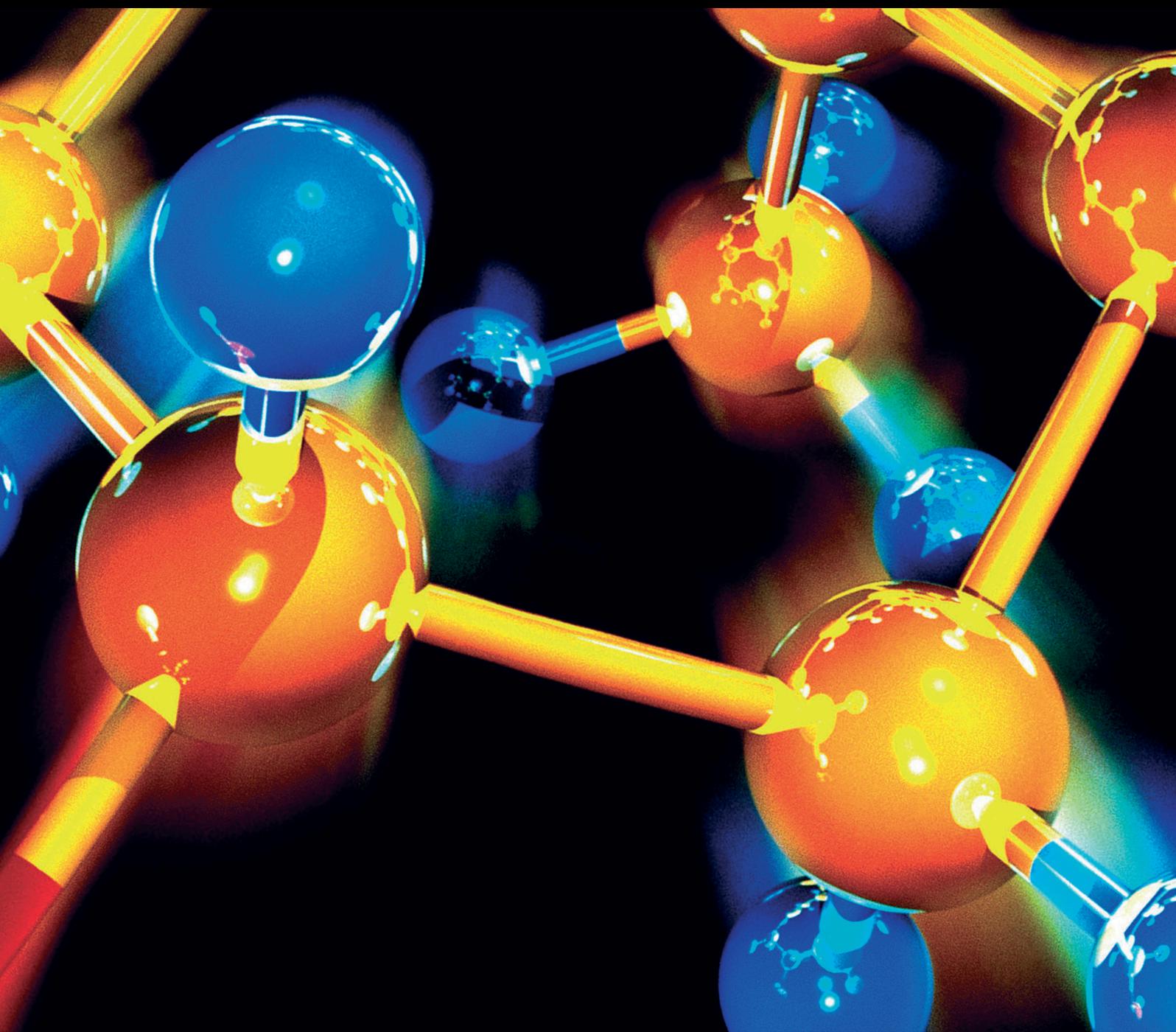


# Advanced Nanomaterials for Green Growth

Lead Guest Editor: Thanh-Dong Pham

Guest Editors: Nguayen Van Noi, Ajit Kumar Sharma, and Van Duong Dao





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# **Advanced Nanomaterials for Green Growth**

Journal of Chemistry

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Research Article (11 pages), Article ID 5602957, Volume 2019 (2019)

## Editorial

# Advanced Nanomaterials for Green Growth

**Thanh-Dong Pham** <sup>1</sup>, **Nguyen Van Noi**,<sup>1</sup> **Ajit Kumar Sharma** <sup>2</sup>, and **Van-Duong Dao** <sup>3</sup>

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Green and sustainable development is widely recognized as a concept of the modern society. This concept has appeared as a state of society where living conditions and resource use continue to meet human needs without undermining the integrity and stability of the natural system. Advanced nanomaterials can be applied to produce cleaner, more efficient, and valuable products to address our present environment-related concerns to a more sustainable future. Thus, the main goal of this issue is to highlight recent advances in synthesis and green applications of nanomaterials. The special issue contains twenty-eight selected research articles relating to nanomaterials. These reported nanomaterials present excellent performance and outstanding stability, have environmental benefits, and are cost-effective.

Most of the selected papers in the special issue reported the synthesis of nanomaterials applying for pollutant treatment. N. M. Phuong et al. reported novel activity of Fe-TiO<sub>2</sub>/Bent-Fe photocatalysts for removal of diazinon pesticides. T. T. V. Ha et al. presented synergistic adsorption and photocatalytic activity of Ag-ZnO/GO photocatalysts for extremely high removal of methylene blue. L. T. T. Thuy et al. reported high photocatalytic activity of C/Fe codoped TiO<sub>2</sub> coated on activated carbon for degradation of Rhodamine B (Rh B). H. Bibova et al. successfully synthesized SiO<sub>2</sub>/TiO<sub>2</sub> composite coating on light substrates for photocatalytic decontamination of oxalic acid and methylene blue in water. L. T. T. Nguyen et al. successfully used the solution combustion method to synthesize MgFe<sub>2</sub>O<sub>4</sub> nanoparticles for methylene blue dye degradation under visible light. N. T. Hanh et al. synthesized of Fe-modified biochar derived from rice straw to apply for arsenic removal.

H. X. Linh et al. reported that their synthesized red mud-activated graphite composites fast and effective in removing methylene blue from aqueous solutions. V. T. Pham et al. studied kinetics, isotherm, thermodynamics, and recyclability of exfoliated graphene-decorated MnFe<sub>2</sub>O<sub>4</sub> nanocomposites for Congo red dye absorption. T. H. Le et al. successfully synthesized MnO<sub>2</sub> nanoparticles on laterite for degradation of methylene blue. X. M. Pham et al. investigated the adsorption of SO<sub>2</sub> and NO<sub>2</sub> over porous Fe<sub>3</sub>O<sub>4</sub> nanoparticles. D. T. C. Nguyen et al. successfully synthesized metal organic framework MIL-53(Fe) as an adsorbent for ibuprofen drug removal from aqueous solutions.

There are four selected papers in the special issue which presented application of nanomaterials as flame retardants. T. A. Nguyen et al. investigated mechanical properties and flame retardancy of epoxy resin/nanoclay/multiwalled carbon nanotube nanocomposites. H. T. Nhung et al. successfully used organoclay to modify expandable graphite/polyurethane foam to use as a flame retardant and thermal insulator. V. Q. Tran et al. successfully used thermal shock combined with ball milling methods to prepare graphene nanoplatelets using flame retardant polymers. T. A. Nguyen et al. studied on fire resistance ability and mechanical properties of composites based on Epikote 240 epoxy resin and thermoelectric fly ash.

There are three selected papers in the special issue which reported catalytic activity of nanomaterials. S. T. Pham et al. reported that Al-incorporated SBA-15 highly efficiently catalyze cellulose conversion to 5-hydroxymethyl furfural (5-HMF). T. H. T. Vu et al. successfully synthesized acidic heterogeneous catalysts with high stability based on

graphene oxide/activated carbon composites for the esterification of lactic acid. M. D. Nguyen et al. reported enhancing activity of Pd-based/rGO modified by Al-Si-Na catalysts in ethanol electro-oxidation in an alkaline medium.

The special issue also presented other useful applications of nanomaterials. C. D. Trinh et al. used the wet chemical method to synthesize  $YVO_4:Eu^{3+}$  nanocrystals for luminescent security ink applications. T. T. P. Nguyen used carbon nanotubes and bismuth oxide to make electrodes for determination of metal concentration by the anodic stripping voltammetry method. T. L. Nguyen et al. successfully utilized platinum nanoflowers to modify electrodes to use as a sensitive sensor for simultaneous detection of lead and cadmium at trace levels. H. T. V. Nguyen et al. successfully used graphene oxide to prepare a hydrophilic polysulfone membrane.

These papers in the issue have been properly selected and concerned most recent progresses in the field of nanomaterials for green growth. The editors hope that the presented objectives of the special issue will be useful not only to working nanomaterial researchers but also to interested engineers as well as students and researchers in other fields. We offer many thanks for reading the enclosed papers and our best wishes for your future research.

### **Conflicts of Interest**

The Guest Editor and Guest Co-Editors declare that there are no conflicts of interest or agreements with private companies, which will prevent us working impartially in the editorial process.

### **Acknowledgments**

We are would like to deeply acknowledge all the authors for their contributions to the special issue and appreciate all the reviewers and related editorial board members for critical assessments and valuable comments to improve the quality of these papers.

*Thanh-Dong Pham  
Nguyen Van Noi  
Ajit Kumar Sharma  
Van-Duong Dao*

## Research Article

# Synthesis of Iron-Modified Biochar Derived from Rice Straw and Its Application to Arsenic Removal

**Thi Hanh Nguyen** <sup>1</sup>, **Thi Huong Pham**,<sup>2</sup> **Hong Tham Nguyen Thi**,<sup>3</sup> **Thi Nham Nguyen** <sup>4,5</sup>, **Minh-Viet Nguyen** <sup>5</sup>, **Trinh Tran Dinh** <sup>5</sup>, **Minh Phuong Nguyen** <sup>5</sup>, **Trung Quang Do** <sup>5</sup>, **Thao Phuong** <sup>5</sup>, **Thu Trang Hoang**,<sup>5</sup> **Thanh Tung Mai Hung**,<sup>6</sup> and **Viet Ha Tran Thi** <sup>7</sup>

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Guest Editor: Ajit Kumar Sharma

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A novel iron-modified biochar (FMBC) derived from rice straw was synthesized using FeCl<sub>3</sub> modification for efficient As(V) removal from aqueous solution. FTIR and SEM-EDX analyses were carried out to determine the mechanism involved in the removal process and also demonstrated that Fe had loaded successfully on the surface of modified biochar. The iron-modified biochar showed higher arsenic removal ability than the raw biochar. The iron-modified biochar showed a maximum adsorption with an initial solution pH of 5.0. Moreover, for the tested biochar, the As(V) removal kinetics data were well fitted by the pseudo-second-order model. Furthermore, the As(V) removal data upon being well fitted by the Langmuir model showed the maximal removal capacity of 28.49 mg/g. The simple preparation process and high adsorption performance suggest that the iron-modified biochar derived from rice straw could be served as an effective, inexpensive, and environmentally sustainable adsorbent to replace typical granular activated carbon (AC) for As(III) removal from aqueous solution.

## 1. Introduction

Arsenic is one of the most abundant elements in the biosphere and in the Earth's crust. Arsenic occurs in most natural waters as As(V), As(III), As(0), and As(-III) oxidation states. As-contaminated water affects a large group of population worldwide, particularly in Vietnam, China, and India. Chronic exposure to inorganic arsenic may lead to cancer or noncancer health effects [1]. Arsenic has been classified as a Class A carcinogen by the United States Environmental Protection Agency (USEPA). According to the World Health Organization (WHO) and USEPA, the limitations for As concentration are 10 µg/L

and 0.2 mg/L in safe drinking water and discharge wastewater, respectively [2]. Ingestion of arsenic, even at low concentration, has resulted in various detrimental health issues such as pulmonary disease, cardiovascular disease, nervous system dysfunction, and also cancer of the lung kidney and skin [3].

Coagulation/precipitation, ion exchange, reverse osmosis, and adsorption processes were utilized for arsenic-contaminated water remediation [4–6]. Among the various techniques, adsorption has been considered the most common and effective technology for removing contaminants from groundwater or wastewater [7]. Adsorption is often utilized at the end of a treatment plan for removal of

contaminants because of its low cost, and it does not generate any secondary waste that needs further treatment.

Biochar (BC), a carbon material produced mainly from the pyrolysis process of low-cost biomass residuals such as rice straw, has received much recent attention because of its many potential environmental abilities such as carbon sequestration, soil improvement, water treatment, and environmental remediation [8, 9]. BC can be utilized as an adsorbent because of its porosity, large surface area, and negative surface charge that can be useful for decontaminating water (organic and inorganic pollutants) [10]. Some BCs can be utilized for removal of heavy metal ions or organic polluted compounds in the aqueous solution. However, the lack of adsorption sites and functional group limits its application to As removal [11, 12]. Many researchers have modified BCs to improve their properties such as enhance the surface functional groups for effective adsorption [13, 14]. Several studies have utilized metal oxyhydroxide surfaces and clay minerals containing Fe, Mn, Al, Cu, and Co to remove As in the aqueous solution [15]. Hematite, an abundant and natural Fe mineral, was a good adsorbent for As removal from groundwater [16]. The hematite mineral was activated by the thermal method to enhance its ability to remove aqueous As [17].

Vietnam is the world's fifth largest rice producer all over the world. The total amount of rice straw generated was approximately 67 million dry ton in 2013. In order to reduce the environmental problem from rice straw burning, it is necessary to find a suitable method to remove the excess rice straw. Therefore, biochar derived from rice straw can be an effective, inexpensive, and environmentally sustainable adsorbent for environmental treatment and can reduce atmospheric pollution from rice straw burning.

In the present study, dried rice straw was used for the preparation of biochar by slow pyrolysis and then modified with the mixture of  $\text{FeCl}_3$  and  $\text{FeSO}_4$  before being applied for the removal of As(V) in aqueous solution.

## 2. Materials and Methods

**2.1. Biochar Production.** In this study, the rice straw biomass was collected from a rice farm in the city of Hanoi, Vietnam. It was pyrolyzed at a temperature of  $500^\circ\text{C}$  for 1 h using a tube-type electrical furnace under  $\text{N}_2$  gas. The biochar was collected from the reactor after being cooled till a room temperature of  $25\text{--}30^\circ\text{C}$  inside the muffle furnace. The iron-modified biochar was synthesized by the following procedure. 10 g of the obtained BC was mixed with 500 ml of 7.3 g  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  and 7.23 g  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  in a glass tube. This mixture was heated at  $50^\circ\text{C}$  to form a stable suspension. The pH was raised to 11 by adding 0.05 M NaOH solution, dropwise. After mixing for 60 min, the organic residues were removed by washing with distilled water ( $\text{H}_2\text{O}$ ) until the pH of the washing solution reached 7.0. The fine powdered modified biochar (FMBC) was vacuum-filtered and then dried overnight at  $50^\circ\text{C}$  in a hot air oven [18].

**2.2. Characterization of Biochar (BC).** The surface architecture of the synthesized BC (FMBC) was examined using a JED-2300 Analysis Station Plus (JEOL) scanning electron microscope (SEM). Energy-dispersive X-ray (EDX) spectroscopy analyses were carried out using a Quantax instrument (Bruker, USA). The infrared (IR) spectra of synthesized materials (as KBr pellets) were analyzed. The surface functional groups of FMBC were analyzed by using an IR spectrophotometer (PerkinElmer FTIR, USA) with an attenuated total reflectance attachment within the wavelength of  $400\text{--}4,000\text{ cm}^{-1}$ .

The point of zero charge (PZC) of FMBC was determined by using the pH drift method of 0.01 M NaCl pH interval of 2 and in the range of pH 2 to 12 [19]. The pH values of solutions were adjusted between 2 and 12 by using 0.1 M HCl or 0.1 M NaOH solution. The initial pH values of solutions were measured. A 0.2 g of biochar was added into a beaker with 20 mL of NaCl solution and left undisturbed for 24 h under  $\text{N}_2$  bubbles to prevent  $\text{CO}_2$  dissolution until the pH value became stable, and then final pH of the solutions was measured. The final pH was measured, and  $\text{pH}_{\text{PZC}}$  was determined as the value at which  $\text{pH}_{\text{final}} = \text{pH}_{\text{initial}}$ .

**2.3. Batch Sorption of Arsenic.** Adsorption experiments were conducted to determine the isotherms of arsenic sorption onto the FMBC sample. About 0.2 g of the FMBC was mixed with 100 mL of As(V) solution for each experiment. The mixture was then shaken in a mechanical shaker (120 rpm) at room temperature ( $22 \pm 2^\circ\text{C}$ ). At the end of each experiment, the remaining As concentrations were determined by using inductively coupled plasma mass spectrometry (ICP-MS) after vacuum-filtered. Duplicate sets of samples were taken for the analysis of residual concentration of As, and the difference of two measurements should be smaller than 10%. All chemical reagents used in the experiments were of high purity grade from Sigma-Aldrich.

The amount of As(V) adsorbed onto the FMBC (adsorbent) was calculated by the concentration difference between the initial and final concentrations of the solution by using the following equation:

$$q_e(\text{mg}\cdot\text{g}^{-1}) = [C_o - C_e(\text{mg L}^{-1})] \times V(\text{L})/W(\text{g}). \quad (1)$$

Hence,  $q_e$  is the equilibrium amount of the As(V) adsorbed ( $\text{mg}\cdot\text{g}^{-1}$ ) on the FMBC,  $C_o$  and  $C_e$  are the initial and equilibrium concentration of As(V) ( $\text{mg/L}$ ),  $V$  is the solution volume of the test sample (L), and  $M$  is the total mass of Fe-modified BC added (g).

**2.4. Adsorption Isotherms and Kinetic Models.** The equilibrium adsorption isotherms were utilized to determine the adsorption mechanism. In this study, Langmuir isotherm and Freundlich isotherm models were utilized to analyze the adsorption process of biochar. Langmuir isotherm is valid for monolayer sorption and expressed in the following equation:

$$\frac{c_e}{q_e} = \frac{1}{q_{\max} K_L} + \frac{c_e}{q_{\max}}, \quad (2)$$

where  $q_{\max}$  ( $\text{mg}\cdot\text{g}^{-1}$ ) indicates the monolayer adsorption capacity and  $K_L$  ( $\text{L}\cdot\text{mg}^{-1}$ ) is the heat of adsorption. The favorability or unfavorability of Langmuir adsorption can be expressed by

$$R_L = \frac{1}{1 + K_L C_0}, \quad (3)$$

where  $R_L$  indicates favorable adsorption and has the range between 0 and 1.

A Freundlich isotherm describes the heterogeneous surface energies by multilayer adsorption and is expressed in the following equation:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e, \quad (4)$$

where  $K_F$  expresses the adsorption capacity ( $\text{mg}\cdot\text{g}^{-1}$ ) and  $n$  is an empirical parameter related to the adsorption intensity, which varies with the heterogeneity of the adsorbent. The increase in  $1/n$  enhanced the adsorption favorability.

The adsorption kinetic is an important characteristic influencing the adsorption efficiency. The pseudo-first-order and pseudo-second-order kinetic models express the adsorption process as follows:

$$\ln(q_e - q_t) = \ln q_e - k_1 t, \quad (\text{pseudo - first - order model}),$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t, \quad (\text{pseudo - second - order model}), \quad (5)$$

where  $q_e$  and  $q_t$  ( $\text{mg}\cdot\text{g}^{-1}$ ) are concentrations adsorbed at equilibrium and at different time  $t$  and the parameters  $k_1$  ( $\text{min}^{-1}$ ) and  $k_2$  ( $\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$ ) are the equilibrium rate constants of pseudo-first-order and pseudo-second-order kinetic models, respectively.

### 3. Results and Discussion

**3.1. Characteristics of BCs.** The SEM analysis was investigated for the determination of shape, size, and surface morphological structure of the raw biochar (RB) and FMBC. Figure 1 reveals the surface morphologies of the two samples are distinctly different. The Fe-modified biochar showed more heterogeneous structure than the raw biochar after modification process that can contribute to enhance the sorption of As(V) in the aqueous solution [20].

The FTIR spectrum of RB and FMBC is shown in Figure 2, representing the functional groups on the RB and FMBC material introduced by the chemical modification process. The peaks found in the spectrum of the RB and FMBC show almost similar wavenumbers. Several peaks obtained around wavenumbers 1,605 and 1,379  $\text{cm}^{-1}$ , which were assigned to C=O and C-O peaks that were attributed to carboxyl and lactone functional groups, respectively [21]. The peaks at 3,409 and 1094  $\text{cm}^{-1}$  correspond to vibration of O-H of the adsorbent [22]. Vibration of the Fe-O peak was

observed on the FMBC at 780  $\text{cm}^{-1}$ . These FTIR results indicated that the chemical modification plays an important role in the changing properties of biochar. The modification process enhanced the functional group intensity on the surface of the biochar; thus, these functional groups can be new active sites for the adsorption improvement on the biochar. The EDX spectra of the RB and FMBC (Figure 3) further indicated the increasing Fe content on the biochar surface after modification. It revealed that magnetite was added to the biochar surface after the modification process.

The point of zero charge (PZC) of a biochar determines the pH at which the surface of the biochar has positive or negative charge [23]. In this work, the points of zero charge of RB and FMBC were 5.44 and 6.88, respectively (Figure 4). The acidic value of the FMBC indicated that arsenic removal is feasible below this pH because the net positively charged surfaces are favorable to attract the anions.

**3.2. Effect of Initial Solution pH.** A pH solution is an important adsorption parameter for the adsorption study because the pH solution demonstrates the  $\text{H}^+$  ions of specific functional groups on the biochar surface and varies the form of As in the solution.  $\text{pH}_{\text{PZC}}$  also plays an important role in the adsorption process. At  $\text{pHs} < \text{pH}_{\text{PZC}}$ , the surface of the FMBC is positively charged and gives a strong electrostatic attraction between surface groups and anion species in the solution that could enhance the adsorption process. The decrease in the adsorption amount observed at pH higher than  $\text{pH}_{\text{PZC}}$  (when the surface of the adsorbent is negatively charged) could lead to increased competition between  $\text{OH}^-$  and anion species for the adsorption sites [24]. The effect of solution pH on the adsorbent's arsenic sorption (removal) was identified by varying the initial solution pH while keeping other sorption parameter constants. The pH effect on adsorption was determined by mixing 1.0 g of modified BC with 100 ml of a 10 mg/l As(V) solution at various pH values ranging from 2.0 to 8.0 for 120 min.

The pH effect ranging from 2.0 to 8.0, on the adsorption of As(V) on biochar, is shown in Figure 5. The removal of As(V) ions was relatively low in the alkaline solution ( $\text{pH} > 6.8$ ) compared with that at lower pH values, ranging from pH 2.0 to 6.8 ( $\text{pH}_{\text{PZC}}$ ), because the  $\text{OH}^-$  ions at alkaline conditions can compete with As(V) anion for active sites under strong alkaline conditions, resulting in the blocking of As(V) adsorption on the surface of the modified BC. This is because As(V) existed in the aqueous solutions in the form of  $\text{H}_3\text{AsO}_4$ ,  $\text{H}_2\text{AsO}_4^-$ ,  $\text{HAsO}_4^{2-}$ ,  $\text{AsO}_4^{3-}$ , and especially  $\text{H}_2\text{AsO}_4^-$  at the pH range of 2.0–6.0 [25]. Therefore, increasing the initial concentration of proton in aqueous solutions increased the level of As(V) removal under acid conditions, ranging from pH 2.0 to 6.8. The highest removal efficiency was 86.3 and 62.3% for FMBC at the condition of  $\text{pH} < 6.0$  and  $\text{pH} > 6.0$ , respectively. The RB showed lower removal efficiency even under the condition of  $\text{pH} < 5.0$ . This demonstrates the feasibility of the FMBC for As(V) removal from wastewater with pH values in the range of 4–7.

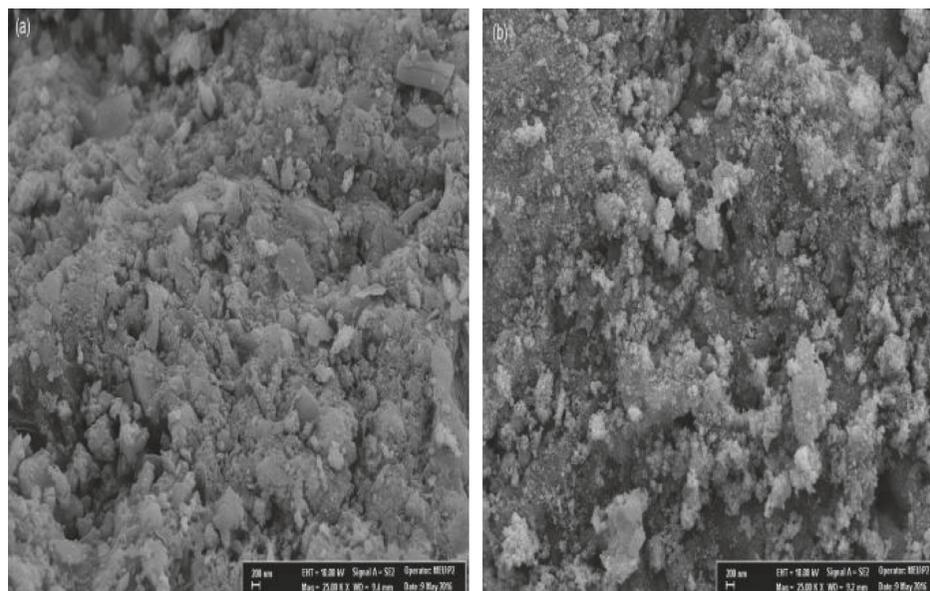


FIGURE 1: SEM images of raw biochar (RB) and iron-modified BC (FMBC).

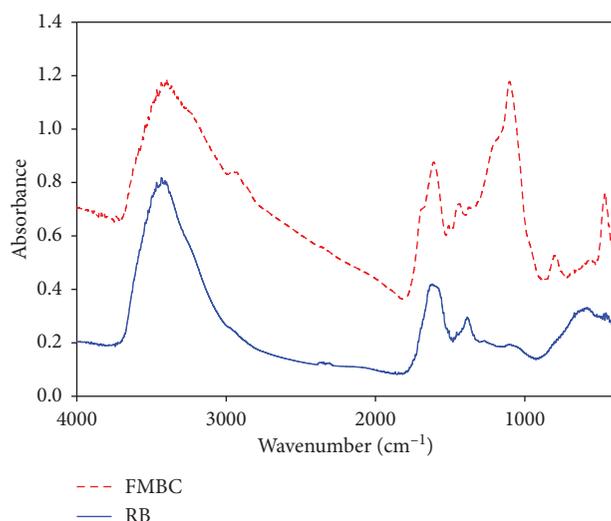


FIGURE 2: FTIR spectra of RB and FMBC.

**3.3. Effect of Initial Concentration.** Figure 6 shows the effect of initial concentration of As(V) ion solution for removal at a pH of 5.0 and a constant agitation speed of 150 rpm for 120 min. The amount of As(V) adsorbed increased with increasing initial concentration up to 30 mg/l, indicating that As(V) removal is highly concentration dependent. At lower concentrations, the amount of ions available for adsorption by a given amount of BC is less than the available sites on the adsorbent. However, at higher concentrations, the number of available sites for adsorption decreases. These results indicate that the adsorption removal of the As(V) ions depends on the initial concentration. Figure 3 shows the removal efficiency of FMBC decreased from 91.5 to 63.5% when the concentration increased from 4 to 30 mg/L.

**3.4. Effect of Phase Reaction Time.** The As(V) removal was also controlled by the reaction time. The rapid interaction of the As(V) ions to be removed by BC is desirable and beneficial for practical removal of arsenic anions from aqueous solutions or wastewater. Figure 7 shows the effects of reaction time for arsenic ion removal by the FMBC. For a given concentration of As(V), the amount of adsorbed As(V) ions was almost proportional to the increasing reaction time up to 45 min. The adsorption equilibrium was obtained at a reaction time of 90 min, with an adsorption capacity of 23.57 mg/g. The adsorption rate was relatively fast at the initial adsorption stage but then slowed down gradually after more sites were occupied by the adsorbed As(V) ions. The slower adsorption was due to the gradual decrease in the number of available adsorption sites.

**3.5. Adsorption Isotherm.** The adsorption isotherm data of FMBC were fitted to the Langmuir and Freundlich isotherms were fitted to the Langmuir adsorption isotherm ( $R^2 = 0.9955$ ) ( $p < 0.01$ ) than the Freundlich isotherm ( $R^2 = 0.9360$ ) (Table 1). The results showed a monolayer As(V) adsorption onto the adsorption sites of the iron-modified biochar. The maximum adsorption capacities ( $q_{\max}$ ) of As(V) decreased in the order of FMBC ( $28.49 \text{ mg}\cdot\text{g}^{-1}$ ) > RB ( $10.3 \text{ mg}\cdot\text{g}^{-1}$ ). The controls showed that the As(V) adsorption capacity of FMBC was higher than that of RB. The adsorption capacity of FMBC may relate to the increasing number of surface functional groups of the modified material. The maximum adsorption capacity of the FMBC for As(V) ions, based on the Langmuir isotherm, was 28.49 mg/g. Table 2 compares this study's result for the As(V) adsorption capacity of FMBC with values reported from other similar studies. The adsorption capacity of FMBC was much higher than that of other commercial material, and the FMBC can be utilized as a green adsorbent for the removal of As(V) in groundwater.

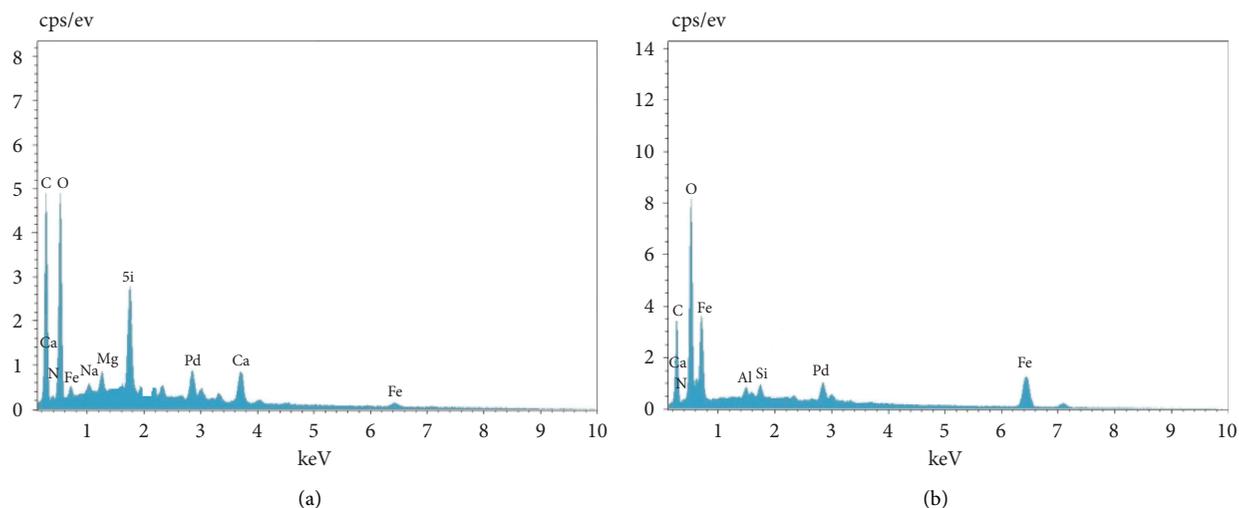


FIGURE 3: EDX spectra of RB (a) and FMBC (b).

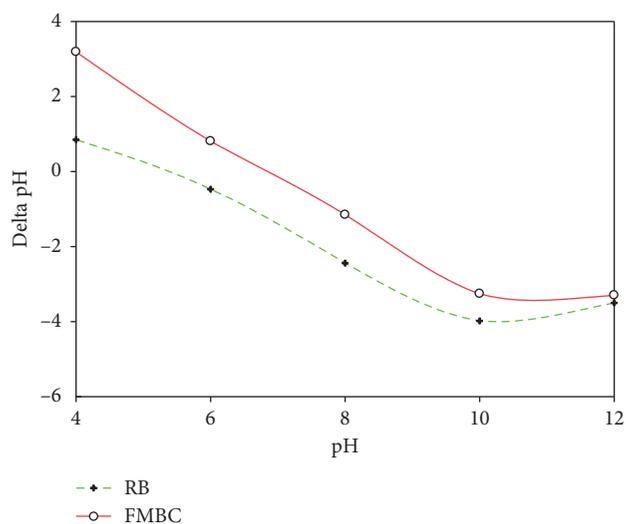


FIGURE 4:  $pH_{pzc}$  of RB and FMBC.

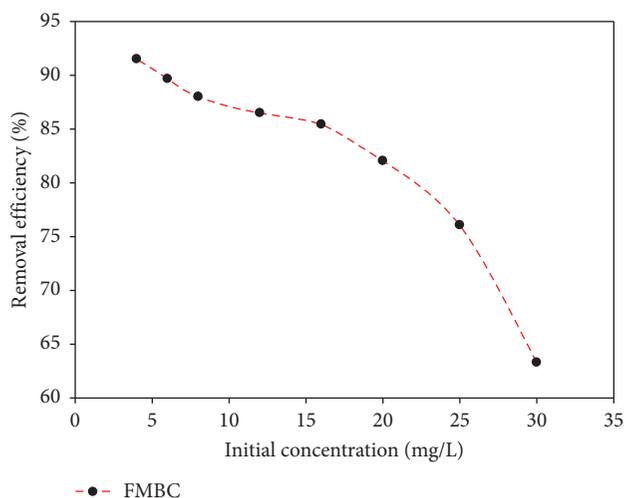


FIGURE 6: Effect of initial concentration for the As(V) removal on FMBC.

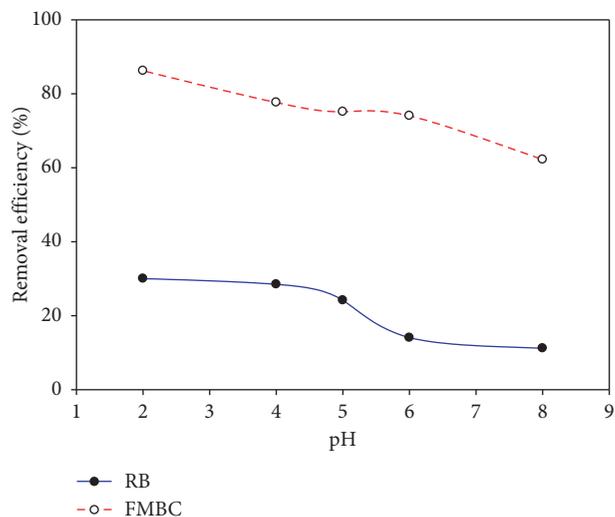


FIGURE 5: Effect of pH for the As(V) removal on RB and FMBC.

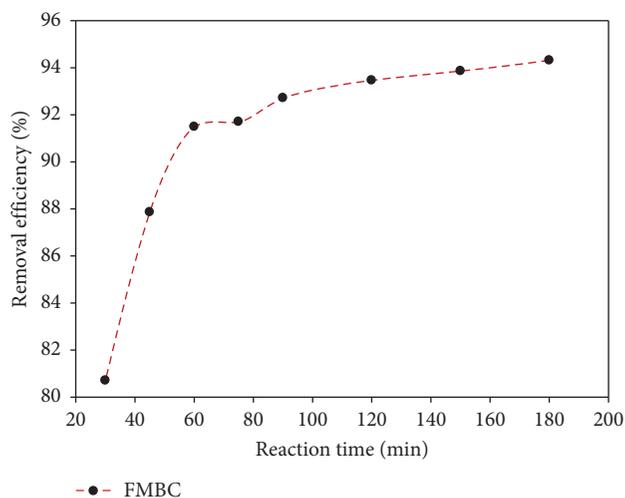


FIGURE 7: Effect of reaction time for the As(V) removal on FMBC.

TABLE 1: Adsorption isotherm of Fe-modified BC.

	Langmuir isotherm			Freundlich isotherm		
	$q_{\max}$ (mg/g)	$K_L$	$R^2$	$\ln K_F$	$1/n$	$R^2$
Fe1-BC	28.49	0.563	0.9955	2.2118	0.5128	0.9360

TABLE 2: Adsorption comparison with other studies.

Material	Adsorption capacity (mg/g)	Reference
TiO <sub>2</sub> -CNTs	1.8	[26]
Biochar	7.21	[27]
Supported nanoscale zero-valent iron on activated carbon	12.0	[28]
Ascorbic acid-coated Fe <sub>3</sub> O <sub>4</sub> nanoparticles	16.56	[29]
Activated carbon	25	[30]
FMBC	28.49	This study
Activated carbon	34.46	[30]
Al <sub>2</sub> O <sub>3</sub> /Fe(OH) <sub>3</sub>	36.63	[31]

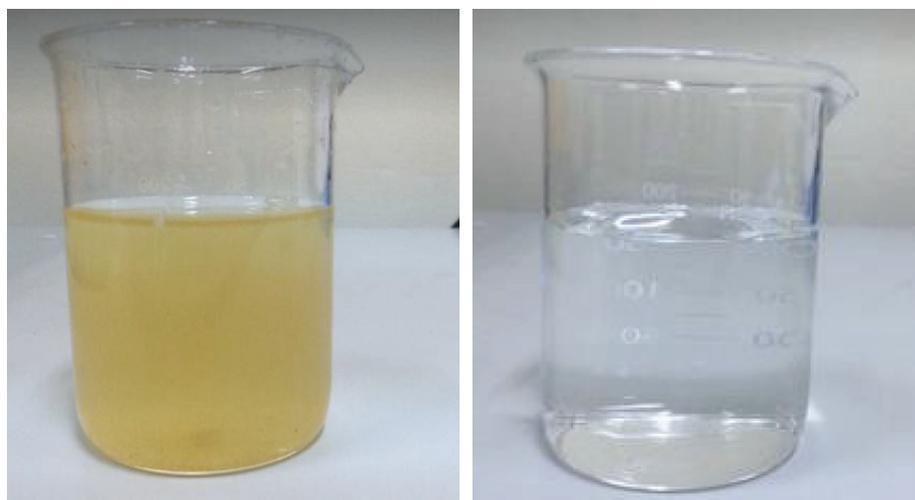


FIGURE 8: Groundwater sample before and after treatment.

The FMBC was applied for the removal of As(V) in the groundwater sample which had the concentration of As(V) 91  $\mu\text{g/L}$ . Figure 8 shows the groundwater sample before and after treatment. The testing experiments showed that 1 kg of the Fe-modified BC can treat 278 and 141 m<sup>3</sup> of contaminated groundwater to clean water of 50  $\mu\text{g/L}$  and 10  $\mu\text{g/L}$  As(V) based on the regulation of Vietnam for water supply and drinking water, respectively.

**3.6. Adsorption Kinetics.** Pseudo-first- and pseudo-second-order models were utilized to determine the kinetics of As(V) removal. The kinetic model of FMBC for As(V) in the aqueous solutions is shown in Table 3. The adsorption experimental data were best described by the pseudo-second-order kinetics that was proved by the obtained values of correlation coefficient ( $R^2 = 0.988$ ) to describe the adsorption behavior of As(V) onto the modified BC. The experimentally obtained adsorption capacity ( $q_{e(\text{exp})}$ ) values were close to the calculated data from the pseudo-second-order model, which also showed good evidence to support the

pseudo-second-order model and chemisorption [32]. For the pseudo-first-order kinetic model, the calculated adsorption capacity ( $q_{e(\text{cal})}$ ) was much lower than the experimental value ( $q_{e(\text{exp})}$ ) and the determination coefficient ( $R^2$ ) was low ( $R^2 = 0.844$ ).

Figure 9 presents the intraparticle diffusion model for sorption by the FMBC. The adsorption processes of As(V) are related by two steps—the first step depicting macropore diffusion and the second micropore diffusion [33]. In the first stage, the sharper portion may be considered as an external surface adsorption or faster adsorption stage. The second phase describes the gradual adsorption stage, where intraparticle diffusion is rate-controlled. These results of As(V) adsorption showed only the pore diffusion adsorption. The rate of uptake might be limited by the size of the adsorbate molecule, the concentration of the adsorbate and its affinity to the adsorbent, the diffusion coefficient of the adsorbate in the bulk phase, the pore-size distribution of the adsorbent, and the degree of mixing [34]. The first and second phases can be attributed to the external mass transfer and intraparticle diffusion mechanisms, respectively [35–

TABLE 3: Kinetic adsorption models.

$q_{e(\text{exp})}$ (mg/g)	Pseudo-first-order model			Pseudo-second-order model		
	$q_{e(\text{cal})}$ (mg/g)	$K_1$ (g/mg/min)	$R^2$	$q_{e(\text{cal})}$ (mg/g)	$K_2$ (g/mg/min)	$R^2$
28.49	3.238	0.0051	0.844	30.53	0.0892	0.988

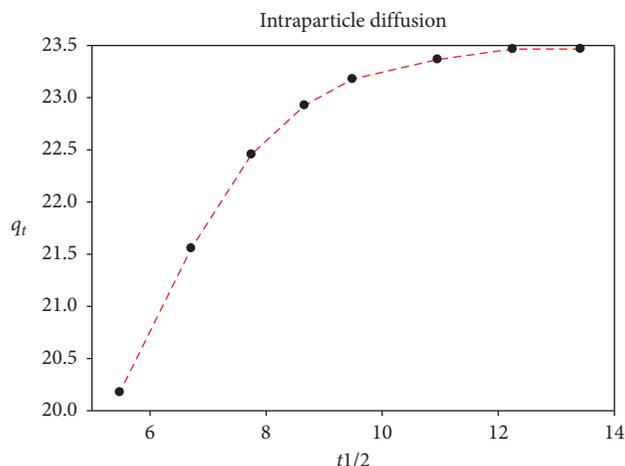
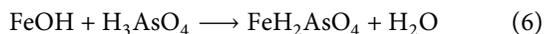


FIGURE 9: Intraparticle diffusion model for As(V) removal by the FMBC.

37]. Furthermore, the regression did not pass through the origin, showing that the intraparticle diffusion is not the only rate-controlling step in the sorption process. Thus, it can be inferred that external mass transfer and intraparticle diffusion occurred simultaneously during the As(V) sorption onto the Fe-modified BC.

The pseudo-second-order model and Langmuir isotherm usually assume that chemisorption of As(V) on FMBC is the rate-limiting step; it is inferred that As(V) was likely adsorbed on the surface of FMBC via chemical interaction. The proposed mechanisms of the removal of As(V) onto the FMBC through the complexation with iron are shown in the following equations:



## 4. Conclusion

This study investigated the removal of As(V) from aqueous solution using iron-modified biochar (FMBC) produced from the slow pyrolysis of rice straw. The FMBC afforded maximum adsorption at a pH of 5.0. The adsorption data were strongly correlated with the Langmuir adsorption isotherm, indicating surface homogeneity and unilayer adsorption. The equilibrium sorption capacity of 28.49 mg · g<sup>-1</sup> for As(V), as determined from the Langmuir isotherm, was very high compared to that of previously reported adsorbents. The As(V) adsorption was well fitted with the pseudo-second-order kinetic model ( $R^2 = 0.988$ )

which showed good evidence to support the chemisorptions of As(V) onto Fe-modified BC. The arsenic removal capacity of the FMBC is comparable to that of many commercial water treatment agents, including AC. Because the FMBC can be produced from rice straw relatively inexpensively, this simple activation method can also be applied to other thermally produced BCs to create an alternative and value-added sorbent for arsenic removal in groundwater.

## Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

## Conflicts of Interest

The authors declare that they have no conflicts of interest.

## Acknowledgments

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## Research Article

# SiO<sub>2</sub>/TiO<sub>2</sub> Composite Coating on Light Substrates for Photocatalytic Decontamination of Water

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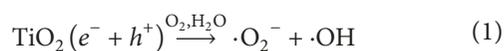
Guest Editor: Ajit Kumar Sharma

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In this study, we describe synthesis and characterization of a floating photocatalyst for water treatment consisting of a light substrate coated by SiO<sub>2</sub>/TiO<sub>2</sub> composite. Three supports of natural origin were used: natural cork, expanded clay (Liapor), and volcanic porous glass (Sorbix). The photoactivity of the coated supports was tested in a laboratory photoreactor, with Liapor being the most photoactive support with good mechanical stability. The corresponding rate constant for the degradation of a model pollutant, 4-chlorophenol, was  $7.8 \times 10^{-5} \text{ s}^{-1}$ . Detail characterization of the coated Liapor was obtained by XRF, SEM/EDX, and UV-Vis diffuse reflectance spectroscopy, and surface area measurements. Outdoor experiments were carried out with calcined Liapor and oxalic acid or methylene blue under sunlight on pilot reactors in the Czech Republic and Vietnam. We demonstrated satisfactory photocatalytic activity, long-term stability, and reusability of the new floating photocatalyst. The photoefficiency to mineralize oxalic acid in water under sunlight was estimated as 6.7% under the applied conditions.

## 1. Introduction

Procedures for contaminated water treatment are still being developed and optimized. Methods using heterogeneous photocatalysis by TiO<sub>2</sub> represent environmental friendly and economical processes that have been investigated for several decades [1]. They are based on the formation of pairs of charge carriers, electron and hole ( $e^- + h^+$ ), in a semiconductor particle upon interaction with photons of sufficient energy (equation (1) [2]). Hydroxyl groups bound on the semiconductor surface are oxidized by migrating holes to hydroxyl radicals ( $\cdot\text{OH}$ ), oxidizing species powerful to accomplish total mineralization of organic compounds and even of microbes. In the presence of oxygen, electrons are consumed under the formation of superoxide radical anions ( $\cdot\text{O}_2^-$ ).

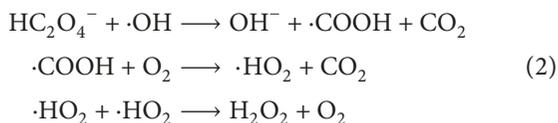


Recently, floating photocatalysts have been increasingly studied due to their advantages, such as easy recovery after the treatment and wide variability of buoyant substrates. Photocatalytic layers were immobilized on various supports, such as graphite [3, 4], perlite [5, 6], vermiculite [7], diatomite powder [8, 9], light-expanded clay aggregate [10, 11], fly ash cenospheres [12–14], palm trunk [15], silica gel beads [16], and others. Besides TiO<sub>2</sub>, other metal oxides deposited on a surface were used (e.g., BiVO<sub>4</sub> [14]).

Photocatalytic efficiency of the materials is often tested by means of a model compound degradation. Halogenated hydrocarbons are stable compounds commonly found as water pollutants due to their wide industrial use. They often show low biodegradability and photodegradability. That is why their representatives, such as 4-chlorophenol (4-CP), are selected as model compounds in photocatalytic studies [17–19]. The proposed mechanism of 4-CP degradation initiated by OH radical attack includes reaction pathways

leading both to the formation of hydroxylated benzene derivatives [20] and to the direct opening of aromatic ring [21].

Oxalic acid (OA) represents another model compound, suitable especially for larger scales and pilot experiments. Its oxidation by hydroxyl radical results directly in the formation of carbon dioxide and hydrogen peroxide (equation (2)) [22]. As a model reactant, OA was used in several studies [22–25].

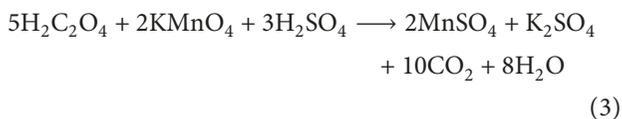


The aim of the presented manuscript is to characterize low-density materials applicable as floating substrates for photocatalytic layers. The required properties of such light supports should include availability, stability, and environmental friendliness. Three different types of supports were selected and used: cork, Liapor, and Sorbix. Photocatalytic efficiency of the supports with immobilized layer of SiO<sub>2</sub>/TiO<sub>2</sub> composite was tested both under the laboratory and outdoor conditions, with the use of 4-CP and OA as model pollutants. We accomplished our study by evaluating the photocatalyst performance in a pilot solar reactor.

## 2. Materials and Methods

4-Chlorophenol (4-CP) (Acros Organics, 99%) was used as a model pollutant in the laboratory-scale experiments. Its concentration was determined by HPLC (Agilent Technology 1200 Series; detection wavelength 254 nm, mobile phase 60:40 water/methanol, flow rate 1 mL/min, injection volume 20 μL, column LiChroCART® 125-4 LiChrosphere 100 RP-18 (5 μm)). Prior to injection, the samples were filtered with 0.45 μm HA filter (Millipore). UV-Vis spectra of the irradiated solutions of 4-CP were measured without filtration by spectrophotometer UV/Vis/NIR Lambda 19 (PerkinElmer).

Oxalic acid (g.r., Lachner, 99.6%) was used for the outdoor experiments. Its concentration was determined by manganometric titration with KMnO<sub>4</sub> (Fluka, ≥99.0% p.a.; H<sub>2</sub>SO<sub>4</sub> was obtained from Lachner, ≥95% p.a.):



Total organic carbon (TOC) was determined by TOC-Vwp Analyzer (Shimadzu). Prior to injection, the samples were filtered with 0.45 μm HA filter (Millipore).

Methylene blue (MB) (Sigma-Aldrich, 82%) was used as a model compound for the outdoor experiments in Vietnam. Its concentration was measured spectrophotometrically at 665 nm by Spectro UV-2550 (Labomed, Inc.).

Water glass (30% SiO<sub>2</sub>, Vodní sklo, a.s.) and TiO<sub>2</sub> P25 (Evonik) were used for the coating of tested floating substrates (experiments in the Czech Republic).

The surface structure and morphology of Liapor and the applied layers were obtained by scanning electron microscopy

coupled with energy dispersive X-ray (SEM/EDX) spectroscopy. SEM Philips XL 30 CP microscope equipped with EDX, Robinson, SE (secondary electron), and BSE (back-scattered electron) detectors were used. Composition of Liapor was measured by X-ray fluorescence (XRF) spectroscopy. The XRF elementary analysis was performed by 4 kW wavelength dispersive X-ray fluorescence spectrometer S4 Pioneer (Bruker AXS) equipped with a rhenium tube operated at 20–60 kV. The samples were prepared and analyzed by the GEO-QUANT method.

Diffuse reflectance spectrum of the SiO<sub>2</sub>/TiO<sub>2</sub> composite layer was measured after the deposition of layers (0.5 mL of the solution was spread on the microscopic glass plate; the procedure and concentration of solutions were otherwise kept same as in the case of the coating of supports) by spectrophotometer UV/Vis/NIR Lambda 19 (PerkinElmer) equipped with the integration sphere. The detail procedure of data evaluation is described by Kočí et al. [26].

The BET specific surface area of Liapor and the applied layers was determined from the adsorption isotherms of N<sub>2</sub> at the boiling point of liquid nitrogen using a Micromeritics ASAP 2010 apparatus [27].

Liapor used for the outdoor experiments in Vietnam was coated by the commercially available suspension of photoactive TiO<sub>2</sub> Protectam FN2 according to the procedure recommended by the manufacturer (Advanced Materials-JTJ, Czech Republic). Protectam FN2 is protected by U.S. patent no. 8,647,565 (2009) and consists of about 74% of Aeroxide TiO<sub>2</sub> P25, the remaining part being an inorganic binder.

**2.1. Floating Support.** In this study, three types of substrates were selected that meet the following criteria: density lower than 1 kg·dm<sup>-3</sup>, large surface area, low cost, easy accessibility, and environmental friendliness (as itself and with regard to possible degradation products) (Figure 1).

As the widely available organic material, raw cork (Korek Jelínek, spol. s.r.o.) was chosen. Inorganic support was represented by expanded volcanic glass perlit “Sorbix” (WB 0/3, Imerys) and expanded clay Liapor (Lias Vintířov). Density and grain size of chosen supports are listed in Table 1.

**2.2. Preparation of Coated Floating Substrates.** The preparation of the photoactive layers is based on the synthesis of SiO<sub>2</sub>/TiO<sub>2</sub> composite described in the utility model [28], modified for the deposition on the studied supports. The synthesis employs general amphoteric properties of solid oxide materials when zero points of charge (pH<sub>zpc</sub>) of TiO<sub>2</sub> and SiO<sub>2</sub> are different. At the appropriate pH value, TiO<sub>2</sub> particles are dominantly protonated while the particles of SiO<sub>2</sub> are negatively charged. As a result, spontaneous association among them occurs. It was found that colloidal suspensions of such composite are stable in a long-term period.

The coating procedure consisted of the following steps:

1<sup>st</sup> layer (water glass): cleaned (washed and dried under room temperature) substrates were dipped in the



FIGURE 1: Floating supports (from the left cork, Sorbix, and Liapor) and demonstration of their stability on water surface.

TABLE 1: Properties of the floating substrates.

	Cork	Sorbix	Liapor
Density ( $\text{kg}\cdot\text{dm}^{-3}$ )	0.15–0.350	0.070	0.25–0.9
Grain size (mm)	0.5–3	<0.125	4–8

suspension of water glass (2 wt.%  $\text{SiO}_2$ ) for 2 hours and then dried at  $80^\circ\text{C}$ . This step was performed in order to improve adhesion of the photocatalyst on the support surface.

2<sup>nd</sup> and 3<sup>rd</sup> layers (photocatalyst): support with the dried water glass layer was dipped in the suspension of 5 wt.%  $\text{TiO}_2$  and 5.99 wt.%  $\text{SiO}_2$  for 2 hours and then dried at  $80^\circ\text{C}$ .

Liapor samples for the outdoor experiments were further calcined at  $250^\circ\text{C}$  for 1 hour (temperature gradient  $1^\circ\text{C}/\text{min}$ ).

The mechanical stability of the deposited layers was tested after washing (5 g) in demineralized water ( $0.1 \text{ dm}^3$ ) for 6 hours under stirring, followed by drying at room temperature.

**2.3. Photoreactors and the Operating Conditions.** Photocatalytic experiments were carried out in the photoreactors of our own design and construction (Figures 2(a) and 2(b)). The laboratory photoreactor (Figure 2(a)) enables to perform series of experiments under the identical conditions, thus reducing random effects. The bottom of the device consists of 6 or 15 magnetic stirrers (Variomag Telesystem) with a cut-out slab to keep the beakers with the tested solutions in constant positions. In the upper part, UV fluorescent lamps are installed that can be switched on/off separately. The inner walls of the photoreactor are covered by the brushed aluminum foil to maximize light reflection and ensure homogeneous irradiation. For the purpose of our study, the photoreactor was equipped with 10 fluorescent black lamps ( $\lambda_{\text{max}} = 365 \text{ nm}$ , 8 watt, Sylvania), and the flux

density at the probe level was  $6.24 \text{ mW}\cdot\text{cm}^{-2}$  measured by UVA probe (ILT 1400-A Photometer, probe UVA #28949).

For the outdoor experiments, solar reactors of a larger scale were used (Figure 2(b)). In the  $40 \text{ dm}^3$  plastic basin, the tested solution ( $25 \text{ dm}^3$ ) is pumped and circulates through the integrated jet system that causes regular rotation and watering of the floating photocatalyst. The solar reactors were covered by UVA transparent glass sheets ( $A_{(300\text{nm})} \leq 0.1$ ) to prevent evaporation of the tested solution. The weather conditions were monitored by an integrated sensor suite (ISS), the measured data sent to ForVantage Pro2 Plus™ console, and evaluated by WeatherLink software.

During the outdoor experiments in Vietnam, the intensity of the incident sunlight was monitored continuously by quantum meter (Apogee Instruments, Inc.).

The course of photocatalytic degradation of the model compound was formally described by the first-order kinetics. The corresponding rate constants were calculated by a nonlinear curve fitting procedure using the relation  $c = c_0 e^{(-kt)}$ , where  $c$ ,  $t$ , and  $k$  represent concentration of 4-CP, time of irradiation, and rate constant, respectively.

### 3. Results and Discussion

**3.1. Comparison of the Supports.** The photoactivity of the supports was monitored by means of 4-CP degradation. Determination of photoactivity of the noncoated substrates was performed with 4-CP ( $2 \times 10^{-4} \text{ mol}\cdot\text{dm}^{-3}$ ,  $0.1 \text{ dm}^3$ ) in the laboratory photoreactor (Figure 2(a)). In the case of Sorbix and Liapor, concentration of 4-CP remains constant during the whole irradiation time, that is, no measurable photoactivity of the floating substrates was found for at least 6 hours under stirring. Cork, on the other hand, releases a small amount of organic matter upon the contact with water. This phenomenon complicates determination of 4-CP concentration due to the high background response detected by UV-Vis spectroscopy and TOC and will be discussed further.

**3.2. Photoactivity and Mechanical Stability of the Deposited Layers.** The kinetics of 4-CP degradation was followed both by HPLC (Figures 3–5) and by the measurement of the relative change of TOC. Although the former value represents direct decrease of 4-CP concentration resulting from hydroxyl radical attack, the latter reflects mineralization to carbon dioxide that proceeds, due to complex degradation mechanism via various intermediates, much slower.

The course of photocatalytic degradation of 4-CP with coated Sorbix and Liapor follows formally the first-order kinetics (Figures 4 and 5). The values of corresponding rate constants and relative changes of TOC are summarized in Table 2.

In the case of using Sorbix as the floating substrate, the deposition of a stable layer is difficult because of the high hydrophobicity of the support. Low wettability of the prepared floating photocatalyst is thus associated with its low photoactivity (Table 2). At a stirring rate of 200 rpm, negligible degradation of 4-CP is observed and even 500 rpm is not

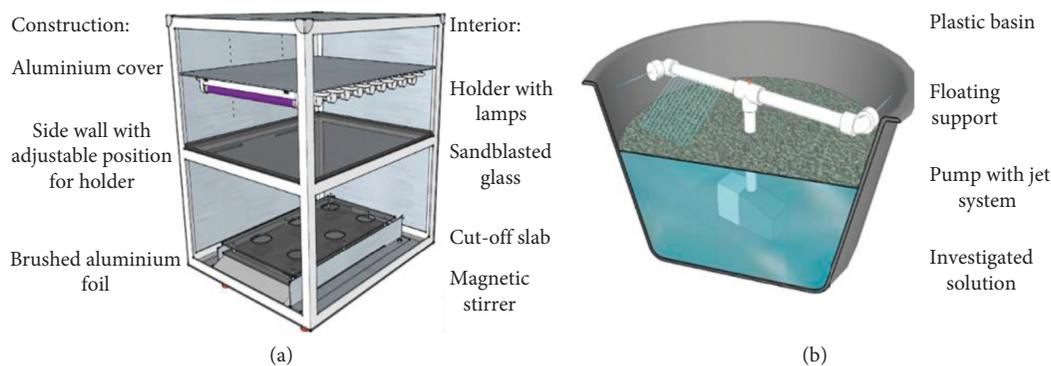


FIGURE 2: Photoreactors of our own design and construction. (a) Laboratory photoreactor. (b) Outdoor photoreactor.

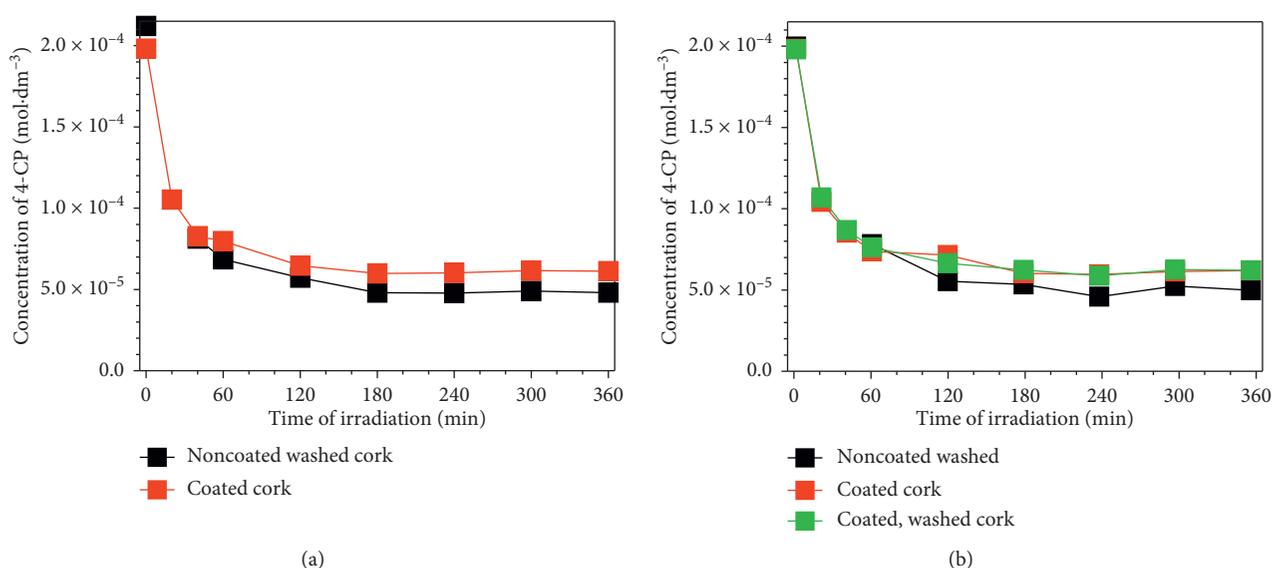


FIGURE 3: (a) Blank—sorption of 4-CP on Noncoated washed cork and coated cork. (b) Photocatalytic degradation of 4-CP (in laboratory photoreactor at a stirring rate of 500 rpm) using noncoated washed, coated, and coated, washed cork.

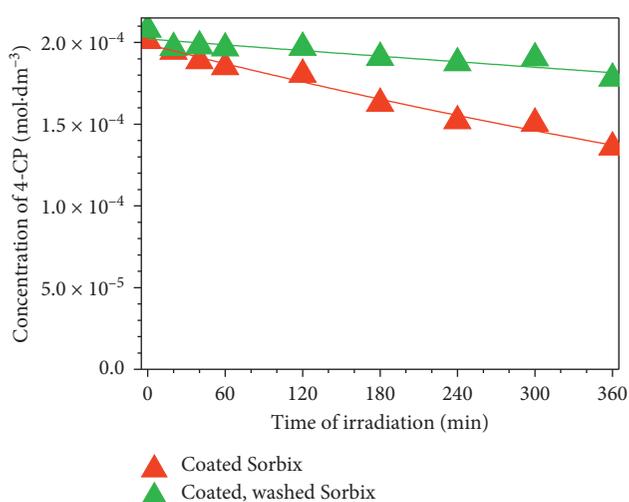


FIGURE 4: Photocatalytic degradation of 4-CP (in laboratory photoreactor at a stirring rate of 500 rpm) using coated Sorbix and coated, washed Sorbix.

sufficient to ensure satisfactory contact with the solution as after 6 hours of the irradiation; the concentration of 4-CP decreased only to 70% of its original value. The mechanical stability of the deposited layer is not satisfactory enough, since by washing, the degradation rate is reduced to one-third and a similar effect is observed in the case of TOC values (Table 2).

The physicochemical properties of Liapor enabled the preparation of a uniform stable layer according to the described procedure (90% of a particle volume was submersed in SiO<sub>2</sub> or SiO<sub>2</sub>/TiO<sub>2</sub> aqueous suspensions). The surface of coated Liapor grains is sufficiently wetted during irradiation, and further increase of stirring rate does not alter the course of 4-CP degradation. Neither the adsorption of 4-CP on Liapor particles (both noncoated and coated) nor any other effects that could affect photocatalytic process were observed under the applied laboratory conditions.

The results of 4-CP degradation with coated Liapor are summarized in Table 2. Within 6 hours of the irradiation, concentration of 4-CP decreased approximately to 10% of its original value ( $k = 7.80 \times 10^{-5} \text{ s}^{-1}$ ). Washing has not changed

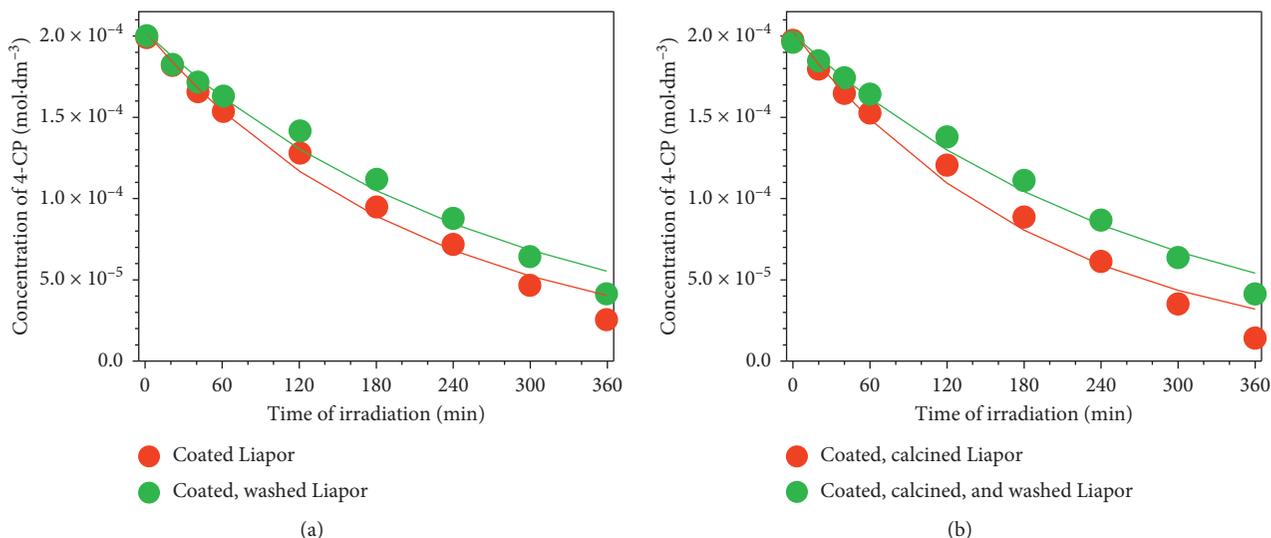


FIGURE 5: Photocatalytic degradation of 4-CP (in laboratory photoreactor at a stirring rate of 500 rpm) using (a) nonwashed and washed Liapor. (b) Calcined, and calcined, washed Liapor.

TABLE 2: Rate constants of 4-CP photocatalytic degradation and relative change of TOC after 6 hours of irradiation.

	Material	Rate constant ( $10^{-5} \text{ s}^{-1}$ )	TOC: relative change (%)
Sc	Sorbix: coated	1.72	76.3
Scw	Sorbix: coated and washed	0.50	89.1
Lc	Liapor: coated	7.80	27.0
Lcw	Liapor: coated and washed	6.22	40.1
Lcc	Liapor: coated and calcined	8.53	15.0
Lccw	Liapor: coated, calcined, and washed	6.08	37.2

the photoperformance of coated Liapor markedly (Figure 5(a) and Table 2).

Calcination of coated Liapor at  $250^\circ\text{C}$  leads to an increase of 4-CP degradation rate ( $8.53 \times 10^{-5} \text{ s}^{-1}$ ) (Figure 5(b)). After washing, almost the same photoactivity of calcined Liapor and Liapor without the heat treatment is observed ( $6.08 \times 10^{-5} \text{ s}^{-1}$ ). From the comparison of the data in Table 2, it can be concluded that Liapor represents the most appropriate floating substrate for the photocatalyst deposition.

Cork used as a support for the photocatalyst layer shows completely different physicochemical properties. Besides the aforementioned release of an organic matter, marked sorption effects occur when 4-CP is exposed to this floating substrate. Blank experiments without irradiation demonstrate significant adsorption of 4-CP on both noncoated and coated cork (Figure 3(a)). According to the experimental data, sorption processes play dominant role and photocatalytic degradation represents only a minor part under the applied experimental conditions, both before and after washing of the cork substrate (Figure 3(b)). Concentration decrease of 4-CP could not be approximated by the first-order kinetics.

**3.3. Characterization of Liapor and the Deposited Layers.** Liapor with deposited photocatalyst layer has been further studied in detail. The results of elemental analyses (XRF and EDS) show that this expanded clay consists of silicone oxide

as the main component (41.02%, Table 3), and of aluminum and iron oxides as less abundant components. Titanium dioxide represents approximately 3% of the total oxide content.

Figure 6 shows SEM images of Liapor sample before the deposition of the photoactive layer. Original Liapor has a heterogeneous surface structure (Figure 6(a)). After water glass deposition, fine cracks typical of silicate layer appear on the surface (Figure 6(b)). The coated layer is thin as evidenced by EDS analysis that provides a similar elemental composition for both uncoated and coated samples (Figure 7(a) and Table 4).

Changes of Liapor surface structure due to the particular steps of the photoactive layer preparation, that is, coating and drying (Figure 8(a)), calcination (Figure 8(b)), and washing (Figure 8(c)) were also followed by SEM technique. Observed smooth layer of the photocatalyst copies depressions and protrusions of the support surface. Formed polygons are separated by numerous cracks. Surface mapping scans of samples show that the polygons consist of the deposited photocatalyst with Si, O, and Ti as the main atomic components (Figure 7(b), Table 4) while in the cracks, the original support surface is observed. The composite layers coated on Liapor substrate show high mechanical stability.

The value of bandgap energy was calculated from UV-Vis diffuse reflectance spectrum of the  $\text{SiO}_2/\text{TiO}_2$  composite layers deposited on a quartz glass. Original coordinates of

TABLE 3: XRF analysis of Liapor.

Formula	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	CaO	K <sub>2</sub> O	MgO	Others
Concentration (%)	41.02	25.67	12.16	3.334	3.079	2.592	2.072	<0.5

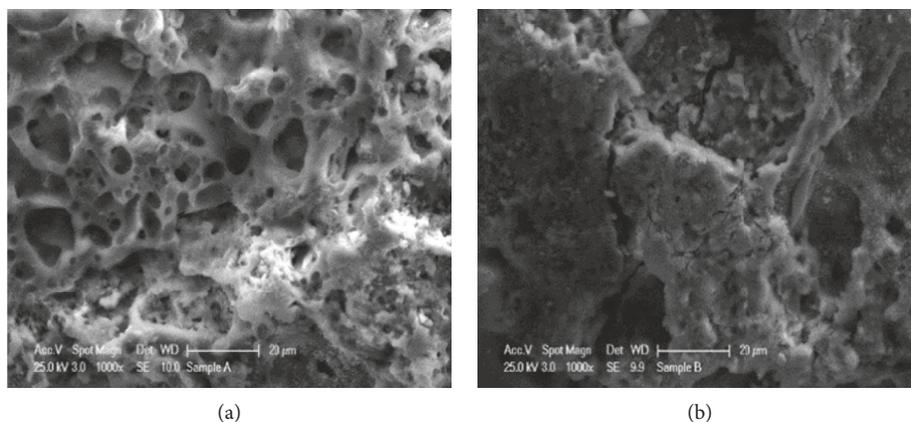
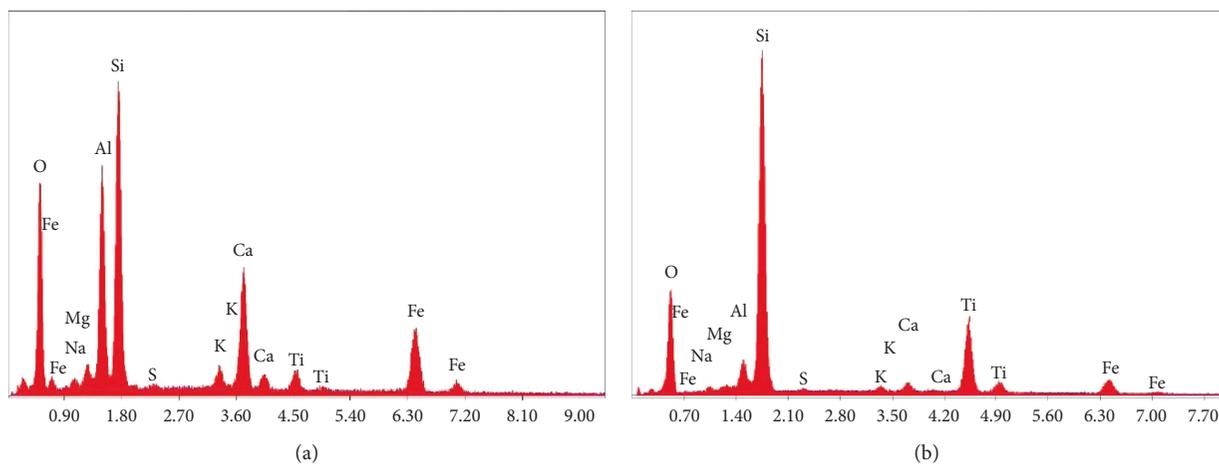
FIGURE 6: SEM images of Liapor. (a) Liapor before coating. (b) Liapor with the first layer of SiO<sub>2</sub>.FIGURE 7: EDS analyses of Liapor. (a) Liapor with the SiO<sub>2</sub> layer. (b) Liapor with the first layer of SiO<sub>2</sub> and two composite layers.

TABLE 4: EDS analysis of Liapor.

Element (wt.%)	Liapor	SiO <sub>2</sub> layer	Composite
O K	41.59	41.59	43.27
Na K	1.14	1.34	1.22
Mg K	2.14	2.08	0.97
Al K	15.13	13.81	3.56
Si K	20.20	19.95	32.54
S K	0.26	0.27	0.34
K K	2.33	1.44	0.63
Ca K	5.41	7.97	1.10
Ti K	1.69	1.76	12.32
Fe K	10.11	9.80	4.04

the spectrum, that is, reflectance vs. wavelength, were transformed to Kubelka–Munk function ( $K$ ) vs. photon energy ( $h\nu$ ). Bandgap energy is usually estimated by extrapolation of the linear part of the dependence; however, we employed a more precise method based on fitting of the

experimental dependences by Boltzmann symmetrical function using nonlinear regression [26]. Then, the calculated crossing point of the tangent line in the inflection point of the Boltzmann fit with its lower asymptote determines the bandgap energy as 3.04 eV (Figure 9).

The surface area of the support and deposited layers was investigated by the measurement of adsorption isotherms of N<sub>2</sub> at 77 K. While the surface area of Liapor is only 0.15 m<sup>2</sup>·g<sup>-1</sup>, a marked increase to 1.2 m<sup>2</sup>·g<sup>-1</sup> is observed after the deposition of SiO<sub>2</sub>. Finally, the composite layer shows the largest value, 4.3 m<sup>2</sup>·g<sup>-1</sup>. The observed trend suggests that the photocatalyst specific surface area is maintained during its application.

**3.4. Outdoor Experiments.** The aim of parallel outdoor experiments was to test the photocatalytic activity of coated Liapor under sunlight. The experiments were carried out in the solar reactor depicted in Figure 2(b). Oxalic acid

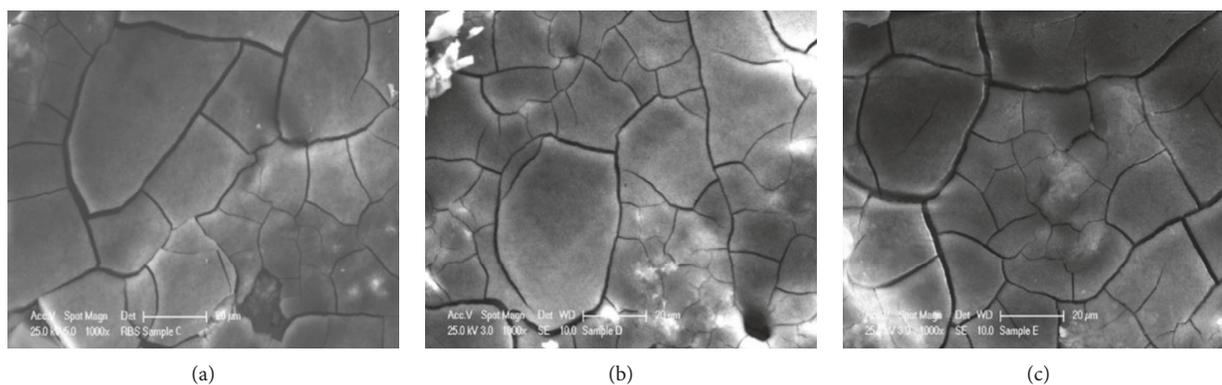


FIGURE 8: SEM images of Liapor coated with SiO<sub>2</sub> layer and two composite layers. (a) Dried at room temperature. (b) Calcined at 300°C. (c) Calcined at 300°C and washed for 6 hours.

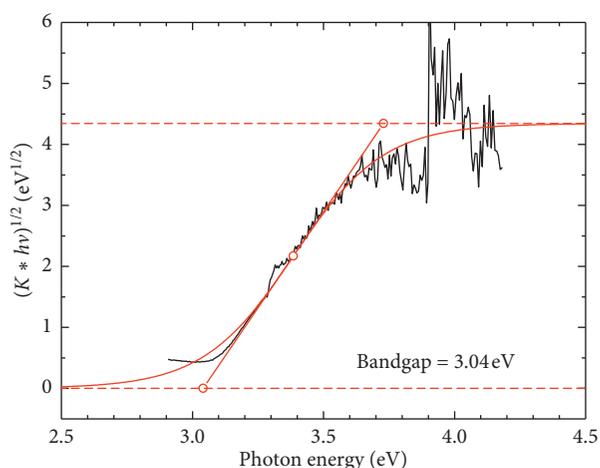


FIGURE 9: Transformed diffuse reflectance spectrum and determination of bandgap energy.

( $3.3 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ ,  $25 \text{ dm}^3$ ) was chosen as a model compound due to its relative nontoxicity that allows its usage in large amounts. During the irradiation, temperature and UV index were monitored by the ISS probe. It was observed that direct photolysis of OA proceeded in parallel to its photocatalytic degradation, although at a much slower reaction rate. Therefore, the higher amount of the coated support, that is, 200 g (60% of water surface covered) was used in order to reduce the contribution of photolysis to the total photodecomposition.

Concentration changes of OA correlated with the solar radiation intensity (Figure 10(a)). At the end of the fourth day of the irradiation, OA was practically decomposed.

An appropriate initial concentration of OA for the experiments under the applied conditions (200 g of coated support, grain size 4–8 mm) was determined on the basis of another series of experiments (Figure 10(b)). While lower concentrations of OA would be decomposed too fast under sunny weather, high initial concentration would lead to unnecessarily long degradation time.

The size of Liapor grains (1–4 mm, 4–8 mm, and 8–16 mm) was another studied parameter (Figure 11(a)). Small grains (1–4 mm) show a large specific area; however, the

smallest beads of expanded clay tend to immerse, thus resulting in the deceleration of the photocatalytic process. On the other hand, large coated grains (8–16 mm) flow easily on the water surface at the cost of a smaller specific area. Photocatalytic performance of both medium and large support grains is comparable.

The stability of the floating photocatalyst was tested by its repeated use under the otherwise same conditions (Figure 11(b)). No significant changes of the photocatalytic performance after one or two experimental cycles compared with the freshly prepared sample (200 g, grain size 4–8 mm) were observed. This fact signifies good stability and durability of the layer deposited on the Liapor substrate, a parameter important for the practical use of any photocatalyst.

### 3.5. Pilot Experiments in the Czech Republic and in Vietnam.

To study the performance of the floating photocatalyst in a scale corresponding to its intended use, pilot experiments were performed. The solar reactor in the Czech Republic (Figure 12(a)) was designed to simulate the remediation of contaminated water in rural areas, for example, in the wells that were left after the bomb attacks during the Vietnam War. It consists of the round plastic pool ( $V=7 \text{ m}^3$ ) equipped with a jet system, pump, and filter. The floating photocatalyst (coated, calcined Liapor) covered almost all water surface and was sprinkled by the jet system. As a model compound, oxalic acid (OA;  $3.3 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ ) was chosen, and instead of distilled water, ordinary tap water was used. This fact shows the importance of such type of experiments, as some cations present in water ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Fe}^{3+}$ ) tend to precipitate as insoluble oxalates. Therefore, these cations were initially removed from the solution by a sufficient excess of OA and subsequent filtration. It was found by EDX analysis that the precipitate contained predominantly Fe(III), indicating the presence of iron ions in the used tap water.

A typical course of the pilot solar experiment with OA in the presence of the floating photocatalyst is shown in Figure 12(b). Stepwise decrease of OA concentration, determined by both manganometric titration and TOC analysis, corresponds well to the day and night period. After

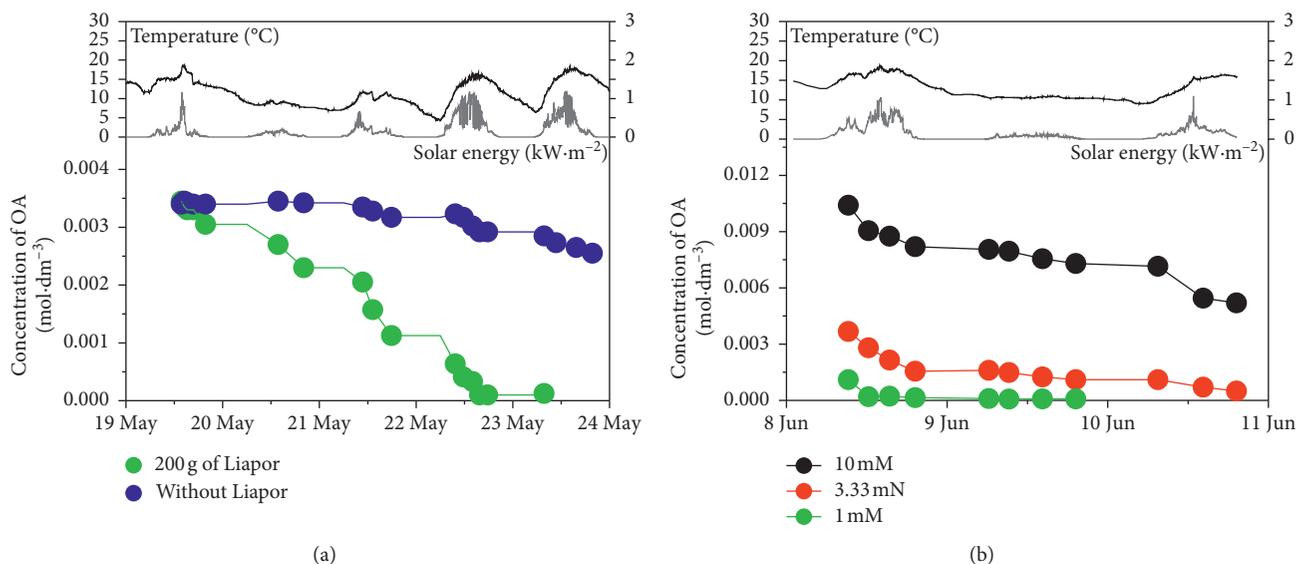


FIGURE 10: Photocatalytic degradation of OA. (a) Without (photolysis) and with coated, calcined Liapor. (b) Influence of OA concentration with coated, calcined Liapor, grain size 4–8 mm.

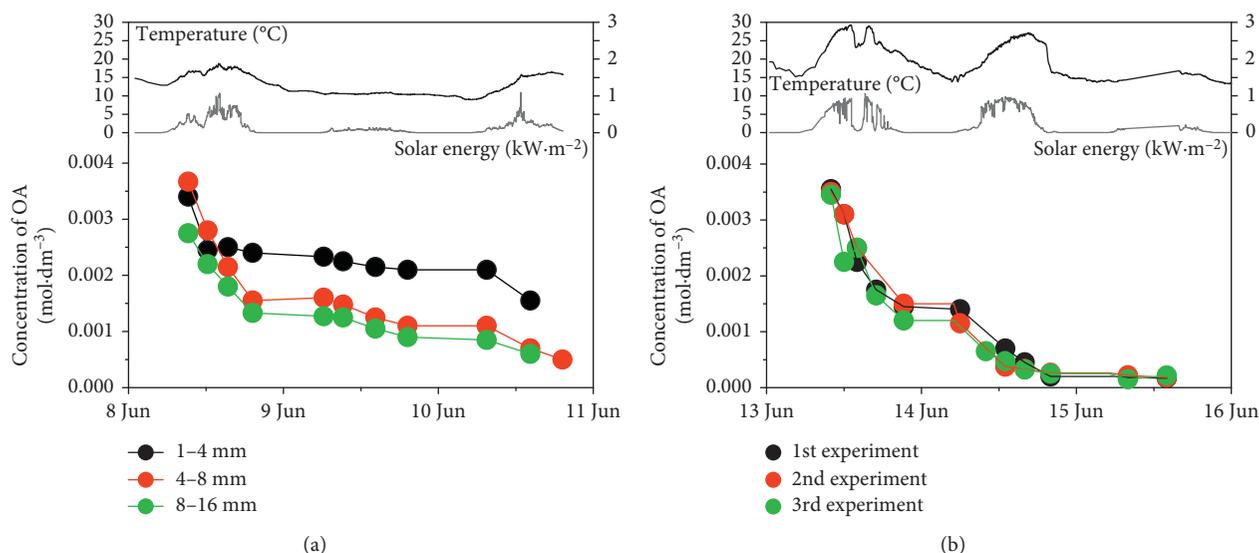


FIGURE 11: Photocatalytic degradation of OA with coated, calcined Liapor. (a) Different grain sizes (1–4 mm, 4–8 mm, and 8–16 mm). (b) Used for the first, second, and third time.

four days of irradiation, no detectable amount of OA remained in the solution and TOC dropped to 11.9% of its original value.

Comparative solar experiments were carried out in Vietnam, employing a special set of batch photoreactors (Figure 13(a)). The device consists of six glass compartments (50 dm<sup>3</sup> each) equipped with aeration, stirring, and a system preventing evaporation. About 2 cm below the solution level, metal plates are placed to prevent immersion of the floating photocatalyst. A typical daily course of solar radiation intensity is shown in the inset of Figure 13(b).

The floating photocatalyst was prepared by coating an expanded clay (analogous to the Liapor) with commercially

available TiO<sub>2</sub> suspension with inorganic additives (Protectam FN2). Two grain sizes of the floating support were tested (5 mm and 10 mm).

As a model compound, methylene blue (MB,  $3.3 \times 10^{-6}$  mol·dm<sup>-3</sup>) was used. Two hours before exposing to solar radiation, the tested solution and floating photocatalyst were left in dark to equilibrate adsorption of MB on the photocatalyst surface. Besides adsorption of MB on the photocatalyst surface, no other interaction was observed. Figure 13(b) shows time dependence of MB concentration during 6 days of solar irradiation. The decrease reflects photocatalytic degradation, in contrast to the overnight periods and the blank experiment, during which MB

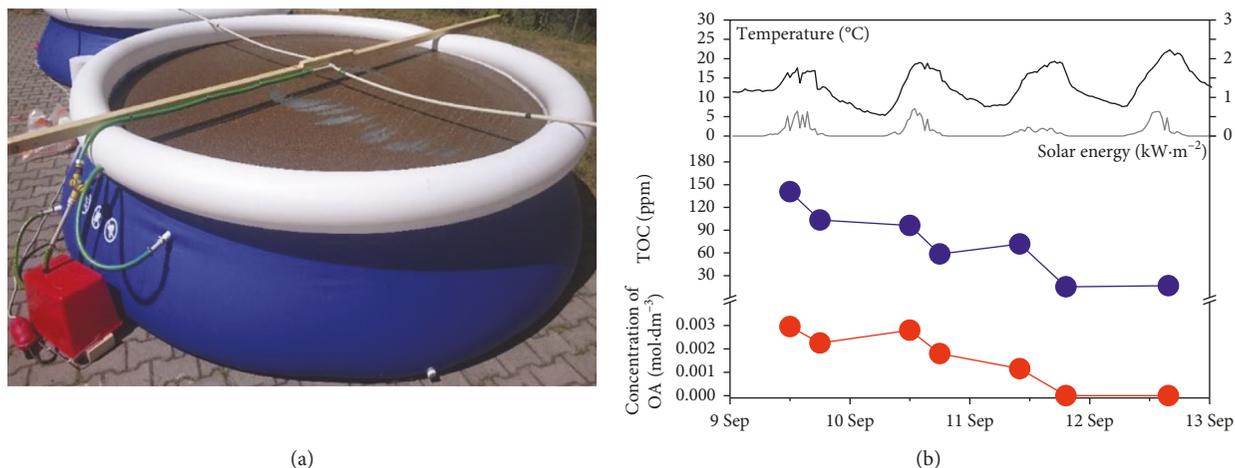


FIGURE 12: Pilot experiments in the Czech Republic. (a) Solar reactor with coated Liapor. (b) Photocatalytic degradation of OA during 4 days of solar irradiation.

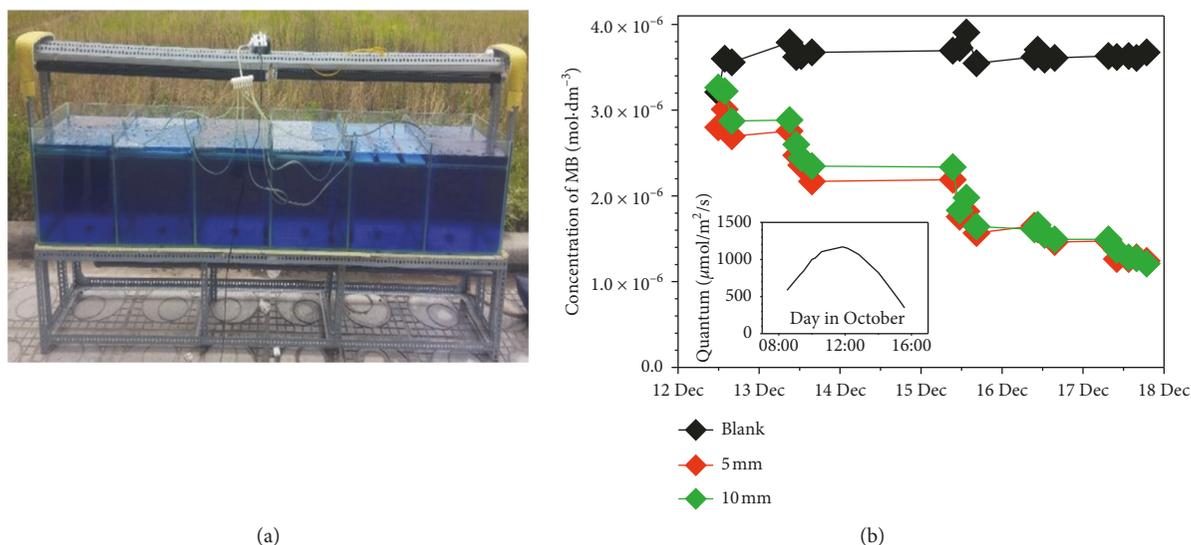


FIGURE 13: Pilot experiments in Vietnam. (a) Set of solar reactors with floating photocatalyst. (b) Photocatalytic degradation of MB during 6 days of solar irradiation.

concentration remained stable. The size of photocatalyst particles did not affect significantly the overall course of the photocatalytic degradation.

**3.6. Estimation of the Photocatalyst Performance under Real Environmental Conditions.** The intensity of solar radiation was measured and integrated during the whole period of outdoor experiments with oxalic acid. Thus, for example, in the case of the three-day experiment in the batch photo-reactor (Figure 11(b)), the integrated solar radiation reached 13.38 kWh·m<sup>-2</sup>, of which 5%, that is, 0.669 kWh·m<sup>-2</sup>, represents UVA radiation available for TiO<sub>2</sub> photocatalysis. Considering, for simplification, UVA photons of a “middle” wavelength 380 nm, the value of 0.669 kWh·m<sup>-2</sup> would correspond to 7.62 mol·m<sup>-2</sup> of incident photons in three days (for detail calculation, see Supplementary Material

(available here)). Applied to the parameters of our outdoor solar reactor and assuming the observed decrease of OA concentration, 0.082 moles of OA were mineralized by 1.23 moles of photons, which corresponds to a quantum efficiency 6.67%. This relatively high value might be partially attributed to a strong adsorption of OA on the photocatalyst surface that could cause its efficient oxidation by direct charge transfer mechanism.

The general capacity of the solar photocatalytic treatment of water can be approximately quantified. Provided that the mineralization of one organic carbon atom may require, on average, two subsequent photo-induced oxidative steps, then under the weather conditions typical of the central Vietnam (5.0 kWh·m<sup>-2</sup>·day<sup>-1</sup>, [29]), up to 0.095 moles of harmful organics can be mineralized by floating photocatalyst (e.g., Liapor with SiO<sub>2</sub>/TiO<sub>2</sub> composite coating) covering area of 1 m<sup>2</sup> of contaminated water

in 1 day, using quantum efficiency calculated above. For a depth of 1 m and the corresponding volume of 1 m<sup>3</sup>, the TOC content of contaminated water would thus be reduced by 1.14 ppm in one sunny day.

This is a promising result implying that solar photocatalysis can represent a method capable to decontaminate not only small water contents in the laboratory scale but also larger surface water amounts intended for cattle watering, fish breeding, etc. Hardly degradable toxic compounds presented in water at extremely low concentrations (such as 2,3,7,8-tetrachlorodioxin and DDT) can thus be successfully mineralized in order of days to weeks.

#### 4. Conclusions

- (i) Photocatalytic performance of SiO<sub>2</sub>/TiO<sub>2</sub> composite deposited on three different floating substrates was tested by means of 4-CP photodegradation
- (ii) Liapor with deposited SiO<sub>2</sub>/TiO<sub>2</sub> composite showed high photoactivity and long-term durability
- (iii) Coated Sorbix was less photoactive due to its high hydrophobicity
- (iv) Cork was experimentally found as a less suitable support due to its strong adsorption properties and release of soluble organic matter
- (v) SiO<sub>2</sub>/TiO<sub>2</sub> composite layer on Liapor was characterized in detail, including atomic composition and surface microscopic images corresponding to each step of the deposition process
- (vi) Pilot solar experiments demonstrated high efficiency, durability, and the ease of use of the new floating photocatalyst necessary for water decontamination
- (vii) The efficiency of the new floating photocatalyst to mineralize organic matter in real contaminated surface water under sunlight was estimated

#### Data Availability

The data used to support the findings of this study are available from the corresponding authors upon request.

#### Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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#### Supplementary Materials

Supplementary Material file contains a calculation procedure for determining the photocatalyst efficiency. (*Supplementary Materials*)

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## Research Article

# Synergistic Adsorption and Photocatalytic Activity under Visible Irradiation Using Ag-ZnO/GO Nanoparticles Derived at Low Temperature

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Ag-ZnO/graphene oxide (AG-ZnO/GO) nanocomposite was synthesized via facile aqueous solution reactions at low temperature in order to improve the photocatalytic activity for cationic dye removal under visible light irradiation. Analytical techniques were carried out in order to determine the abilities including structure, state of elements, morphology, and surface area of synthesized materials. Ag-ZnO/GO nanocomposite presented an extremely high removal rate of methylene blue (MB) not only under UV light (over 99% removal) but also under visible light (85% removal) during the same irradiation time. In this study, initial process parameters of catalyst dosage, MB concentration, and pH of the solution were also examined for MB removal efficiency effects. The proposed mechanisms for the increased removal of MB by Ag-ZnO/GO nanocomposite under visible irradiation include increased photocatalytic degradation, mainly due to increased charge transfer capacity by lowering band gap energy; minimized recombination of the excited electron-hole pairs of ZnO with the addition of Ag into the ZnO crystal lattice; and an increased adsorption capacity with the addition of GO with high surface area and semiconductor function with zero band gap energy.

## 1. Introduction

Developing semiconductor photocatalysts has been considered a promising green technology for solving environmental issues. Among various semiconductors, zinc oxide (ZnO) has been considered one of the most promising photocatalysts because of its outstanding properties, such as physical and chemical stability, low cost, and nontoxicity. Thus, ZnO has been widely used for many different applications such as in optical materials, sensors, solar energy conversion devices, and photocatalysts for pollutant treatment. ZnO also has

several advantages over TiO<sub>2</sub>—the most popular photocatalyst [1], which includes higher thermal stability and easier and less expensive synthesis [2]. However, the photocatalytic performance of ZnO is reduced because of its wide band gap (theoretical ~ 3.2 eV at room temperature) [3] and high recombination rate between photogenerated electrons from the conduction band (CB) and holes from the valence band (VB) [4]. Such a noble metal modification can also influence the surface properties, in particular, by introducing hydroxyl groups on the surface of the photocatalysts [5–7]. However, these modifications require calcination at high temperature

(400–600°C) and the consequent need for strict control which hinders large-scale production.

Graphene sheets possess a unique two-dimensional layered structure of  $sp^2$ -hybridized carbon atoms, and thus, they can exhibit novel electronic properties as zero band gap semiconductors. Ahmad et al. synthesized graphene-Ag/ZnO nanocomposite via a solvothermal method [8]. However, it is not easy to synthesize due to high levels of impurities with graphene; thus, oxidized forms are usually used as a substitute for graphene in many research studies. In addition, graphene oxide (GO) provides a large scaffold for anchoring various substances owing to its large specific surface area [9] and two-dimensional planar conjugated structure. For example, GO bonding with  $TiO_2$  or  $WO_3$  composites has been widely investigated [10, 11]. Moreover, GO-based photocatalysts can avoid the aggregation of nanoparticles anchored on graphene sheets, which can provide more reactive sites for the photocatalytic degradation process. For instance, Nasrollahzadeh et al. reported on the synthesis and use of graphene oxide/ZnO nanocomposite as a heterogeneous catalyst for the synthesis of various tetrazoles [12]. Easy separation of the GO-based photocatalysts used for organic removal from water systems offers other benefits for repeated catalyst use and wide industrial applications [13, 14]. However, most of the derived nanoparticles need to be calcinated at high temperature; thus, GO can form reduced GO (rGO) or other forms of GO. Raj Pant et al. synthesized Ag-ZnO/rGO nanocomposite in an autoclave at 140°C [15], and Gao et al. synthesized sulfonated graphene oxide-ZnO-Ag photocatalyst at 300°C [13]. Only limited reports are available for different fabrication methods of Ag-ZnO/GO to treat organic pollutants under UV light [16].

Herein, we report a novel fabrication method of Ag-ZnO/GO nanocomposite and its characterizations, and then apply it for use in effective removal of the cationic dye methylene blue (MB) in an aqueous solution. This study also aims to save energy and costs by using a novel synthesis method at low temperature, with visible lamps rather than UV lamps as the light source of the photocatalytic process. A suitable photocatalytic degradation mechanism for enhanced MB removal was also proposed.

## 2. Materials and Methods

**2.1. Preparation of Photocatalysts.** Sodium hydroxide (NaOH), silver nitrate ( $AgNO_3$ ), zinc sulfate heptahydrate ( $ZnSO_4 \cdot 7H_2O$ ), ascorbic acid ( $C_6H_6O_6$ ), and MB ( $C_{16}H_{18}N_3S$ ) were purchased from DaeJung Chemicals & Metals Co., Ltd., Korea. GO was purchased from Sigma-Aldrich Co LLC. All purchased chemicals were used without any further purification. Distilled water was used for experiments.

ZnO nanoparticles were prepared by dropwise addition of 25 mL of NaOH 0.4 mol/L into 25 mL of  $ZnSO_4$  0.2 mol/L at an approximate addition rate of 5 mL/min. After stirring with a magnetic stirrer (GLHPS-G, Global Lab., Ltd.) at a speed of 150 rpm for 60 min, the solution was kept at 60°C for 2 h.

The Ag-ZnO composite nanoparticles were prepared by adding 6 mL of ascorbic acid 0.01 mol/L and 13 mL of  $AgNO_3$  0.01 mol/L into the solution of NaOH and  $ZnSO_4$ , while stirring under the same condition as in the first experiment, and again the solution was kept at 70°C for 2 h.

For the preparation of Ag-ZnO/GO, the steps of the Ag-ZnO synthesis procedure were repeated. At the same time, 50 mg of GO was mixed into 50 mL water in an ultrasonicator (D250H, DAIHAN Scientific, Co., Ltd.) for 30 min at room temperature. The two solutions were then mixed, and the final solution obtained was kept at 70°C for 2 h. In the last step, the synthesized products were centrifuged and washed with deionized water several times and dried in a vacuum at 70°C for 24 h.

**2.2. Characterization.** The synthesized reaction products were characterized by X-ray diffraction (XRD; Bruker AXS D8 ADVANCE) to identify the structure and phase composition. Wide-angle patterns were recorded from  $2\theta = 10^\circ$  to  $80^\circ$  using a step size of  $0.1^\circ$ . Their surface morphologies and microstructures were examined using field emission scanning electron microscopy (FE-SEM; JEOL, JSM-6500F, 10 kV) and transmission electron microscopy (TEM; JEOL, JEM-2100F). Composition mapping of the major elements on the material surface was carried out using energy dispersive X-ray spectroscopy (EDS; JEOL, JSM-6500F). The surface compositions and chemical states were measured by using X-ray photoelectron spectroscopy (XPS; Thermo Fisher Scientific, ESCALAB 250XI). The specific surface areas of the compounds were determined by the Brunauer–Emmett–Teller (BET) method using nitrogen gas adsorption. Room temperature photoluminescence (PL) spectra were recorded using a fluorescence spectrometer.

The visible light absorption of the synthesized products was measured in the range of 400 to 800 nm using a UV-Vis spectrophotometer (GENESYS™ 10S UV-Vis., USA) with integrating sphere accessories. To plot the calibration curve of MB dye, aqueous dye solutions were prepared at a concentration ranging from 1 to 25 mg/L by using distilled water. The concentrations of the MB solutions were determined using the obtained calibration curve. The dye removal efficiency was calculated based on following equation:

$$\text{Removal efficiency (\%)} = \frac{C_0 - C}{C_0} \times 100\%, \quad (1)$$

where  $C_0$  (mg/L) is the concentration of the MB solution at the initial time  $t = 0$  (min) and  $C$  (mg/L) is the concentration after the treatment reaction in a dark condition or after UV-visible light irradiation.

**2.3. Photocatalytic Activity Measurement.** The photocatalytic activity of the synthesized materials was estimated by using an illumination system consisting of five lamps [visible lamp (EFTR 20EX-D, Kumho Co., Ltd., Republic of Korea)/UV lamp (AL-2220D1 20W, Alim Co., Ltd, the Republic of Korea)] as irradiation sources. In a typical process, 20 mg of the synthesized photocatalyst was suspended in 20 mL of MB

with a concentration of 15 mg/L in a cylindrical glass reactor. Before starting the photocatalytic reaction, the suspension was stirred for 30 min in a dark condition to obtain an adsorption/desorption equilibrium between the dye and the photocatalyst. Photocatalytic reactions were carried out under a stable condition (stirring speed of 80 rpm at intervals of 3 h under light irradiation).

To clarify the dominant radical or ion on the photocatalysis reaction, the experiments using different radical scavengers were performed. Scavengers including *tert*-butyl alcohol, benzoquinone, ammonium oxalate, and  $K_2S_2O_8$  were used for  $OH^\bullet$ ,  $O_2^\bullet$ , holes and electrons, respectively. The experiment was carried out similar to the removal experiment with the added radical scavenger (0.1 mmol).

### 3. Results and Discussions

#### 3.1. Characterization of Material

**3.1.1. XRD Pattern Analysis.** Figure 1 showed the XRD patterns of the ZnO and Ag-ZnO/GO samples. The Ag-ZnO/GO spectrum included a diffraction peak at  $2\theta=11.5^\circ$  of pristine GO [17, 18], indicating that the major form of graphene in the synthesized material was GO. In both ZnO and Ag-ZnO/GO spectra, the observed diffraction peaks at  $2\theta=32, 34,$  and  $36^\circ$  confirmed the presence of the hexagonal wurtzite structure of ZnO. In general, the intensity of the diffraction peaks decreases greatly with the increase in doping concentration [19]. Thus, it can be observed that the peak intensity of ZnO in the Ag-ZnO/GO sample was decreased as compared with that of the ZnO sample. Besides, the XRD pattern of Ag-ZnO/GO mainly showed a small silver peak at  $2\theta=38^\circ$  [20–22], and this confirmed the doping activity of Ag onto the structure of ZnO. Simultaneously, a small amount of Ag entered the ZnO crystal structure, as confirmed by the broadening at  $2\theta=32, 34,$  and  $36^\circ$  in the Ag-ZnO/GO peaks compared to ZnO peaks [23, 24]. The value of full width at half maximum (FWHM) of diffraction peak is showed on Table 1.

**3.1.2. Morphology and Microstructure by SEM and TEM Analysis.** FE-SEM and TEM analyses were used to identify the morphology and microstructure of the synthesized materials. The SEM images of ZnO before addition of Ag and GO exhibited high degree of uniformity in the nanosized ZnO particles (Figures 2(a) and 2(b)). When GO was introduced into the composites, numerous Ag-ZnO nanoparticles were deposited on the GO sheets (Figures 2(c) and 2(d)). In the Ag-ZnO/GO heterostructure, GO sheets were consistently decorated with Ag and ZnO nanoparticles. TEM images revealed a hexagonal shape for ZnO (Figure 2(e)) with a diameter 50–60 nm, which is in good agreement with the diameter of ZnO revealed in SEM images. Figure 2(f) shows the TEM image of Ag-ZnO/GO composite, demonstrating the attendance of few-layered GO sheets decorated with Ag and ZnO particles which may result in better adsorption capacity and electron-hole separation.

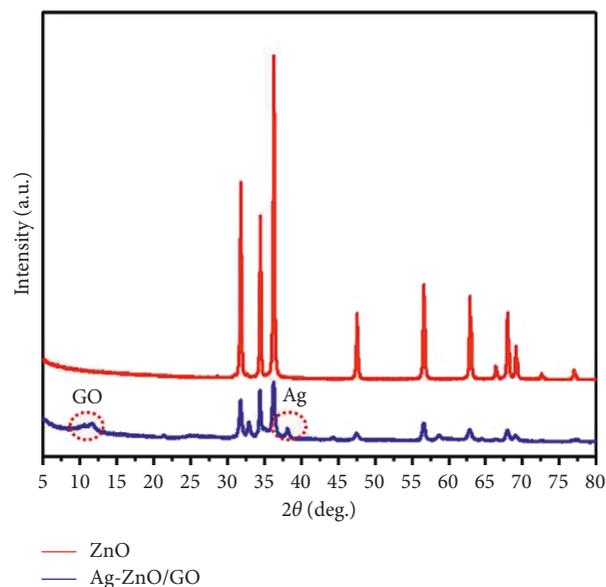


FIGURE 1: XRD patterns of the ZnO and Ag-ZnO/GO samples.

TABLE 1: FWHM in the samples.

Sample	FWHM ( $cm^{-1}$ )
ZnO	0.2210
Ag-ZnO/GO	0.2377

The chemical compositions of ZnO and Ag-ZnO/GO were analyzed by energy dispersive spectrometry (EDS) and mapping technique in conjunction with SEM (Figure 3). All the peaks were ascribed to Zn, Ag, and O in the ZnO sample, and peak of C elements appeared in the composite sample. The mapping results confirmed the presence and uniform distribution of zinc, silver, and oxygen on the GO surface. In combination, these elemental mapping and SEM and TEM results demonstrate the capability of GO to function as an effective scaffold for ZnO and silver.

**3.1.3. XPS Analysis.** The surface element composition and chemical state of the as-synthesized samples were analyzed by XPS analysis, as shown in Figure 4. The peaks of Zn  $2p_{3/2}$  and Zn  $2p_{1/2}$  of the synthesized ZnO and Ag-ZnO/GO were observed at around 1,021.8 eV and 1,045.1 eV, respectively, which are very similar to the peaks of pure ZnO (Figure 4(a)). This finding, therefore, demonstrated the presence of the  $Zn^{2+}$  form in both samples [19, 25]. In the C1s spectra of Ag-ZnO/GO (Figure 4(b)), the presence of C was attributed to the GO addition. Compared to ZnO, the C peaks of the Ag-ZnO/GO nanocomposite were shifted toward a slightly lower binding energy. In the ZnO sample, the presence of C originated from the vacuum oil used in the pretreatment system before the XPS testing. The four peaks in the Ag-ZnO/GO sample at 282.4, 284.8, 286.1, and 288.6 eV were ascribed to Zn-C, C-C/C=C, Zn-O-C, and C=O, respectively [26, 27]. The presence of abundant carbon species on the surface of the Ag-ZnO/GO composite increased the photodegradation because it facilitated the

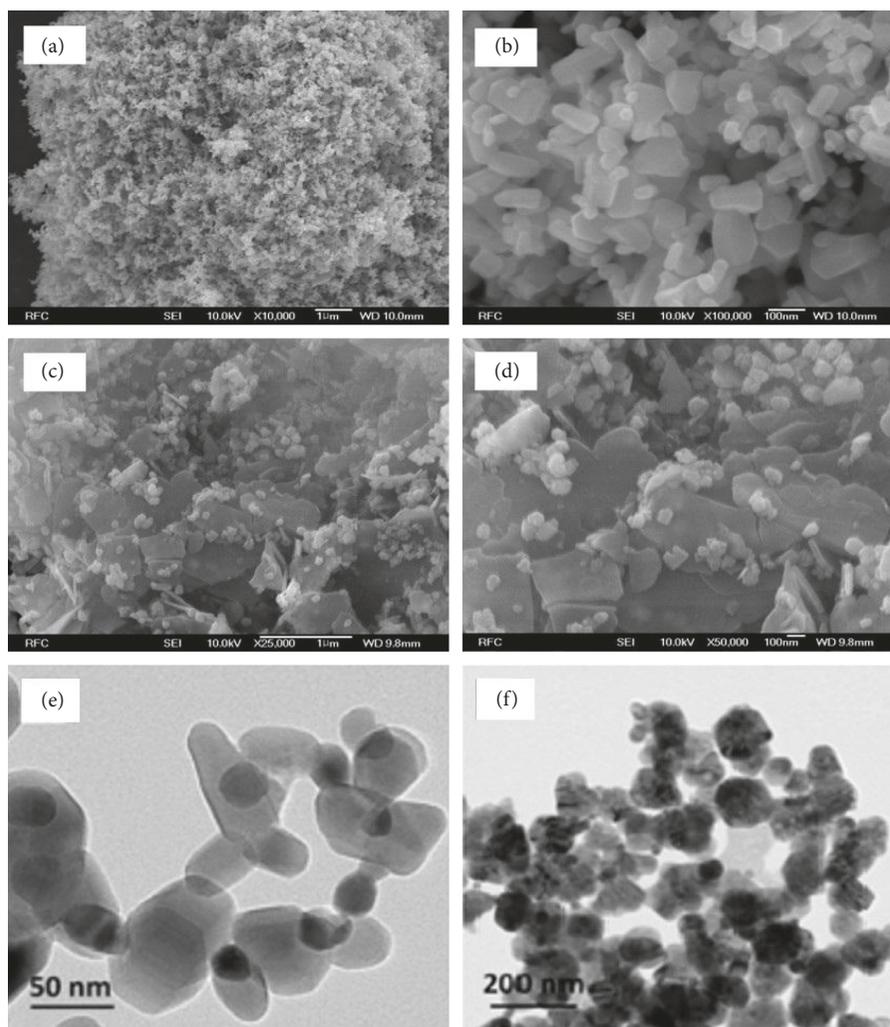


FIGURE 2: FE-SEM and TEM analyses of synthesized materials.

contact with organic pollutant molecules. The high resolution spectra of the strong O1s peak (Figure 4(c)) at 531.3 eV in the ZnO sample was due to the oxygen in the ZnO crystal lattice (Zn-O bonds) [28, 29]. Two O1s peaks at 531.5 and 531.8 eV in the Ag-ZnO/GO composite sample revealed the presence of surface oxygen complexes in the carbon phase [21, 28]. These oxygen-containing groups increased the photocatalytic activities due to their involvement in the production of active radicals, which play an important role in the photodegradation process. The Ag 3d XPS peaks of Ag-ZnO/GO, shown in Figure 4(d) located at 367.7 and 374.0 eV, were ascribed to Ag 3d<sub>5/2</sub> and Ag 3d<sub>3/2</sub>, respectively [30, 31]. The XPS results were in good agreement with the aforementioned XRD and EDS results. These observations in Figure 4 further confirmed the successful preparation of Ag-ZnO/GO nanoparticles and viability of Ag-ZnO/GO as a superior nanocomposite material.

**3.1.4. UV-VIS Reflectance Spectra and Band Gap.** The optical absorption properties of the synthesized nanomaterials were investigated by UV-VIS reflectance spectra (Figure 5). The doping activity induced a shift from the UV light

absorption of ZnO to the visible light absorption of Ag-ZnO/GO. The optical band gaps of the synthesized materials were calculated by using the following Tauc equation:

$$\alpha h\nu = A(h\nu - E_g)^n, \quad (2)$$

where  $\alpha$  is the absorption coefficient,  $E_g$  is the band gap,  $A$  is a constant, and  $n$  is an index that characterizes the optical absorption process (for direct band gap semiconductor material  $n = 1/2$ ). By extrapolating the linear region of the plot  $(\alpha h\nu)^2$  vs.  $h\nu$ , the band gap could be estimated. The band gap values for ZnO and Ag-ZnO/GO are given in Figure 5. Band gap of Ag-ZnO/GO (2.92 eV) is smaller than that of synthesized ZnO (3.15 eV). This decreased band gap may have been due to the introduction of silver and carbon as dopants in the ZnO lattice. Similar phenomena have been observed in ZnO-based material systems in other studies [19, 32, 33].

**3.1.5. BET Surface Area.** The specific surface area of the synthesized materials was measured using the BET method with N<sub>2</sub> adsorption-desorption (Figure 6). The identified surface area of Ag-ZnO/GO was almost 3.6 times larger than

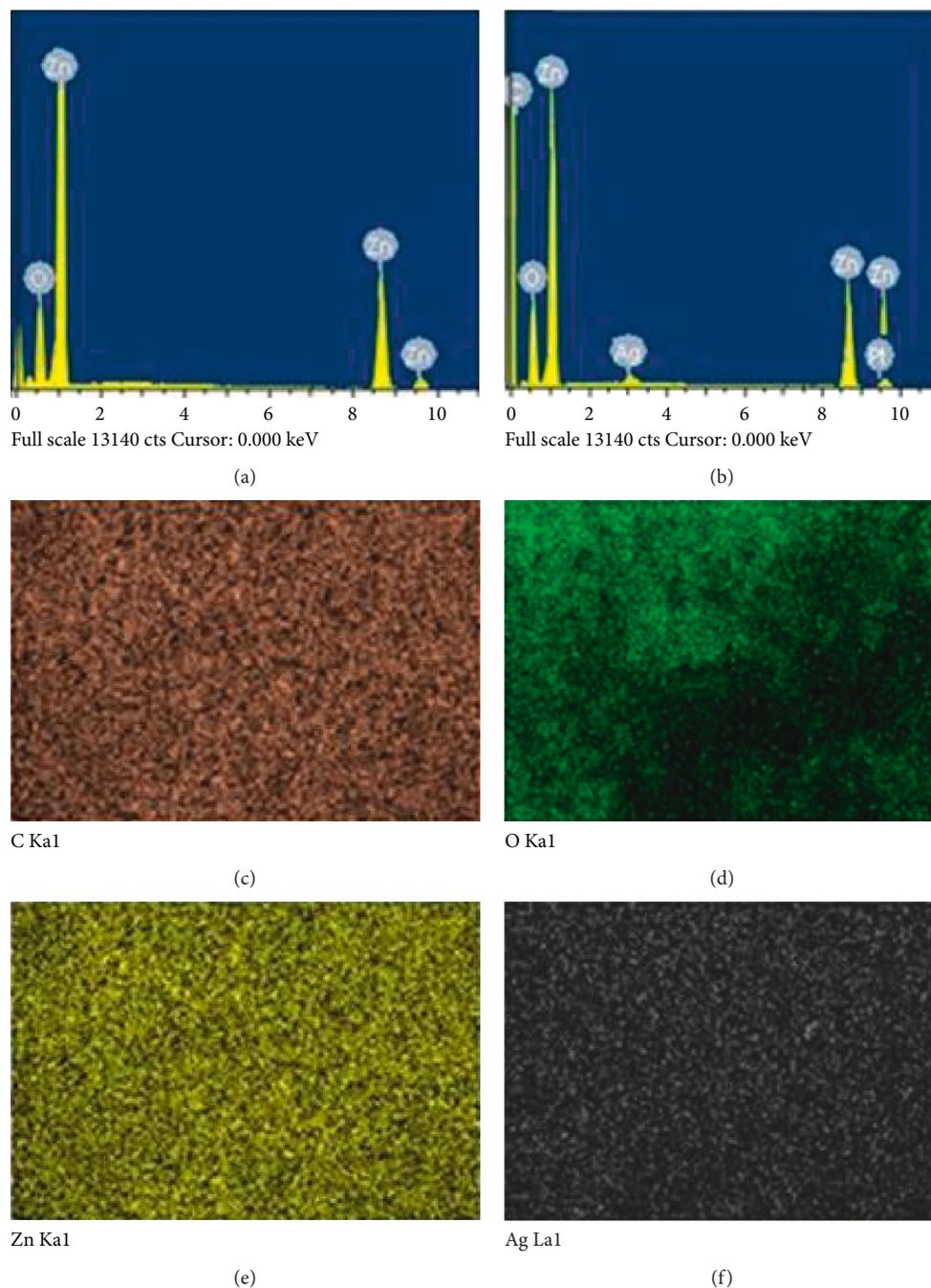


FIGURE 3: EDS and mapping analyses of synthesized materials.

that of ZnO. With Ag-ZnO/GO present in a dark condition, pollutant adsorption is mainly assisted by the increased specific surface area ( $S_{\text{BET}}$ ). In general, graphene has a very high specific surface area [34], and thus, it could provide a high adsorption capacity. GO, the oxidized form of graphene, contains oxygen functional groups on its surface that can become adsorption sites. Therefore, the enhanced degradation capacity under visible light can be attributed to the adsorption power of GO combined as a semiconductor or adsorption substrate [35, 36]. In addition, the increased pore size of Ag-ZnO/GO nanocomposite could lead to the increases in adsorption efficiency.

**3.1.6. PL Spectra.** The PL spectra of as-prepared ZnO and Ag-ZnO/GO at room temperature are presented in Figure 7. As observed, the PL intensities of the samples increase in the following order: Ag-ZnO/GO and ZnO. The PL intensity of the composite sample is weaker as compared with that of the ZnO sample, indicating that the fluorescence of the composite is quenched more efficiently than that of ZnO. It also indicated that the incorporation of ZnO with Ag and GO can improve the separation of photoinduced electrons and holes. Thus, there is a high agreement with the order of PL intensities when compared with the result from the removal experiments, and the recombination process can be

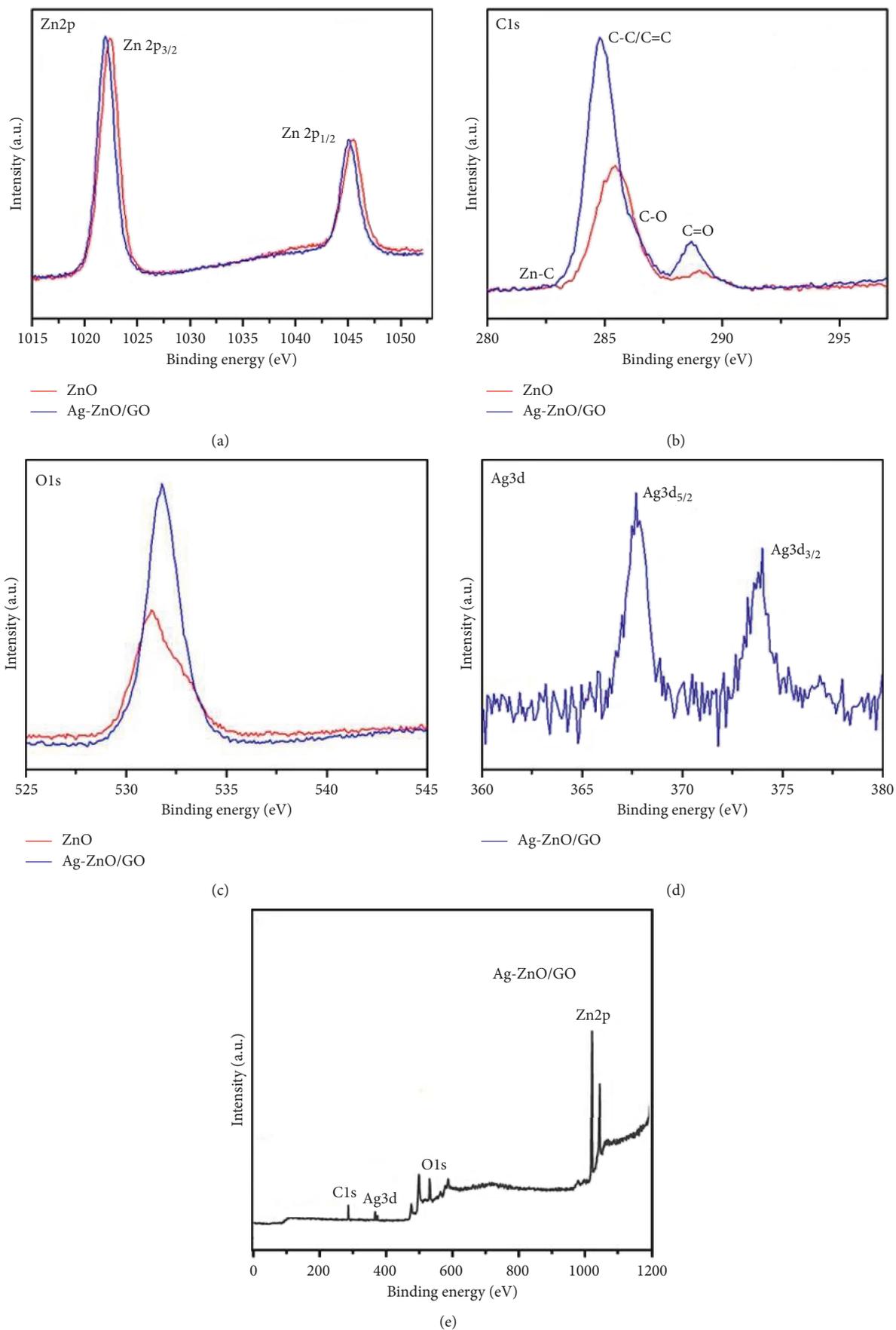


FIGURE 4: XPS analyses of synthesized materials.

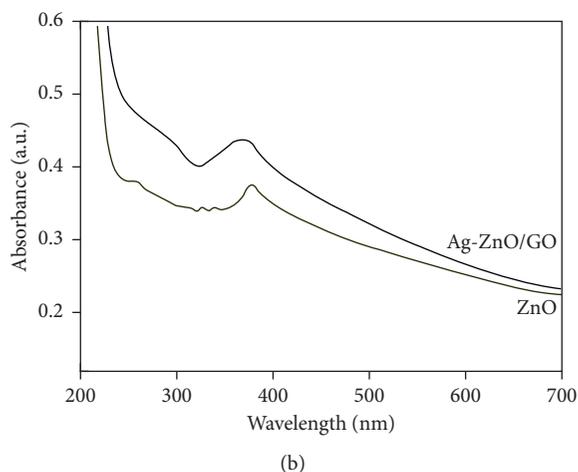
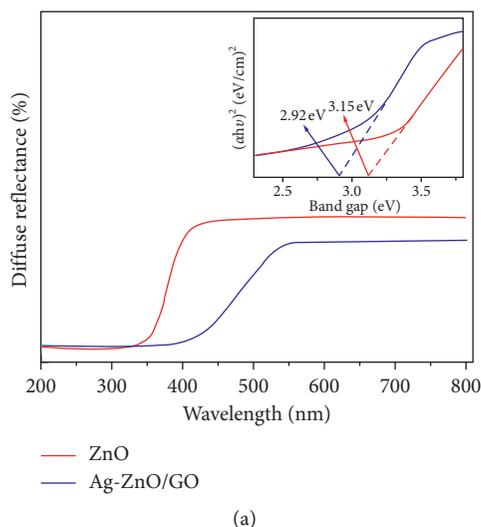


FIGURE 5: UV-VIS reflectance spectra and band gap of synthesized materials.

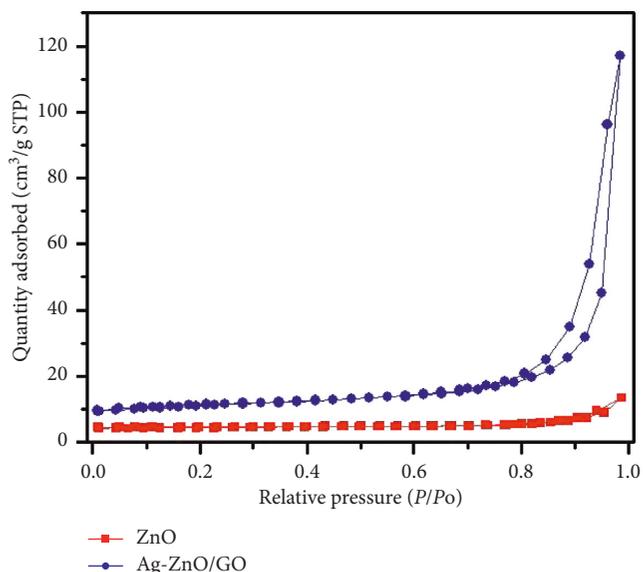


FIGURE 6: BET analysis data of synthesized materials.

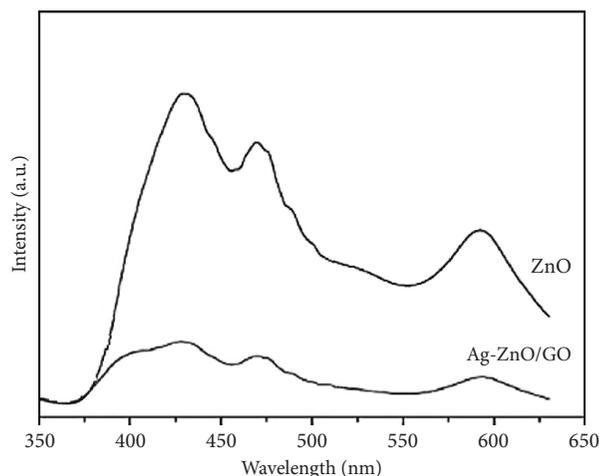


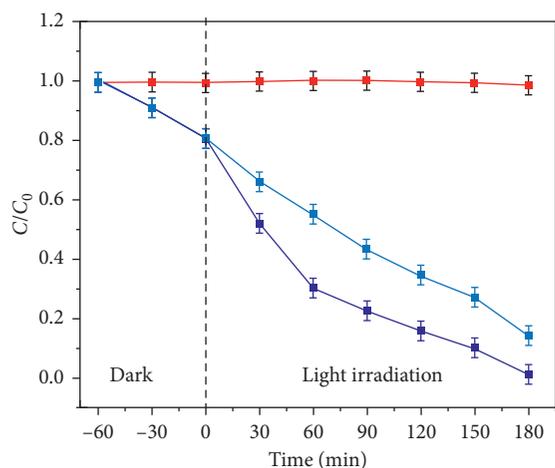
FIGURE 7: PL spectra of synthesized materials.

significantly suppressed through the combination of ZnO with Ag and GO.

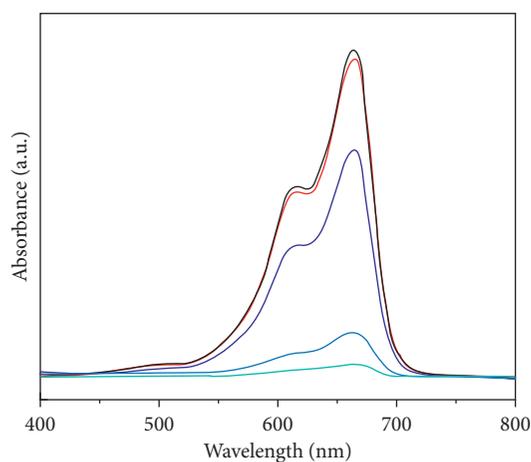
**3.2. Removal of MB Dye Using Synthesized Materials.** It is commonly accepted that most dyes are resistant to biodegradation and direct photolysis, and many N-containing dyes such as MB undergo natural reductive anaerobic degradation to yield potentially carcinogenic aromatic amines [31]. In this study, therefore, MB was chosen as a model contaminant to evaluate the photocatalytic activity of the synthesized photocatalysts.

Figures 8(a) and 8(b) show the UV-Vis absorption spectrum and removal efficiency of MB degraded by using synthesized materials under dark and light (visible and UV) irradiation conditions, respectively. ZnO did not show any significant adsorption of MB, when the addition of Ag-ZnO/GO into the MB solution without any light source afforded an MB removal efficiency of around 20%. After the adsorption, visible light or UV light was directed at the MB removal system containing Ag-ZnO/GO added into MB solution as a photocatalyst. The addition of Ag-ZnO/GO into the MB solution under visible light and UV light irradiation increased the MB removal efficiency after 3 h by up to 85% and 99%, respectively. The comparison of the light absorption results between the dark and light irradiation conditions clearly demonstrated that most of the MB removal effects were due to photocatalytic degradation by the Ag-ZnO/GO nanocomposite. Under visible light, MB removal was significantly increased by Ag-ZnO/GO because of the combination effects of the adsorption and photocatalytic degradation. Under UV conditions, removal efficiency reached up to 99% because of the high photon energy in UV light, and so photodegradation could occur more strongly than under the visible light. The photocatalytic activity by Ag-ZnO/GO under visible light is explained in the mechanism section.

To clarify the role of photogenerated radical species in the removal process, different scavengers were used. It is observed from the scavenger tests' result that the degradation level of MB was significantly inhibited when tert-butyl



(a)

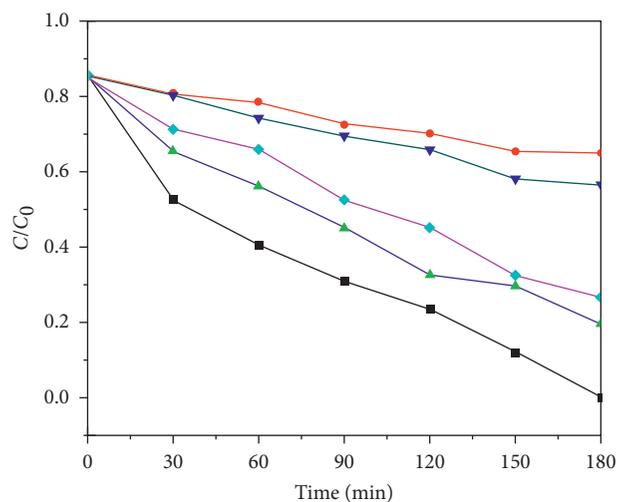


(b)

FIGURE 8: Removal of MB by using synthesized materials.

alcohol and ammonium oxalate were added. Thus, it is clear that most of the reactive radicals responsible for catalytic activity are found to be  $\text{OH}^\bullet$  and photogenerated holes (Figure 9).

Synthesized composite material have higher surface area and greater numbers of active sites as compared with ZnO, where the photogenerated charge carriers react with absorbed molecules to form hydroxyl and superoxide radicals. A set of experiments was carried out in order to check the reusability and stability of the composite catalysts. The photodegradation experiment was duplicated eight times after the centrifugation and cleaning process. As shown in Figure 10, the photocatalytic activities were almost stable in the first 4 cycles. From the 5<sup>th</sup> cycle, the removal of MB was decreased; it might be due to the loss of adsorption properties after several centrifugation and cleaning process. The particles readily form aggregates, leading to the loss of the



Without scavenger      Ammonium oxalate  
 tert-Butyl alcohol       $\text{K}_2\text{S}_2\text{O}_8$   
 Benzoquinone

FIGURE 9: Evaluation of reactive radical species using various scavengers for photocatalytic degradation of MB by using Ag-ZnO/GO.

original structure and active sites, thus decreasing the photocatalytic efficiency.

**3.3. Effect of Initial Process Parameter.** pH of the solution has been reported as one of the most important factors affecting the removal efficiency of organic pollutants by photocatalytic processes in an aqueous solution [37, 38]. Interpreting the pH effects on the MB dye removal process is a difficult task because it is affected by multiple factors. The effect of pH on the removal of MB dye was investigated in the pH range 3 to 12. The pH of the point of zero charge (pH pzc) of ZnO was about 8.6 [39]. At pH above pH pzc, the surface of the ZnO particles was mostly positively charged. As the solution pH increases from the acidic range up to pH pzc of ZnO ( $\text{pH} < 8.6$ ), the decreased  $\text{H}_3\text{O}^+$  concentration produces less repulsion of Ag-ZnO/GO with the positively charged MB molecules, resulting in increased adsorption of MB. As the solution pH further increases above pzc ( $\text{pH} > 8.6$ ), the increased  $\text{OH}^-$  produces more electron repulsion of Ag-ZnO/GO with negatively charged MB molecules, leading to less adsorption. Therefore, pH 8.5–9 was chosen as the optimal pH for MB adsorption (Figure 11(a)).

Figure 11(b) shows the effects of different Ag-ZnO/GO loadings on the MB removal process under visible light irradiation. As the dosage of Ag-ZnO/GO increased up to 1.0 g/L, the MB removal effect also increased. The increased Ag-ZnO/GO dosage led to more active sites for adsorption and thus more moiety availability for photocatalytic degradation of MB molecules. However, even the MB removal efficiency decreased as the dosage loading was increased above 1 g/L. At higher dosages, there was excessive increase in the amount of suspended Ag-ZnO/GO, with excessive addition, disturbing the penetration of visible light into the reaction system. This also led to reduction in the generation

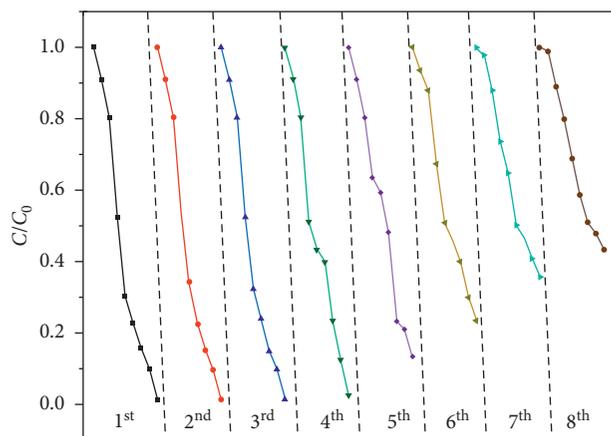


FIGURE 10: Reusability of the synthesized composite material.

of the electron-hole pairs and subsequent reduction in the production of oxy-radicals and hydroxyl radicals [40]. Furthermore, excessive photocatalyst dosage increases the pollutant removal costs. Hence, 1 g/L was determined to be the optimum Ag-ZnO/GO dosage.

Different initial MB solution concentrations, ranging from 1 mg/L to 25 mg/L, were used to evaluate the MB removal effect by Ag-ZnO/GO (Figure 11(c)). The MB removal efficiency decreased when the initial MB concentration was more than 15 mg/L within 3 h of irradiation. When the MB concentration was beyond the limit of 15 mg/L, the MB molecules adsorbed on the adsorbent/photocatalyst surface repulsed further MB molecules from approaching the adsorbent/photocatalyst, thereby decreasing MB removal. In addition, a high initial MB concentration hindered visible light penetration due to increased turbidity, as explained in the previous section, which decreased the light irradiation effect for photocatalytic degradation of MB [41, 42].

**3.4. Photocatalytic Mechanism.** Three mechanisms proposed to explain the increased photocatalytic degradation of MB dye by Ag-ZnO/GO under visible light irradiation are schematically shown in Figure 12.

The first proposed mechanism for the increased MB removal is associated with GO addition to the photocatalytic system (Figure 12(a)). GO was used as a better substrate for the photocatalytic reaction by increasing the surface area of the photocatalyst. Moreover, the photocatalytic degradation efficiency of MB by Ag-ZnO/GO was improved by combining it with a zero band gap semiconductor, GO [43, 44]. Some previous studies have reported that GO can also enhance the photocatalytic ability of ZnO under visible light irradiation due to

resonance effects, including the increased surface area with added GO and increased formation of  $\pi$ - $\pi^*$  interactions between the dye molecules [25]. The high surface area of GO can contribute to the effective adsorption of MB molecules on the photocatalyst surface. MB is a sensitive chromophore that absorbs light in a wide range of wavelengths, including the visible region [45, 46], and thus, MB molecules easily enter an excited status. The electrons in the excited MB\* can jump to the conduction band (CB) of ZnO through GO [47] and then be transferred to various Ag levels (Figures 12(b) and 12(c)). This series of excited electron transfer can minimize or delay the recombination of electrons with holes. Therefore, the excited electrons can have more delayed recombination, while simultaneously increasing the charge transfer capacity from the valence band (VB) to the CB of ZnO.

The second mechanism for the enhanced photocatalytic degradation of MB could be due to the Ag doping effect into the ZnO crystal lattice (Figure 12(c)). It is well known that band gap is a region of energy with no allowed states. The density of states versus energy depends on the chemical composition of the material, and the state density distribution will be changed if the chemical composition is changed. In this case, Ag dopant is the impurity, so the chemical composition was changed by doping. When the doping density is high enough, the dopant states generate a band. If this band is very close to the valence or conduction band edge, the band gap will decrease. The electrons transferred to the CB of ZnO tend to be transferred to Ag at that time, which prevents delay of the recombination of the excited electrons and holes. Addition of Ag led to the formation of “stairs” that allow the excited electrons to move easily to higher energy levels with visible light irradiation rather than directly moving down to the holes. The minimized recombination of the excited electrons in the CB with the holes in the VB can increase the opportunity for the production of oxy-radicals by reaction with O<sub>2</sub> molecules, leading to the oxidative degradation of MB molecules.

The third proposed mechanism is based on the narrowed band gap of the semiconductor (Figure 12(b)). The major limitation of ZnO is its restriction to UV light irradiation because of its wide band gap. This weakness was improved through Ag doping into the ZnO lattice by narrowing the band gap. Dotted green lines (Figure 12(c)) represent a new band gap for ZnO, which was narrowed by the interaction between ZnO, Ag, and GO during the synthesis of the Ag-ZnO/GO nanocomposite [48]. The major oxidative and reductive processes for the photodegradation of MB by using Ag-ZnO/GO with a narrowed band gap under visible light illumination can be explained as shown in equation (3) to (11).



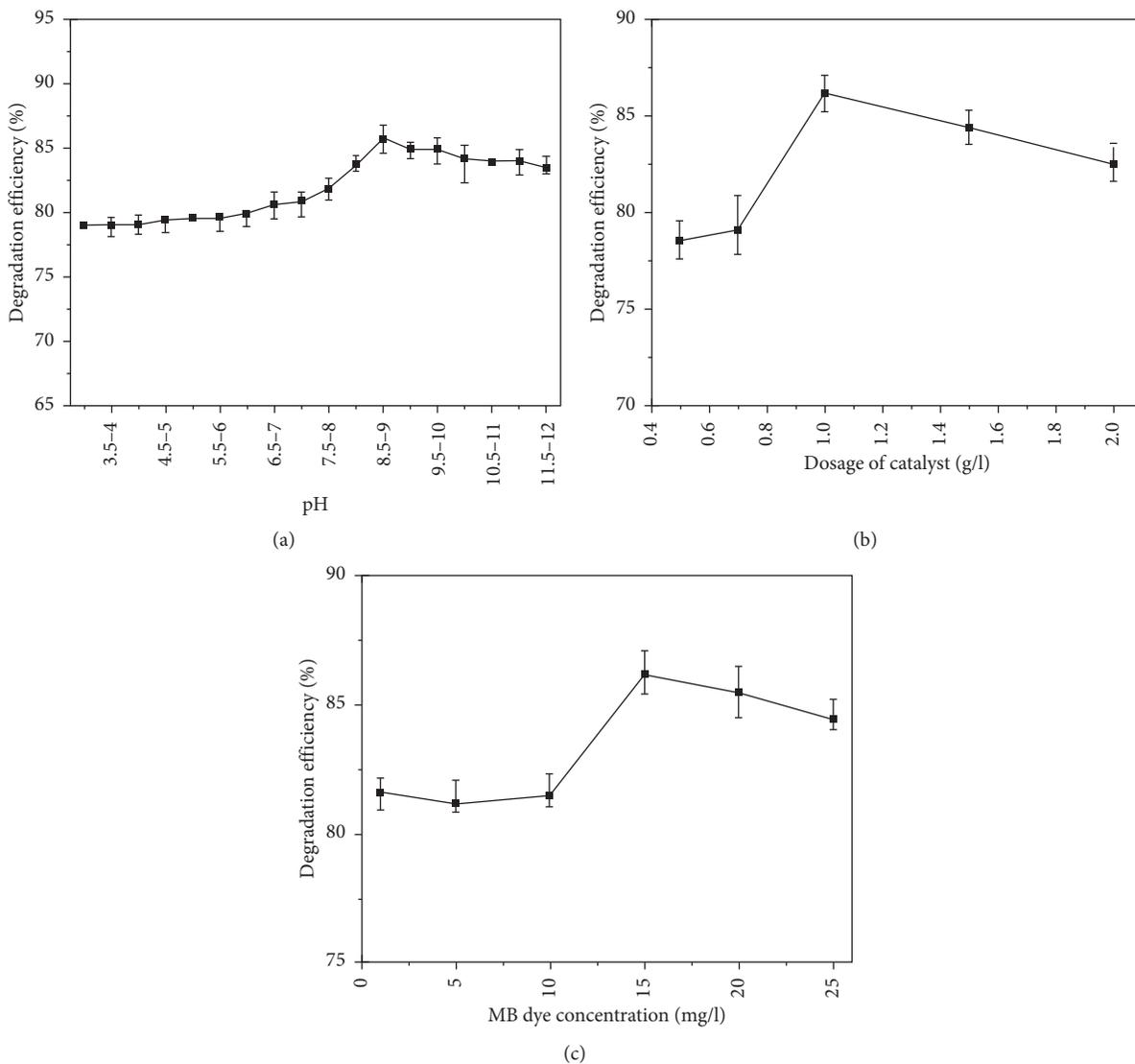


FIGURE 11: Effect of the initial parameter on the MB removal efficiency.

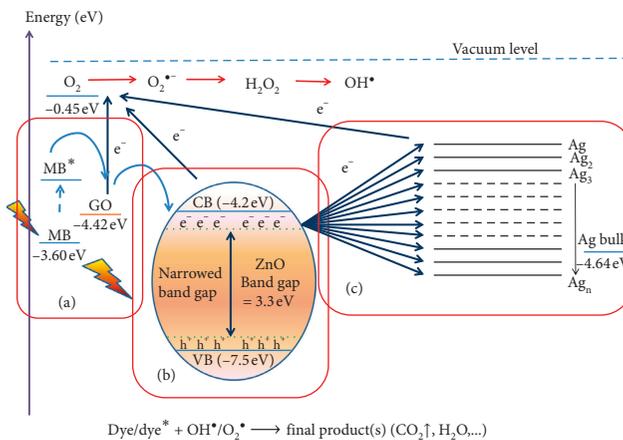
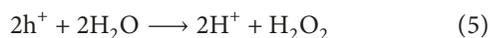
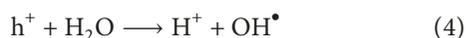
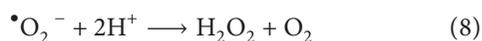


FIGURE 12: Proposed mechanism for MB removal using synthesized material.

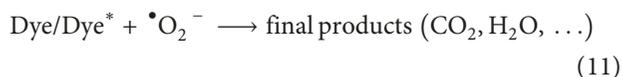
TABLE 2: Comparison between previous and current studies for MB removal using photocatalytic degradation.

Photocatalyst	Chemical ingredients	Calcination temperature	Light source	Adsorption	Photocatalysis	Total removal	Remark	Ref.
Sulphonated GO-ZnO-Ag	Zn(CH <sub>3</sub> COO) <sub>2</sub> ·2H <sub>2</sub> O, HMTA, EG, AgNO <sub>3</sub> , HCl, ClCH <sub>2</sub> CH <sub>2</sub> SO <sub>3</sub> H, AgNO <sub>3</sub> , NaNO <sub>3</sub> , KMnO <sub>4</sub> , H <sub>2</sub> O <sub>2</sub> , H <sub>2</sub> SO <sub>4</sub>	160	Visible	20%	78%	98%	Sulfonated GO high calcination temperature	[13]
Ag-ZnO/RGO	GO, bis-hexamethylene triamine, Zn(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O, AgNO <sub>3</sub> , ethanol	140, in autoclave	Visible		Not separated	65%	Reduced GO high calcination temperature in autoclave	[15]
Graphene-Ag/ZnO	Graphene, EG, CH <sub>3</sub> COOAg, Zn(CH <sub>3</sub> COO) <sub>2</sub> ·2H <sub>2</sub> O, NaOH	160	Visible	28.6%	65.6%	94.4%	Graphene expensive high calcination temperature	[8]
Ag/ZnO/GO	Graphite oxide, ZnO, AgNO <sub>3</sub>	55	UV		Not separated	98%	GO UV light high energy safety issue	[16]
Ag-ZnO/GO	Graphene oxide, AgNO <sub>3</sub> , ZnSO <sub>4</sub> ·7H <sub>2</sub> O, C <sub>6</sub> H <sub>6</sub> O <sub>6</sub>	70	Visible UV	25% 25%	60% 74%	85% 99%	GO visible light low energy high safety UV light high energy safety issue	This study This study

## (I) Oxidative reactions with holes

(II) Reduction reaction with O<sub>2</sub>

## (III) Photocatalytic oxidation with oxy-radicals



3.5. *Energy and Cost Issue.* Nowadays, the demand and market for the use of nanoparticles or nanocatalysts in pollutant removal are increasing. As discussed above, ZnO nanoparticle is one of the most promising materials for wastewater treatment. Performance of ZnO can be enhanced by adding some ingredients to make better nanocomposite. The methods currently developed for making better ZnO nanomaterials mainly consist of sol-gel template and hydrothermal methods. However, the requirement of high crystallinity is a major problem in ZnO synthesis. With the

sol-gel method, calcination of gels or thermal annealing of emulsions is therefore required to induce crystallization of the nanoparticle, and thus, normally a high temperature of more than 200°C is required. Hydrothermal methods are directly carried out at slightly lower temperatures than sol-gel methods (but not less than 120°C). However, nanocrystals formed with hydrothermal methods agglomerate and thus are insoluble in most solvents, and thus, some stabilizing agents are required to prevent agglomeration. Their characteristics from previous relevant study outcomes are summarized in Table 2 with comparisons.

The search for a simple and economic synthesis method to derive nanoparticles with good size and shape at low temperature is still an open challenge. The ability to produce nanomaterials at lower temperatures is needed for the purpose of saving energy and increasing safety for large-scale production. In this study, we demonstrate that it is possible to cost effectively produce nanomaterials at low temperature in considerable quantities, with increased safety in a wide range of applications. By adding the noble metal Ag as a dopant and GO as a high surface area adsorption substrate, firstly, our nanomaterial can work excellently for adsorption and also as a photocatalyst, even under visible light. Researchers have previously used UV light in their studies to irradiate the photocatalyst, and the removal efficiency of their process was very high. However, the price of a UV lamp is at least two times as high as the price of a visible lamp. Furthermore, UV waves are invisible but very harmful for human eyes. Secondly, for processing our current method, only a calcination temperature of around 70°C is needed without any requirements for complex instruments. From an economical view, such fabrication may offer better opportunities to significantly lower the cost of manufacturing nanomaterials, while bringing environmental advantages such as low energy consumption and reduced CO<sub>2</sub> emissions. Thirdly, the simplicity of the synthesis procedure

would make it safe for workers and easy to apply to industrial manufacturing.

#### 4. Conclusion

Ag-ZnO/GO nanocomposite was successfully synthesized by facile aqueous solution reactions at low temperature. The MB removal efficiency increased up to 99% under the UV light and 85% under visible light. The optimum conditions for maximum removal efficiency of MB were pH 8.5–9, temperature 35°C and dosage 1 g/L at MB concentration 15 mg/L. The significant increase in photocatalytic degradation for MB removal exhibited by Ag-ZnO/GO was due to the combined effects of the two semiconductors, ZnO and GO, and Ag doping into the ZnO crystal lattice. The proposed mechanism for enhanced removal includes an increase in adsorption by adding GO with a high surface area and an increase in photocatalytic activities due to improved charge transfer capacity achieved through lowering the band gap energy of ZnO, thus minimizing the recombination of the excited electrons in the CB with the holes in VB of ZnO, leading to higher removal rate of MB.

#### Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

#### Conflicts of Interest

The authors declare that they have no conflicts of interest.

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## Research Article

# Preparation of Manganese Dioxide Nanoparticles on Laterite for Methylene Blue Degradation

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The laterite-coating manganese dioxide nanoparticle material (M2) prepared by the immersion method was used for the efficient removal of methylene blue (MB) from aqueous solution. The adsorption and heterogeneous Fenton catalytic oxidation experiments of M2 were investigated by changing the effective factors such as time, pH, amount of M2, and concentration of MB. The adsorption data of M2 showed good fitting with the Langmuir isotherm, suggesting that the adsorption of MB on the surface of M2 is a heterogeneous and physical adsorption process. Degradation of MB was also carried out to evaluate the heterogeneous Fenton catalytic oxidation characterization of a new catalytic oxidation material (M2). The results show that the M2 material has both adsorption and heterogeneous Fenton catalytic oxidation. However, the heterogeneous Fenton catalytic oxidation of the M2 material is the main performance. Hence, our groups have investigated the ability of the catalytic column treatment with high efficiency of 98–100% and the degradation efficiency after the sample running through the column almost does not change much. This proves that heterogeneous Fenton catalytic activity of the catalytic column is completely unaffected and reused many times after oxidizing MB. Specifically, even if the M2 material is reused for five times, the degradation efficiency still reaches 98.86%.

## 1. Introduction

Methylene blue (MB) is an organic compound which used in the treatment of cyanide poisoning, treatment of impetigo, pyoderma, urogenital antiseptic, and dying tissues in some diagnostic operations (bacterial staining, etc.) [1]. In addition, methylene blue is a chemical that is widely used in the dyeing industry of fabrics, nylon, leather, wood, and ink production. Moreover, a large amount of MB remain in the wastewater of textile dyeing process [2]. Hence, the removal of MB has attracted considerable attention in the

environmental field. Over the past few years, several physical methods and chemical methods have been employed for removing MB [3]. There are several treatment processes that have been applied for treatment of dye wastewater such as photocatalytic degradation [4, 5], membrane separation [5, 6], adsorption-precipitation processes [7, 8], ultrafiltration [9, 10], chemical-biological degradation [6, 11], Fenton system and heterogeneous Fenton-like catalytic reactions [12–14], and adsorption on activated carbon and electrolysis [15, 16]. However, some of these techniques are rarely used due to insensitivity to a toxic substance, the complexity of

the design, and high cost. Therefore, development of an effective, cheap, and eco-friendly method is of crucial importance for the removal of dye wastewater.

Recently, manganese oxide nanoparticles have been also widely used for dye removal due to the effect of the chemical and physical interactions which occur between the organic (polymer) and inorganic (manganese dioxide nanoparticles) components [17, 18]. Manganese dioxide nanoparticles material is not only nontoxic but also has highly active and strong oxidations because the oxidation number of Mn is +4. In addition, manganese oxide nanoparticles have been used as adsorbents and catalytic materials [19–22]. Hence, most research focus on investigating the ability of Fenton catalytic oxidation of manganese oxide, especially manganese dioxide ( $\text{MnO}_2$ ), for degradation of dye molecules. Dantas et al. [23] studied the ability of catalytic oxidation reaction of methylene blue with  $\text{H}_2\text{O}_2$  under catalysts of  $\beta$ - $\text{MnOOH}$ ,  $\alpha$ - $\text{FeOOH}$ ,  $\gamma$ - $\text{Mn}_3\text{O}_4$ , and treated methylene blue at 30 mg/L in 40 minutes. In addition, Zhang et al. [24] synthesized  $\beta$ - $\text{MnO}_2$  with size about 30–400 nm and applied  $\beta$ - $\text{MnO}_2$  to form bars and columns, with the surface area of 68.82  $\text{m}^2/\text{g}$ , as a catalyst to remove methylene blue. The degradation percentage of methylene blue using  $\beta$ - $\text{MnO}_2$  is 100% in 40 minutes. Furthermore, Liangjie Yuan [1] studied the ability of the catalyst carbon nanometre coated  $\text{MnO}_2$  to treat MB by adding  $\text{H}_2\text{O}_2$  agent. In addition, Yang et al. [2] also studied the ability of the catalysts to remove hexanol of amorphous  $\text{MnO}_2$  oxide and pyroluzite ( $\beta$ - $\text{MnO}_2$ ). The study found that 99% of hexanol was treated in 60 minutes. Han et al. [25] also synthesized  $\text{Mn}_3\text{O}_4/\text{SBA-15}$  to treat ethanol with a concentration of 100 ppm under the  $\text{H}_2\text{O}_2$  agent. The study of Han et al. group and Liangjie Yuan group also demonstrated that manganese oxide nanoparticles are a oxidation catalytic to induce free radicals  $\text{OH}^*$ ,  $\text{O}_2^*$ , and  $\text{HO}_2^*$ , leading to potential application of it in heterogeneous Fenton catalytic. Thus, manganese dioxide nanoparticles are not only degradation MB by physical adsorption but also degradation MB by heterogeneous Fenton catalytic oxidation. However, the use of manganese dioxide nanoparticles has several disadvantages due to self-aggregation, difficulty in solid-liquid separation, and leaching of nanoparticles with the treated effluents. These limitations can be avoided by anchoring the particle on the substrates with high sorption capacity of adsorbents and Fenton catalytic activity such as laterite ore. Therefore, manganese oxide nanoparticles were then mixed with denaturated laterite (iron-rich ore, available in Vietnam) to create new high-performance materials because impregnation or coating with nanoparticles enhances the sorption capacity of adsorbents and Fenton catalytic activity. Therein, the manganese oxide nanoparticle is the catalysts effective material, and the laterite is the adsorption efficiency material for degradation MB. Therefore, the combination of these two effective materials can result in the best adsorbent and catalytic oxidation material for MB removal. The objectives of this study are to synthesize colloidal manganese dioxide nanoparticles ( $\text{MnO}_2$  NPs), to prepare mixed material by mixing colloidal  $\text{MnO}_2$  NPs and denaturated laterite, and to investigate the adsorption and heterogeneous Fenton catalysts of the mixed material for MB removal.

## 2. Materials and Methods

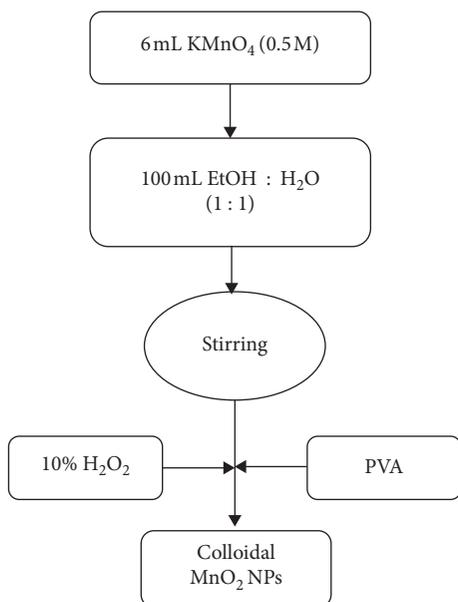
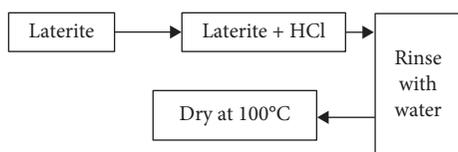
**2.1. Chemicals and Characterization.** All chemical reagents, including manganese sulfate monohydrate ( $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ ), potassium permanganate ( $\text{KMnO}_4$ ), hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), ethanol ( $\text{C}_2\text{H}_5\text{OH}$ , 99.5%), polyvinyl alcohol (PVA,  $M_w \sim 31,000$ ), and methylene blue, were purchased from Merck. In our experiment, we use laterite ore from Cao Bang Province, VietNam.

X-ray diffraction (XRD) spectra of absorption materials were obtained using D8 Advance (Bruker, Germany) and D5005 (Siemens, Germany). The scanning electron microscopy and energy dispersive X-ray spectroscopy (EDX) were performed with S-4800 (SEM, Hitachi). The transmission electron microscopy (TEM) was performed with a JEOL JEM1010 operated at 80 kV. UV-Vis absorption spectra were obtained on an UV1800, Japan.

**2.2. Synthesis of Colloidal Manganese Dioxide Nanoparticles ( $\text{MnO}_2$  NPs).** The colloidal  $\text{MnO}_2$  NPs are synthesized as shown in Scheme1 [26]. 6 mL of the diluted potassium permanganate ( $\text{KMnO}_4$  0.5 M) solution was added into 100 mL mixture solvent of EtOH :  $\text{H}_2\text{O}$  (1 : 1) at room temperature. The mixture was stirred, and then 10%  $\text{H}_2\text{O}_2$  and polyvinyl alcohol (PVA) were added. The polyvinyl alcohol (PVA) was used a coreduction agent to obtain  $\text{MnO}_2$ . Soon after adding 10%  $\text{H}_2\text{O}_2$  and polyvinyl alcohol (PVA), the brown precipitate began to appear. The brown precipitate was collected by centrifugation and washed with ethyl alcohol (three times). To remove polyvinyl alcohol (PVA), the mixture was precipitated with ethanol as a solvent and hexane as an antisolvent. Finally, colloidal  $\text{MnO}_2$  NPs were obtained as brown powder.

**2.3. Preparation of Laterite-Based Materials.** The laterite ore was collected from Cao Bang Province, Vietnam. The laterite ore was crushed and sieved. The fraction small laterite particle is thermally denaturated by following the procedure in Scheme2. 100 g of laterite powder was treated with 40 mL of HCl in a 250 mL beaker. The mixtures were soaked for 2 hours and then decant a liquid. The remaining powder was rinsed with distilled water and dried at 100°C. Finally, we obtained the substrate material, referred to as M1.

**2.4. Preparation of Mixed.** In the final step, the prepared colloidal  $\text{MnO}_2$  NPs were mixed with denaturated laterite by the immersion method. 50 g of the denaturated laterite particle (0.5 mm) was added into the beaker which contained the colloidal  $\text{MnO}_2$  NPs. The mixture was impregnated for 12 hours and then dried at 105°C for 8 hours. The power was rinsed by distilled water to remove the remaining salt. Finally, we obtained the mixed adsorbent material symbolized as M2.

SCHEME 1: Synthesis of colloidal MnO<sub>2</sub> NPs.

SCHEME 2: Thermal denaturation of laterite ore.

To determine the shape, phase composition, particle size, particle distribution of colloidal MnO<sub>2</sub> NPs (M1), and M2 materials, we use the transmission electron microscopy (TEM), scanning electron microscopy (SEM), and X-ray diffraction (XRD) pattern (XRD) analysis.

The adsorptive and catalytic activities of the mixed material (M2) were assessed by using methylene blue. The methylene blue concentrations before and after treatment were determined by the absorption intensity of the UV spectrum at the maximum absorption wavelength of 664 nm, which is explained in detail in Supplementary Materials.

**2.5. Adsorption Experiments.** Adsorption experiments were investigated by changing the effective factors such as time, pH, and concentration of methylene blue (MB). The residual concentration of MB was determined with the help of the calibration plot of MB solution at a fixed wavelength (667 nm) with varying initial ion metal concentration which is explained in detail in Supplementary Materials. The amount of adsorbed MB ( $C_a$  mg/L) was found out using the following formula [27]:

$$C_a = C_0 - C_e \text{ (mg/L)}, \quad (1)$$

where  $C_0$  is the initial concentration and  $C_e$  is the residual concentration of MB. The adsorption percentage was calculated by the following equation:

$$\text{Adsorption (\%)} = \frac{C_a}{C_0} \times 100, \quad (2)$$

where  $C_a$  is the adsorbed concentration (mg/L) of MB and  $C_0$  is the initial concentration of MB.

The equilibrium adsorption capacities of M2 for methylene blue (MB) were calculated by the following equation [27]:

$$q_e = \frac{V_0(C_0 - C_e)}{m}, \quad (3)$$

where  $q_e$  is the equilibrium adsorption capacity (mg/g),  $C_0$  and  $C_e$  are the initial and residual concentrations (mg/L) of MB solution, respectively,  $V_0$  is the volume of the initial solution (L) use for sorption, and  $m$  is the weight of the adsorbent (g).

**2.5.1. Determination of Equilibrium Time.** The equilibrium time was determined by taking 1.0 g of the adsorbent M2 with 100 mL MB (80 mg/L) solution at pH equal to 7, followed by stirring at room temperature at various time intervals ranging from 0 to 7 h.

**2.5.2. Adsorption Isotherm.** The adsorption isotherms of MB were investigated by taking 1.0 g of M2 material with 100 mL of MB solution with different initial concentrations (varying from 10 to 300 mg/L) at pH about 7 under room temperature with stirring for 6 hours.

**2.5.3. Kinetic Adsorption Experiment.** The adsorption kinetic is described by the Langmuir adsorption model and the Freundlich adsorption model. The Langmuir equation is generally expressed as follows [28]:

$$\frac{1}{q_e} = \frac{1}{q_{\max} K_L C_e} + \frac{1}{q_{\max}}, \quad (4)$$

where  $q_e$  and  $q_{\max}$  are the equilibrium adsorption capacity and a maximum capacity of adsorbent (mg/g), respectively,  $C_e$  is the equilibrium MB concentration in solution (mg/L), and  $K_L$  is the Langmuir adsorption constant pertaining to the energy of adsorption (L/mg).

The Freundlich equation is generally expressed as follows [28]:

$$\lg q_e = \lg K_F + \frac{1}{n_F} \lg C_e, \quad (5)$$

where  $n = 1/n_F$  is the slope of Freundlich isotherm and  $K_L$  is the Freundlich adsorption constant.

**2.6. Heterogeneous Fenton Catalytic Oxidation Experiments.** Degradation of MB was carried out to evaluate the heterogeneous Fenton catalytic oxidation characterization of a new catalytic oxidation material (M2). Sodium hydroxide and hydrochloric acid were used for modifying the pH of the solutions. 30% hydrogen peroxide was used as the oxidation agent to enhance the degradation of MB. The degradation experiments were performed as a function of time, pH of MB

solution, and the amount of 30% hydrogen peroxide under room temperature. The degradation percentage of MB was calculated according to the following equation [1]:

$$\text{degradation (\%)} = \frac{C_0 - C_e}{C_0} \times 100, \quad (6)$$

where  $C_0$  is the initial concentration of MB solution and  $C_e$  is the residual concentration of MB solution after treating with the catalyst oxidation material M2.

**2.6.1. Effect of Amount of Hydrogen Peroxide.** The effect of amount of 30%  $\text{H}_2\text{O}_2$  on the degradation of methylene blue (MB) was evaluated by stirring 1.0 g M2 material with 100 mL of MB solution (20 mg/L) for various volumes of 30%  $\text{H}_2\text{O}_2$  solution from 0.2 to 5 mL, at pH 7.0, followed by stirring for 45 min. Then, the MB solutions were separated by centrifugation to determine the methylene blue concentration by using the UV-Vis spectrophotometer.

**2.6.2. Effect of Time.** The effect of time on the degradation of MB was evaluated by stirring 1.0 g M2 material and adding 1.5 mL 30%  $\text{H}_2\text{O}_2$  and 100 mL of MB solution (20 mg/L) at various time intervals ranging from 0 to 180 min, at pH 7.0. Then, the MB solutions were separated by centrifugation to determine the methylene blue concentration by using the UV-Vis spectrophotometer.

**2.6.3. Effect of pH.** The effect of pH of metal ion solutions on degradation of MB was examined. 1.0 g of M2 material was added to 100 mL of MB 20 mg/L solution with varying pH values ranging from 2 to 12, at room temperature, followed by stirring for 45 min. The pH of metal ion solutions was adjusted to the desired value by using HCl 0.1 M or NaOH 0.1 M.

**2.6.4. Effect of Catalyst Oxidation Material M2 Mass.** The effect of amount of M2 on the degradation of MB was tested by stirring different amounts of M2 (0.2, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, and 5.0 g) and adding 1.5 mL 30%  $\text{H}_2\text{O}_2$  and 100 mL of MB solution (20 mg/L) at pH 7.0, followed by stirring for 45 min. Then, the MB solutions were separated by centrifugation to determine the methylene blue concentration by using the UV-Vis spectrophotometer.

### 3. Results and Discussion

**3.1. Characterization of Colloidal  $\text{MnO}_2$  NPs, Laterite, and Mixed Material (M2).** Figure 1 shows the transmission scanning electron microscopy (TEM) image of colloidal  $\text{MnO}_2$  NPs. The average sizes of the  $\text{MnO}_2$  NPs are about 50 nm. The TEM image clearly shows that the spherical particle of  $\text{MnO}_2$  NPs sample is formed, and their size distribution is narrow. Moreover, the TEM results of  $\text{MnO}_2$  NPs sample show those particles which aggregate to form a block with a porous structure.

The surface structures of laterite (M1) and mixed material (M2) were analysed by the scanning electron

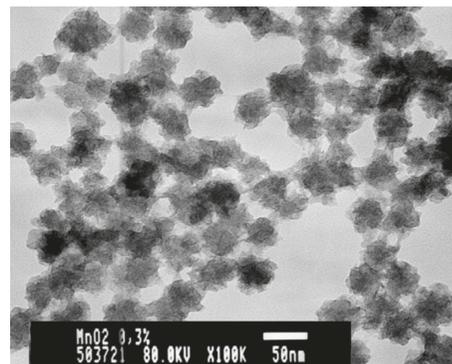


FIGURE 1: TEM micrograph of  $\text{MnO}_2$  nanoparticles.

microscopy (SEM) in Figures 2(a) and 2(b). The SEM results show that the surface of the laterite after the immersion process has been coated by the nanoparticle layer. In addition, the average sizes of laterite particles are about 5  $\mu\text{m}$  in Figure 2(a). Therefore, we believe that the nanoparticle layer is  $\text{MnO}_2$  NPs, which coats on the laterite surface.

Figure 3 shows X-ray diffraction (XRD) patterns of M1,  $\text{MnO}_2$  NPs, and M2 materials. The XRD results of laterite (M1) and laterite after coating with  $\text{MnO}_2$  nanoparticle (M2) showed some similar main peaks at  $2\theta$  of 24.2, 34.1, 35.8, 54.6, 62.7, 21.0, 26.7, 50.10, and  $60^\circ$  which were associated with hematite and quartz [29]. In addition, the XRD result of  $\text{MnO}_2$  NPs does not show any peaks. Thus, these results prove that the  $\text{MnO}_2$  NPs layer coats on laterite in an amorphous structure.

The composition of the laterite after coating  $\text{MnO}_2$  nanoparticle (M2) is also analysed by energy dispersive X-ray spectroscopy (EDX). Figure 4 shows that these M2 materials are composed of mainly Fe element (from  $\text{Fe}_2\text{O}_3$ ), Si element (from the  $\text{SiO}_2$ ), Al element (from the  $\text{Al}_2\text{O}_3$ ), O element (from  $\text{Fe}_2\text{O}_3$ ,  $\text{SiO}_2$ , and  $\text{Al}_2\text{O}_3$ ), and S element. Furthermore, the manganese element is detected in the EDX result which shows that  $\text{MnO}_2$  NPs had been coated on the surface of the laterite particle.

#### 3.2. The Adsorption of the Mixed Material (M2)

**3.2.1. Effect of Time.** The adsorption process is time dependent, as shown in Figure 5 and Table S1 (Supplementary materials). The results of MB showed that when increasing the adsorption time, the adsorption percentage increased. In Figure 5, adsorption occurs rapidly in the first 5 hours, and then the adsorption rate slowed down and almost reached equilibrium at 6 hours. Hence, 6 hours have to be considered as an optimized time for the adsorption of MB.

The adsorption isotherms of MB were investigated by taking 1.0 g of M2 adsorbent material with 100 mL of MB solution with different initial concentrations (varying from 20 to 100 mg/L) at pH of about 7 under room temperature with stirring for 6 hours. The results in Table S4 (Supplementary materials) show that when the concentration of MB gradually increases, the adsorption capacity increases and the percentage decreases.

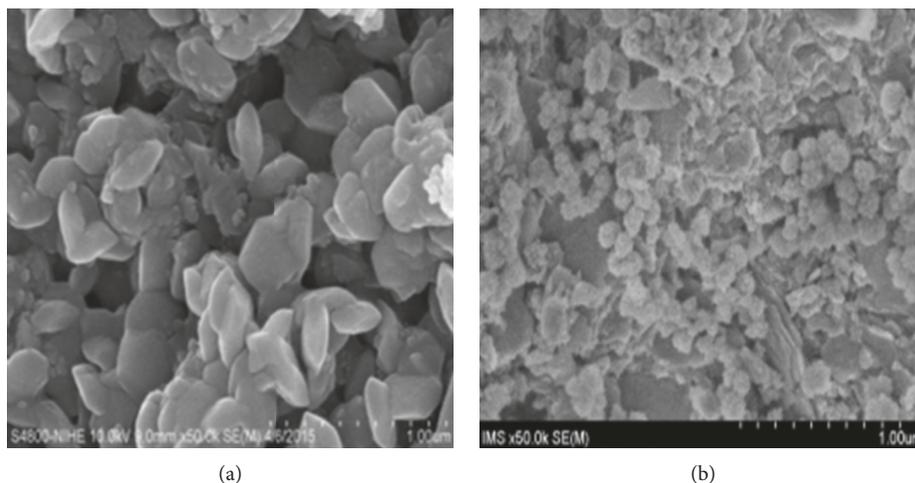


FIGURE 2: SEM micrographs of (a) laterite (M1) and (b) laterite after coating with MnO<sub>2</sub> nanoparticles (M2).

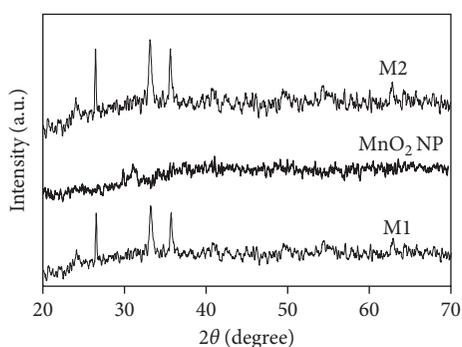


FIGURE 3: Powder X-ray diffraction pattern of M1, MnO<sub>2</sub> NP, and M2 samples.

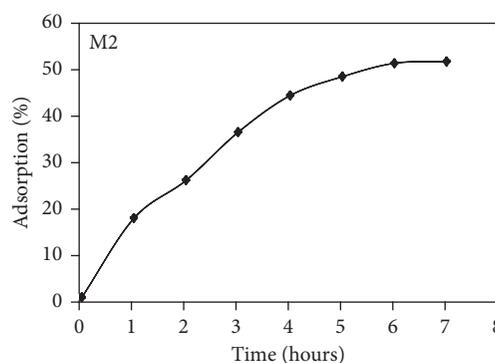


FIGURE 5: Effect of time on the adsorption process of MB.

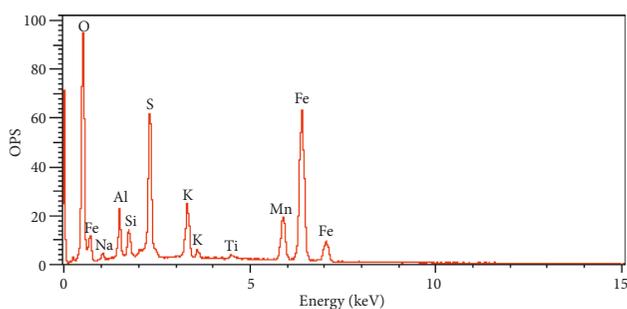


FIGURE 4: Energy-dispersive X-ray (EDX) spectra of the mixed laterite after MnO<sub>2</sub> NP (M2) coating.

**3.2.2. Adsorption Isotherm.** The adsorption kinetic is described by the Langmuir adsorption model and the Freundlich adsorption model [28]. The linear equation was used to fit the MB adsorption process on M2, as shown in Figures 6(a) and 6(b) and Table S2 (Supplementary materials). The Langmuir adsorption isotherm assumes that the monolayer adsorption occurs on a homogeneous surface of the adsorbent, while Freundlich adsorption isotherm assumes that the multilayer adsorption occurs on a heterogeneous surface of the adsorbent. Results show that the Freundlich model ( $R^2 = 0.966$ ) is better than the Langmuir

model ( $R^2 = 0.8717$ ) in simulating the adsorption experiments. This suggests that the adsorption process is a heterogeneous process. The maximum adsorption capacity for MB was 10.63 mg/g. The  $n_F$  value in the Freundlich equation (Table 1) is used to determine adsorption whether it is linear adsorption ( $n_F = 1$ ), chemical adsorption ( $n_F < 1$ ), or physical adsorption ( $n_F > 1$ ) [28]. Moreover, the adsorption of M2 on MB powder is the physical adsorption process due to the  $n_F$  value ( $n_F = 2.6$ ) larger than 1 (Table 1).

Moreover, to assess the adsorption performance of laterite after coating MnO<sub>2</sub> NP material (M2) in environmental treatment, our group investigated large-scale survey adsorption performance by preparing one adsorption column with a diameter of 15 cm, height of 15 cm, and weight of M2 material about 50 g. The ability absorption MB of the column was carried out with the initial concentration of methylene blue 40 mg/L and flow rate 2 mL/min. The results of column processing absorption are given in Table 2.

The results of Table 2 show adsorption performance of the laterite-coating MnO<sub>2</sub> NP material (M2). These results suggest the MB adsorption over the laterite after coating MnO<sub>2</sub> NPs (M2) proceeds rather through weak and physical type adsorption than chemical type adsorption. Moreover, the adsorption time reached equilibrium at 6 hours with low adsorption percentage of MB of 50%.

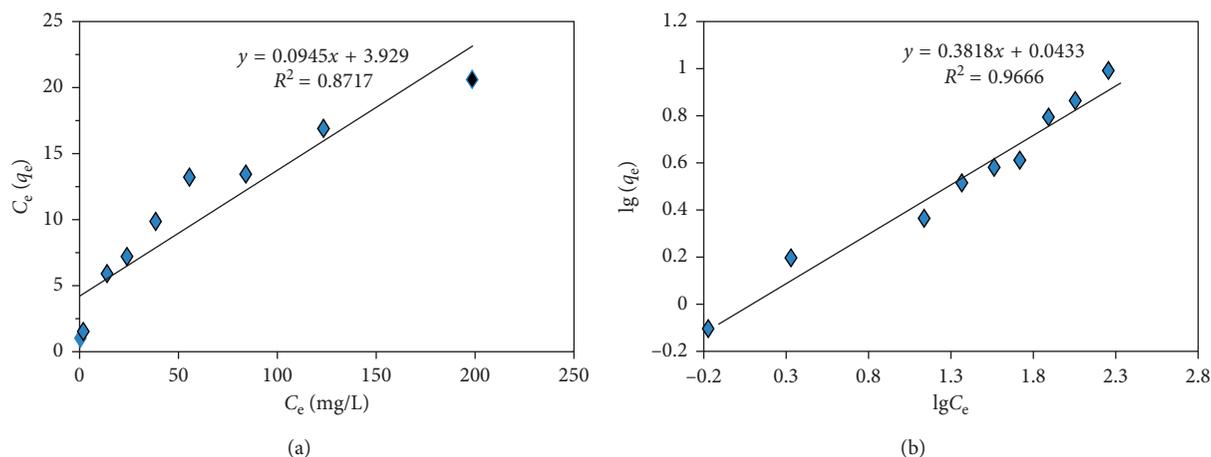


FIGURE 6: Adsorption isotherm of MB: (a) Langmuir isotherm and (b) Freundlich isotherm.

TABLE 1: Kinetic parameter and correlation coefficient of two kinetic equations.

Langmuir			Freundlich		
$K_L$ (L/mg)	$q_{max}$ (mg/g)	$R^2$	$n_F$	$K_F$	$R^2$
0.024	10.6	0.871	2.6	1.10	0.966

TABLE 2: Results of the large-scale surveys on adsorption performance of M2.

No.	$V$ (mL)	Output concentration of MB (mg/L)
1	2000	—
2	1000	0.2
3	900	0.91
4	800	1.35
5	700	3.79
6	600	5.11
7	400	8.77
8	200	16.66
9	100	27.80
10	50	33.79
11	25	36.84
12	15	38.01
13	10	39.17
14	5	40.00

Amount of methylene blue absorbed on column is 2.51 g

### 3.3. The Catalytic Oxidation Activity of the Mixed Material (M2)

**3.3.1. Effect of  $H_2O_2$  Concentration.** As mentioned above, thanks to the outstanding advantage of removing organic pollutants, the highly biodegradable organic matter (POP) enhanced the oxidation process based on free radicals  $HO^*$  of  $H_2O_2$ , which is considered a “key gold” to solve the challenging problems of the century for the current water and wastewater treatment industries. Thus, we investigate the effect of  $H_2O_2$  concentration on the degradation of MB in Figure 7. In Figure 7 and Table S3 (Supplementary materials), the effect of hydrogen peroxide concentration on the degradation of methylene blue shows that in the range of 0.2

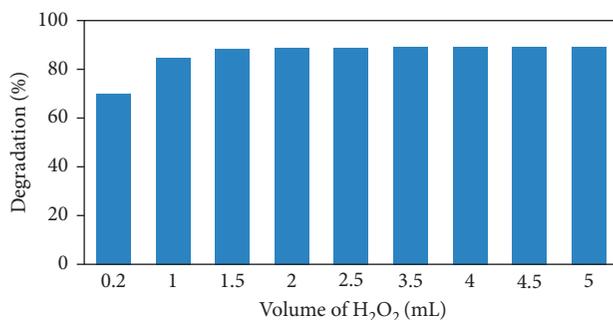


FIGURE 7: Effect of the hydrogen peroxide concentration on the degradation percentage of MB.

to 1.5 mL of 30%  $H_2O_2$ , the degradation percentage increases strongly from 70 to 89.01%. Thus, MB efficiency degradation is proportional to the concentration of  $H_2O_2$ . This result is explained by the increase in the number of free radicals ( $HO^*$ ) generated from  $H_2O_2$  over the laterite after  $MnO_2$  NP (M2) catalyst coating.

When the amount of  $H_2O_2$  increased over 1.5 mL, the excessive  $H_2O_2$  reacts with the availability of  $HO^*$  to release the hydroperoxyl radicals ( $HOO^*$ ) (Equation (7)). Moreover, the hydroperoxyl radicals ( $HOO^*$ ) react immediately with  $HO^*$  (Equation (8)) to induce  $H_2O$  and  $O_2$  (Equation (8)) resulting in a reduction of the availability of  $HO^*$  [30].



The consumption of free radical  $HO^*$  reduced the catalytic ability, leading to reduction in the efficiency of treatment. Thus, it can be seen that the optimal amount of  $H_2O_2$  for methylene blue treatment is 1.5 mL of 30%  $H_2O_2$ .

**3.3.2. Effect of Time.** The survey results of the effect of time (Figure 8 and Table S4 (Supplementary materials)) show that

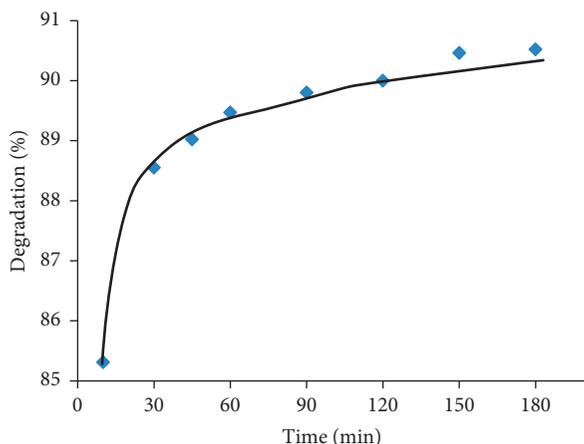
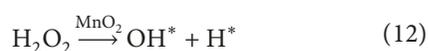
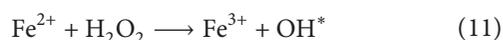
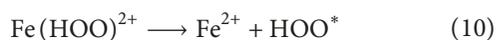
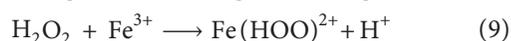


FIGURE 8: Effect of time on the degradation percentage of MB.

the first 45 min of processing speed increased rapidly and reached a quite high efficiency of 89.96% and then increased slowly. Thus, during the next survey, it is recommended to select the optimal time of 45 min.

**3.3.3. Effect of pH.** The pH of the solution plays an important role in determining the adsorption ability of M2 for methylene blue. The effect of pH on the MB removal was investigated at a pH range of 2–12. The results obtained are presented in Figure 9 and Table S5 (Supplementary materials). The results of surveying the effect of pH show that when the pH was 2–5, the MB degradation efficiency was low. When the pH is from 6 to 8, the degradation efficiencies of MB increase strongly from 80 to 89%. Especially, the maximum degradation efficiency of MB is 100% in the pH region of 9–12. Therefore, we choose pH 7 for further studies.

**3.3.4. Effect of Catalyst Dosage.** The effect of the amount of the laterite after MnO<sub>2</sub> NP (M2) catalyst coating on the removal of methylene blue is investigated and is shown in Figure 10 and Table S6 (Supplementary materials). The result shows that the degradation efficiency increases with increasing catalyst content, due to the increase in the catalytic active sites on the surface of the catalyst and the associated generated free hydroxyl radicals (equations (9)–(12)) [29, 30]. Especially, the degradation efficiency increases rapidly in the range of 0.5 to 1.5 g of M2 (Figure 10):



However, when the amount of M2 increased over 1.5 g, the degradation efficiency did not change so much. This

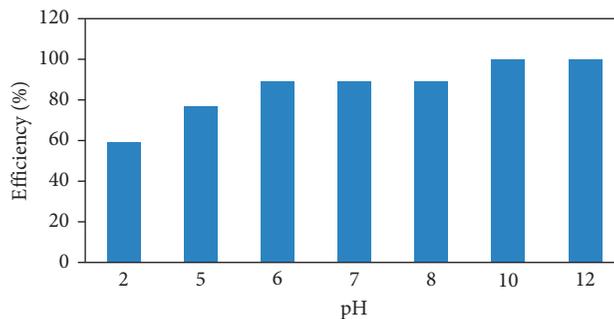


FIGURE 9: Effect of pH on the degradation percentage of MB.

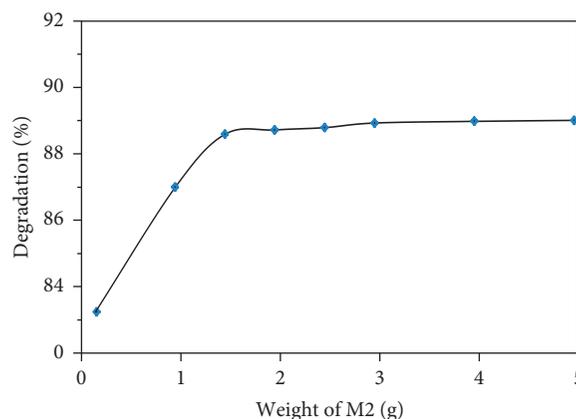
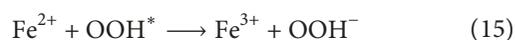
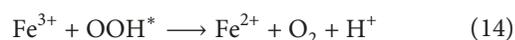
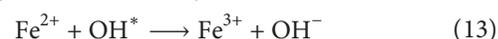


FIGURE 10: The effect of the amount of mixed material M2 on the degradation percentage of MB.

phenomenon is attributed to the scavenging effect of HO<sup>\*</sup> radicals during unwanted side reactions over the catalyst surface M2, resulting in a reduction of the availability of HO<sup>\*</sup> and degradation efficiency [29]:



Thus, in the next survey, we conducted the selection of catalyst amount of about 1.5 g. Moreover, the increase of catalyst dosage should be accompanied by an increase in H<sub>2</sub>O<sub>2</sub> concentration, and an optimum concentration ratio has to be maintained.

To assess the heterogeneous Fenton catalytic oxidation performance of laterite after coating MnO<sub>2</sub> NP material (M2) in environmental treatment, our group conducted large-scale surveys by preparing one catalytic column with a diameter of 15 cm, height of 15 cm, and weight of M2 material on the column of about 50 g. The ability degradation MB of the catalytic column was carried out with 3 mL H<sub>2</sub>O<sub>2</sub> 30%, the initial concentration of methylene blue of 40 mg/L and flow rate 2 mL/min. The results of columns processing capacity are given in Table 3.

The results in Tables 2 and 3 show that the laterite-coating MnO<sub>2</sub> nanoparticle material (M2) has both

TABLE 3: Results of the large-scale surveys on the heterogeneous Fenton catalytic oxidation performance of M2.

No.	V (mL)	Output concentration of MB (mg/L)
1	1200	—
2	1000	—
3	1000	—
4	1000	0.21
5	900	0.26
6	800	0.27
6	700	0.29
7	600	0.32
8	500	0.34
9	400	0.41
10	300	0.45
11	300	0.48
12	200	0.53
13	200	0.57
14	200	0.62
15	100	0.63
16	100	0.64
17	50	0.65

TABLE 4: The degradation efficiency of MB after reusing the catalyst five times.

No.	1	2	3	4	5
Degradation efficiency (%)	99.85	99.68	99.53	98.92	98.86

adsorption and heterogeneous Fenton catalytic oxidation performances. However, the heterogeneous Fenton catalytic oxidation performance is the domain because the degradation efficiency of MB after the sample running through the catalytic column almost does not change much and is about 96–100% (Table 3). This is consistent with that of the previous studies [1, 25, 31]. Specifically, our group has investigated the possibility of catalytic reuse of M2 material with 3.0 mL of 30% H<sub>2</sub>O<sub>2</sub>, 10 L of methylene blue of 40 mg/L, and flow rate 2 mL/min. The number of reusing the catalyst (M2) is five as shown in Table 4, the degradation efficiency of MB still reaches 98.86%. Therefore, these results prove that heterogeneous Fenton catalytic oxidation performances of the M2 material with 3.0 mL H<sub>2</sub>O<sub>2</sub> 30% is completely unaffected after oxidizing MB and reusing at least five times.

#### 4. Conclusions

In conclusion, the adsorption and heterogeneous Fenton catalytic oxidation experiments of laterite-coating manganese dioxide nanoparticle material (M2) were investigated by changing the effective factors such as time, pH, and concentration of MB. The results show that the laterite-coating MnO<sub>2</sub> NP material (M2) shows both adsorption and heterogeneous Fenton catalytic oxidation performances. However, the heterogeneous Fenton catalytic oxidation performance is the domain. Hence, our groups have investigated the ability of catalytic column treatment with high degradation efficiency after the MB solution running through the column almost does not change much. These results prove that the heterogeneous Fenton catalytic activity

of laterite-coating MnO<sub>2</sub> NP material (M2) is completely unaffected by the number of times the MB solution runs through the column. Moreover, this M2 material can be reused five times with the degradation efficiency still being 98.86%. Based on these catalytic performances, the laterite-coating MnO<sub>2</sub> NP material is worthy to be seriously considered in the design of sustainable and readily affordable wastewater treatment solutions in developing tropical countries.

#### Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

#### Conflicts of Interest

The authors declare that they have no conflicts of interest.

#### Acknowledgments

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#### Supplementary Materials

Figure S1: the calibration graph of MB solution at  $\lambda_{\max}$  to about 644 nm. Table S1: the effect of time on adsorption percentage of M2 for MB. Table S2: the effect of MB concentration solution on the adsorption capacity. Table S3: the effect of hydrogen peroxide concentration on the degradation percentage of MB. Table S4: the effect of time on the degradation percentage of MB. Table S5: the effect of pH on the degradation percentage of MB. Table S6: the effect of the amount of the M2 on the degradation percentage of MB. (*Supplementary Materials*)

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## Research Article

# Using Electrode Made of Carbon Nanotubes and Bismuth Oxide for the Determination of Metal Concentration by Anodic Stripping Voltammetry

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We have successfully manufactured a new electrode modified with bismuth oxide ( $\text{Bi}_2\text{O}_3$ ) using carbon nanotubes (CNTs). The electrode was fabricated to detect cadmium (Cd), lead (Pb), and indium (In) by differential pulse anodic stripping voltammetry (DP-ASV). The electrode surface was studied by scanning electron microscopy (SEM), and the reduction and oxidation processes were studied by cyclic voltammetry (CV) techniques. Operational parameters such as electrode size, bismuth concentration, and electrolytic background were optimized. The DP-ASV method used fabricated electrodes with a linear response range from  $1.5\text{--}20\ \mu\text{g}\cdot\text{L}^{-1}$  with Cd(II) and Pb(II) and  $2.5\text{--}20\ \mu\text{g}\cdot\text{L}^{-1}$  with In(III); low detection limit (LOD) of  $0.22\ \mu\text{g}\cdot\text{L}^{-1}$  with Cd(II),  $0.65\ \mu\text{g}\cdot\text{L}^{-1}$  with In(III), and  $0.26\ \mu\text{g}\cdot\text{L}^{-1}$  with Pb(II); and good repeatability with relative standard deviations (RSD) of 2.65%, 2.51%, and 3.34% with Cd(II), Pb(II), and In(III), respectively ( $n=8$ ). The electrode can be used to test the content of Cd(II), In(III), and Pb(II) in water.

## 1. Introduction

The Cd and Pb determination is very important because of their toxic effects to environment and humans [1]. Several compounds of In can cause cancer and are toxic [2]. Some analytical methods such as atomic absorption spectrometry (AAS) [3–8], inductively coupled plasma-mass spectrometry (ICP-MS) [9–11], and inductively coupled plasma-atomic emission spectroscopy (ICP-AES) [12–16] have been applied to analyse Cd(II), In(III), and Pb(II). These techniques have high selectivity and sensitivity, but they are very expensive and time-consuming. The electroanalytical method not only has high accuracy and sensitivity but also is low cost, has good repeatability, and allows in situ measurement [17]. Carbon paste electrodes (CPEs) have been widely applied in analytical chemistry in some recent years [18–21]. Nowadays, CNTs are

also used in CPEs because they have high mechanical strength, electrical conductivity, and surface area [22–25]. The electrochemical analysis methods using various working electrodes (WEs) have been widely used, in which mercury electrodes have been most commonly used. However, mercury is very toxic. Bismuth is less toxic than mercury, and it has some similar electrochemical characteristics of mercury, so it has been used a lot to replace mercury in electrochemical analysis [26–35]. In this study, we manufactured a new modified CNT electrode with  $\text{Bi}_2\text{O}_3$  as replacement for mercury electrodes, and this electrode is used as a WE in electrochemical analysis equipment for the simultaneous analysis of Cd(II), In(III), and Pb(II). The method was tested successfully on water samples. In addition, the results were compared with those of graphite furnace atomic absorption spectroscopy (GF-AAS). The accuracy of the method is

evaluated by using the sediment certified reference material (CRM) and graphite furnace atomic absorption spectrometry (GF-AAS).

## 2. Experimental

**2.1. Chemicals and Reagents.**  $\text{CH}_3\text{COONa}$ , KI, KCl,  $\text{NaNO}_3$ , paraffin oil,  $\text{CH}_3\text{COOH}$  (100%, m/v), and  $\text{HNO}_3$  (65%, m/v) were purchased from Merck (Germany). Multiwalled carbon nanotubes (MWCNTs 95%, diameter  $\times$  length: 10–35 nm  $\times$  1–10  $\mu\text{m}$ ). Bismuth oxide ( $\text{Bi}_2\text{O}_3$ , grain size  $< 10 \mu\text{m}$ ) was provided by Sigma-Aldrich. Working standards for Pb, Cd, and In were prepared using standard solutions supplied by Merck (standard solutions of 1000 ppm for Cd, Pb, and In).

**2.2. Apparatus.** The Metrohm 797 VA Computrace (Switzerland) with the working electrode (WE) was the CPE modified with  $\text{Bi}_2\text{O}_3$  using CNTs. For AAS measurements, a PerkinElmer 3300, USA, was used. For SEM measurements, a field emission SEM S-4800, Hitachi, Japan, was used.

**2.3. Fabrication of Electrodes.** CNTs (heated at 700°C for 15 min) and paraffin oil (6 : 4, w/w) were mixed with an agate mortar and pestle, and then they were transferred into test tubes with the help of ultrasonic agitation for 2 h. By continuous mixing of carbon paste with  $\text{Bi}_2\text{O}_3$  by mixing similar to the abovementioned method, the modified carbon nanotube paste was obtained. This modified carbon nanotube stuff was packed into a Teflon tube. Electrode surface was cleaned with a filter paper.

**2.4. Procedures.** The analytical solution was added into the electrolyte beaker. The measurement conditions were as follows: the deposition potential ( $E_{\text{dep}}$ )  $-1.2 \text{ V}$ , deposition time ( $t_{\text{dep}}$ ) 120 s, speed 15 mV per second, and pulse amplitude ( $\Delta E$ )  $50 \text{ mV}\cdot\text{s}^{-1}$ . After a rest time, 20 s, the DP-ASV was saved. The DP-ASV of blank solution was saved with the similar measurement conditions. Before the test, oxygen was removed from the analytical solution by exposing to pure nitrogen gas for 5 minutes.

## 3. Results and Discussions

**3.1. Influence of Electrode Diameters.** In stripping voltammetry analysis, all preconcentration and stripping processes happen on the surface of the WE, so the electrode diameter has a great influence on the limit diffusion line. So, we study the influence of different electrode diameters (diameters are 1.8, 2.2, 2.5, 3, 3.5, and 4.0 mm) on the peak ( $I_p$ ) of metal ions. The results are shown in Figure 1. At 3 mm electrode diameter,  $I_p$  of all 3 ions are high, the peak is balanced, and the repeatability is good. Therefore, we chose 3 mm as the optimum electrode diameter.

**3.2. Influence of  $\text{Bi}_2\text{O}_3$ .** The simultaneous analysis of Cd(II), Pb(II), and In(III) by DP-ASV using a CPE modified with 1%, 3%, 5%, and 8% (w/w)  $\text{Bi}_2\text{O}_3$  was researched. The CPE

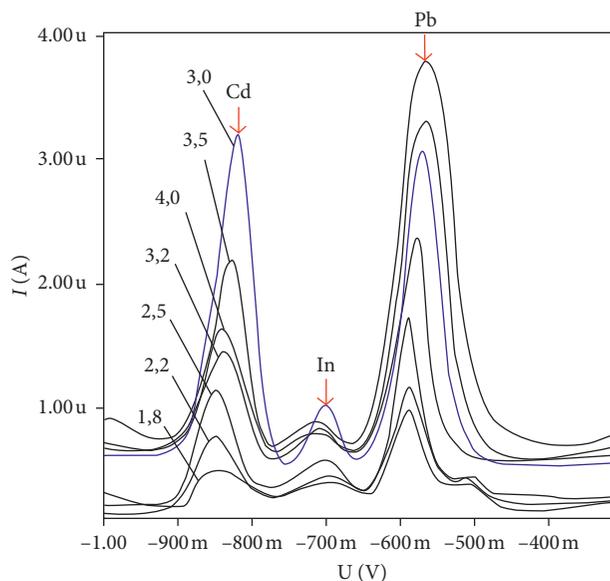


FIGURE 1: Effect of the electrode diameters at a modified CPE with 5%  $\text{Bi}_2\text{O}_3$  (w/w) in the supporting electrolyte mixture of 0.1 M KI and acetate buffer. Conditions:  $E_{\text{dep}} = -1.2 \text{ V}$ ;  $t_{\text{dep}} = 120 \text{ s}$ ;  $\Delta E = 50 \text{ mV}\cdot\text{s}^{-1}$ ; speed =  $15 \text{ mV}\cdot\text{s}^{-1}$ .

modified with 5% (w/w)  $\text{Bi}_2\text{O}_3$  produced the highest Cd, In, and Pb peaks; resolution is high, and repeatability is good. Therefore, the CPE modified with 5% (w/w)  $\text{Bi}_2\text{O}_3$  was used for the further studies.

**3.3. Influence of  $E_{\text{dep}}$  and  $t_{\text{dep}}$ .** Influence of  $E_{\text{dep}}$  on the  $I_p$  of Cd(II), Pb(II), and In(III) has been investigated with  $E_{\text{dep}}$  from  $-0.9$  to  $-1.4 \text{ V}$  (Figure 2). The effect of  $t_{\text{dep}}$  in the range from 30 s to 300 s was also researched (Figure 3). The best stripping signal was obtained at  $E_{\text{dep}} -1.2 \text{ V}$  and  $t_{\text{dep}} 120 \text{ s}$ . From these results,  $E_{\text{dep}}$  and  $t_{\text{dep}}$  of  $-1.2 \text{ V}$  and 120 s were selected for the further studies.

**3.4. Cyclic Voltammetry (CV).** The reduction and oxidation processes were studied by potential scanning from  $-1.2$  to  $0.3 \text{ V}$  and continuous scanning from  $0.3 \text{ V}$  to  $-1.2 \text{ V}$  at a speed of 15 mV per second. The results are shown in Figure 4. In Figure 4, the anodic scan resulted in a peak potential of Bi which was  $-0.12 \text{ V}$  that reflects the oxidation of the metallic bismuth.

**3.5. Morphological Surface Characterization.** Figure 5 shows the scanning electron micrograph (SEM) surface image of the CPE containing 5%  $\text{Bi}_2\text{O}_3$  (w/w) before and after reduction at  $E_{\text{dep}} -1.2 \text{ V}$  with  $t_{\text{dep}}$  of 120 s. After the electrochemical reduction, the electrode surface was changed because  $\text{Bi}_2\text{O}_3$  was converted to Bi at  $-1.2 \text{ V}$  for 120 s following the reaction [36]



According to the SEM image, the electrode surface has got a porous structure, and the surface is relatively uniform.

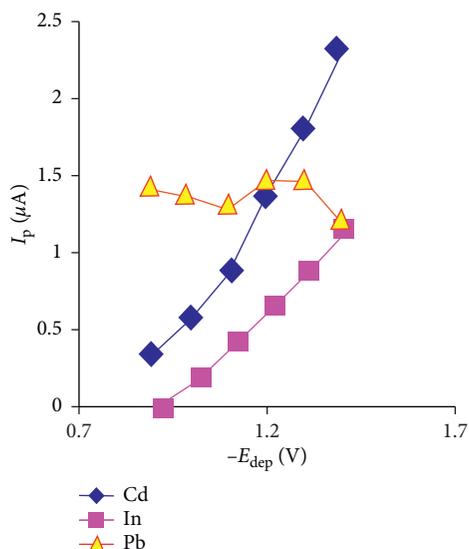


FIGURE 2: DP-ASV of Cd, In, and Pb at different  $E_{\text{dep}}$  values. Conditions: supporting electrolyte mixture of 0.1 M KI and acetate buffer;  $t_{\text{dep}} = 120$  s;  $\Delta E = 50 \text{ mV}\cdot\text{s}^{-1}$ ; speed =  $15 \text{ mV}\cdot\text{s}^{-1}$ .

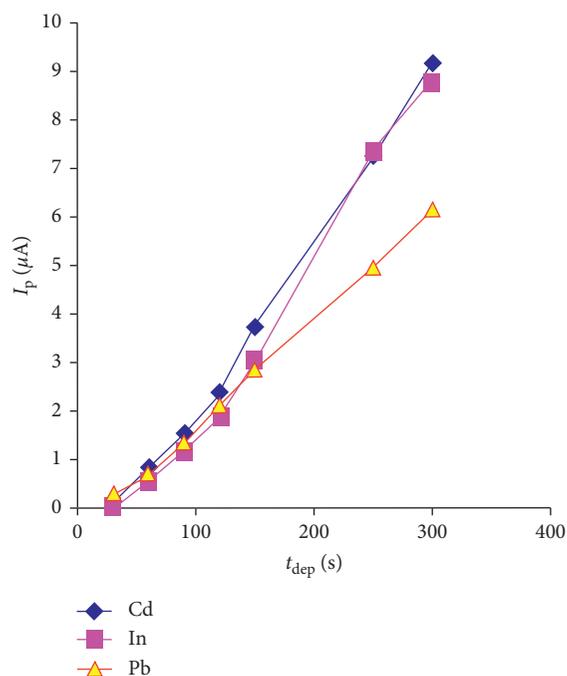


FIGURE 3: DP-ASV of Cd, In, and Pb at different  $t_{\text{dep}}$ . Conditions: supporting electrolyte mixture of 0.1 M KI and acetate buffer;  $E_{\text{dep}} = -1.2$  V;  $\Delta E = 50 \text{ mV}\cdot\text{s}^{-1}$ ; speed =  $15 \text{ mV}\cdot\text{s}^{-1}$ .

Therefore, it is supposed to be beneficial for the stripping analysis.

**3.6. Influence of Supporting Electrolytes.** The influence of the background electrolytes, acetate buffer, mixture of  $\text{NaNO}_3$  and acetate buffer,  $\text{KCl}$  and acetate buffer, and  $\text{KI}$  and acetate buffer, on the  $I_p$  of metals were studied. The results are shown in Figure 6. According to [37], simultaneous measurement of

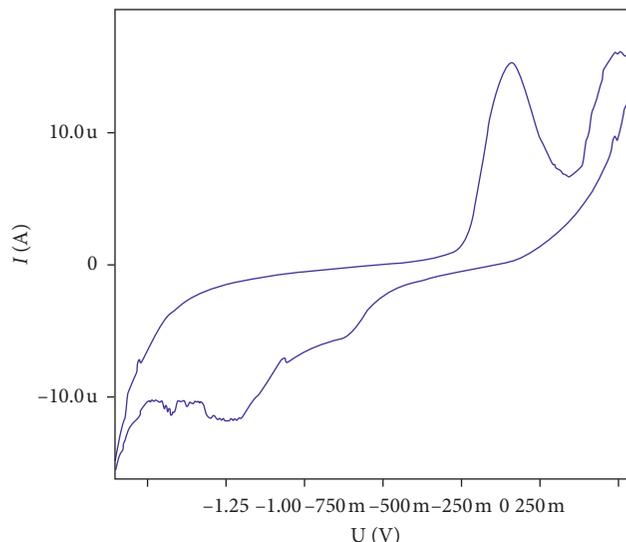


FIGURE 4: Cyclic voltammograms at a modified CPE with 5%  $\text{Bi}_2\text{O}_3$  (w/w) in the supporting electrolyte mixture of 0.1 M KI and acetate buffer. Conditions:  $E_{\text{dep}} = -1.2$  V;  $t_{\text{dep}} = 120$  s;  $\Delta E = 50 \text{ mV}\cdot\text{s}^{-1}$ ; speed =  $15 \text{ mV}\cdot\text{s}^{-1}$ .

$\text{Cd(II)}$ ,  $\text{Pb(II)}$ , and  $\text{In(III)}$  is possible if there is a difference of peak potential of at least 100 mV. In Figure 6(a), the resolution between Cd and In signals in acetate buffer as well as the mixture of  $\text{NaNO}_3$  and acetate buffer and  $\text{KCl}$  and acetate buffer solution is not good. Amongst these mentioned electrolytes, the supporting electrolyte mixture of 0.1 M KI and acetate buffer is the best choice with the best resolution, and largest peak current is for  $\text{Cd(II)}$ ,  $\text{Pb(II)}$ , and  $\text{In(III)}$  (Figure 6(b)). Therefore, a medium containing 0.1 M KI and acetate buffer was selected.

**3.7. Linear Response Range, LOD, and Reproducibility.** The DP-ASV at different concentrations was recorded. The results of linear range are shown in Figure 7(a), and the calibration curves are shown in Figures 7(b)–7(d). The linear response ranges were  $1.5\text{--}20 \mu\text{g}\cdot\text{L}^{-1}$  with  $\text{Cd(II)}$  and  $\text{Pb(II)}$  and  $2.5\text{--}20 \mu\text{g}\cdot\text{L}^{-1}$  with  $\text{In(III)}$ .

The CPE modified with  $\text{Bi}_2\text{O}_3$  using MWCNTs also demonstrated LOD ( $S/N = 3$ ) of  $0.22 \mu\text{g}\cdot\text{L}^{-1}$  with  $\text{Cd(II)}$ ,  $0.26 \mu\text{g}\cdot\text{L}^{-1}$  with  $\text{Pb(II)}$ , and  $0.65 \mu\text{g}\cdot\text{L}^{-1}$  with  $\text{In(III)}$  (at  $t_{\text{dep}} = 120$  s). The method has a fine reproducibility with RSD of 2.65%, 3.34%, and 2.51%, respectively ( $n = 8$ ) (with the concentration of  $\text{Cd(II)}$ ,  $\text{Pb(II)}$ , and  $\text{In(III)}$  to be  $10 \mu\text{g}\cdot\text{L}^{-1}$ ).

Various Bi precursor-modified and  $\text{Bi}_2\text{O}_3$ -modified carbon electrodes for analysis of  $\text{Cd(II)}$ ,  $\text{Pb(II)}$ ,  $\text{In(III)}$  are shown in Table 1.

**3.8. Influence of Ions.** The influence of several ions  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Fe}^{3+}$ , and  $\text{Cu}^{2+}$  at concentration range from 0.1 to  $100 \text{ mg}\cdot\text{L}^{-1}$  on the peak of  $\text{Cd(II)}$ ,  $\text{Pb(II)}$ , and  $\text{In(III)}$  was examined. No signal changes were observed on the  $I_p$  of  $\text{Cd(II)}$ ,  $\text{Pb(II)}$ , and  $\text{In(III)}$  (changes in peak currents  $< 10\%$ ). The influence of cetyltrimethylammonium

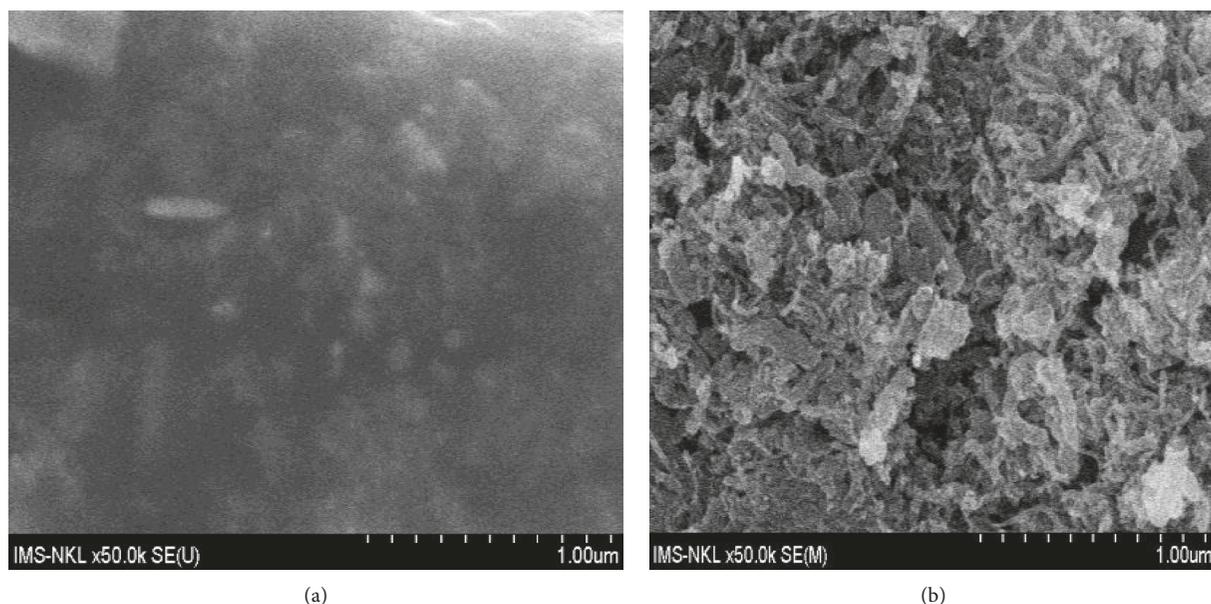


FIGURE 5: Scanning electron micrographs of the CPE modified with 5% Bi<sub>2</sub>O<sub>3</sub> (w/w) (a) before and (b) after electrochemical reduction at -1.2 V for 120 s in the supporting electrolyte mixture of 0.1 M KI and acetate buffer solution. Other conditions are as in Figure 1.

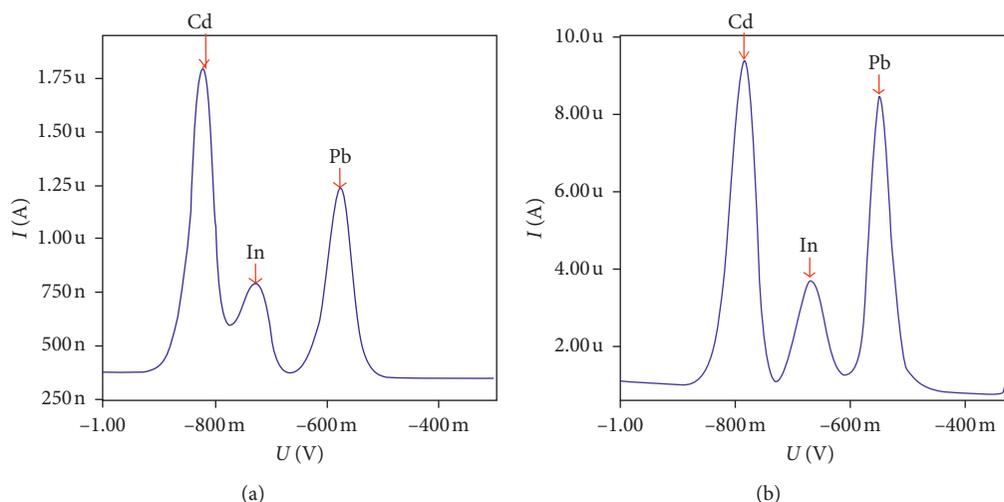


FIGURE 6: DP-ASV of Cd, Pb, and In supporting electrolytes: (a) acetate buffer (pH = 4.5); (b) mixture of 0.1 M KI and acetate buffer (pH 4.5). Conditions: [Cd(II)] = 5 μg·L<sup>-1</sup>; [Pb(II)] = 5 μg·L<sup>-1</sup>; [In(III)] = 10 μg·L<sup>-1</sup>. Other conditions are as in Figure 1.

bromide and Triton X-100 surfactants in range from 0.1 to 10 mg·L<sup>-1</sup> concentrations was also studied. A decrease in the  $I_p$  value was found for Cd(II), Pb(II), and In(III) determination on increasing the amount of the surfactant. Nevertheless, this surfactant interference was reduced by the UV irradiation with a UV lamp at 254 nm wavelength in 90 min.

**3.9. Determination of CRM.** The accuracy of the method was studied by analysis of sediment CRM (MESS-2). The results are shown in Table 2. The results of these five trials were not significantly different from the certified values following Student's  $t$  test ( $t_{\text{exp}} = 2.52$  greater than  $t(0.05, 4)$ ).

**3.10. Determination of River Water Samples.** Water pollution in some rivers of Hanoi, Vietnam, has been a serious problem, with high concentration of metal ions and other ions [38, 39]. So, we took some river samples in Hanoi to analyse Cd(II), In(III), and Pb(II). The samples were acidified by 10% HNO<sub>3</sub>, and then the solution was filtered using the 0.45 μm membrane filter. The sample was treated with UV light for 90 minutes at wavelength 254 nm.

After filtering, 10.0 mL of the solution was taken, and the mixture of 0.1 M KI and acetate buffer was added. Content analysis of Cd, In, and Pb in 3 different river samples by DP-ASV was performed using the manufactured CPE. The content of Pb(II) in the samples ranged from 1.45 ± 0.01 μg·L<sup>-1</sup> to 1.93 ± 0.20 μg·L<sup>-1</sup>. The content of Cd(II)

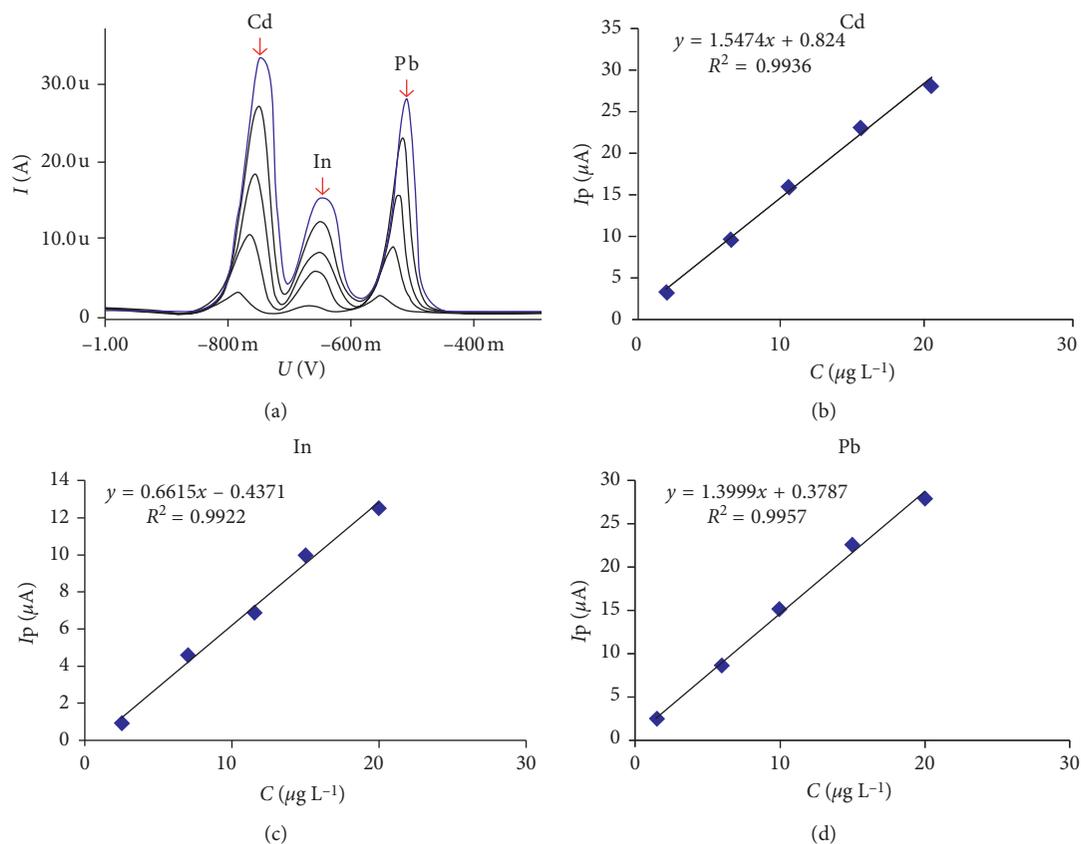


FIGURE 7: (a) DP-ASV of Cd(II), Pb(II), and In(III) and the calibration curve of (b) Cd(II), (c) In(III), and (d) Pb(II). Conditions: [Pb(II)]; [Cd(II)] = 1.5, 6, 10, 15, and 20  $\mu\text{g}\cdot\text{L}^{-1}$ ; [In(III)] = 2.5, 7, 11.5, 15, and 20  $\mu\text{g}\cdot\text{L}^{-1}$ ; supporting electrolyte mixture of 0.1 M KI and acetate buffer. Other conditions are as in Figure 1.

TABLE 1: Various Bi precursor-modified and  $\text{Bi}_2\text{O}_3$ -modified carbon electrodes for analysis of Cd(II), Pb (II), and In(III).

Electrode material	Voltammetric	Studied ions	LOD	Linear range	Reference
$\text{Bi}_2\text{O}_3/\text{SPE}$	SW-ASV	Pb	5 $\mu\text{g}\cdot\text{L}^{-1}$ (at pH = 1.2) 10 $\mu\text{g}\cdot\text{L}^{-1}$ (at pH = 4.5)	5–150 $\mu\text{g}\cdot\text{L}^{-1}$ (at pH = 1.2) 10–150 $\mu\text{g}\cdot\text{L}^{-1}$ (at pH = 4.5)	[28]
		Cd	2.5 $\mu\text{g}\cdot\text{L}^{-1}$ (at pH = 1.2) 5 $\mu\text{g}\cdot\text{L}^{-1}$ (at pH = 4.5)	5–150 $\mu\text{g}\cdot\text{L}^{-1}$ (at pH = 1.2) 10–150 $\mu\text{g}\cdot\text{L}^{-1}$ (at pH = 4.5)	
$\text{Bi}_2\text{O}_3/\text{SPE}$	SW-ASV	Pb	2 $\mu\text{g}\cdot\text{L}^{-1}$	50–300 $\mu\text{g}\cdot\text{L}^{-1}$	[29]
$\text{Bi}_2\text{O}_3/\text{SPE}$	DP-ASV	Pb	1.0 $\mu\text{g}\cdot\text{L}^{-1}$		[30]
$\text{Bi}_2\text{O}_3/\text{SPE}$	SW-ASV	Pb	2.3 $\mu\text{g}\cdot\text{L}^{-1}$	20–100 $\mu\text{g}\cdot\text{L}^{-1}$	[31]
		Cd	1.5 $\mu\text{g}\cdot\text{L}^{-1}$	20–100 $\mu\text{g}\cdot\text{L}^{-1}$	
$\text{Bi}_2\text{O}_3/\text{SPE}$	SW-ASV	Pb	1.1 $\mu\text{g}\cdot\text{L}^{-1}$	0–80 $\mu\text{g}\cdot\text{L}^{-1}$	[32]
		Cd	2.1 $\mu\text{g}\cdot\text{L}^{-1}$	0–160 $\mu\text{g}\cdot\text{L}^{-1}$	
$\text{Bi}_2\text{O}_3/\text{SPE}$	SW-ASV	Pb	5 $\mu\text{g}\cdot\text{L}^{-1}$		[33]
		Cd	5 $\mu\text{g}\cdot\text{L}^{-1}$		
BONPs-IL/CPE	SW-ASV	Pb	0.21 $\mu\text{g}\cdot\text{L}^{-1}$	3–30 $\mu\text{g}\cdot\text{L}^{-1}$	[34]
		Cd	0.15 $\mu\text{g}\cdot\text{L}^{-1}$		
BiOCl/MWCNT-GCE	SW-ASV	Pb	1.9 $\mu\text{g}\cdot\text{L}^{-1}$		[35]
		Cd	4 $\mu\text{g}\cdot\text{L}^{-1}$		
$\text{Bi}_2\text{O}_3/\text{MWCNT-CPE}$	DP-ASV	Pb	0.26 $\mu\text{g}\cdot\text{L}^{-1}$	1.5–20 $\mu\text{g}\cdot\text{L}^{-1}$	This study
		Cd	0.22 $\mu\text{g}\cdot\text{L}^{-1}$	1.5–20 $\mu\text{g}\cdot\text{L}^{-1}$	
		In	0.65 $\mu\text{g}\cdot\text{L}^{-1}$	2.5–20 $\mu\text{g}\cdot\text{L}^{-1}$	

SPE: screen printed electrode; GCE: glassy carbon electrode; SW-ASV: square wave anodic stripping voltammetry; BONP: bismuth oxide nanoparticle; IL: ionic liquid; BiOCl: bismuth-oxychloride.

TABLE 2: Cd(II), Pb(II), and In(III) determination in CRM by the DP-ASV method (using the CPE modified with Bi<sub>2</sub>O<sub>3</sub>) and  $\mu$  value of CRM.

Ion	$\bar{X}$ ( $\mu\text{g/g}$ )	$\mu$ ( $\mu\text{g/g}$ )
Pb(II)	20.5	21.9
In(III)	<LOD	<LOD
Cd(II)	<LOD	0.24

Note.  $\bar{X}$  is the average value of the DP-ASV method (5 measurements).

TABLE 3: Pb(II) content in water samples identified by the DP-ASV method (using the CPE modified with Bi<sub>2</sub>O<sub>3</sub> using CNTs) and the GF-AAS method.

Samples	GF-AAS	DP-ASV	Recovery (%)	$t_{\text{exp}}$
1	1.86	1.93	96.37	2.52
2	1.62	1.76	108.64	2.35
3	1.47	1.45	98.64	1.68

Note. All concentrations are expressed in  $\mu\text{g}\cdot\text{L}^{-1}$ ; the result of the DP-ASV method is the average value of 5 measurements.

and In(III) in samples was smaller than the limit of quantitative. The results of Pb(II) in this sample using the DP-AAS method with CPE modified with Bi<sub>2</sub>O<sub>3</sub> using MWCNTs were compared with GF-AAS and are shown in Table 3. The results of these five measurements were not significantly different from the certified values.

## 4. Conclusions

The CPE modified with 5% (w/w) Bi<sub>2</sub>O<sub>3</sub>, 3 mm diameter, using CNTs was applied for simultaneous analysis of the concentration of Cd(II), Pb(II), and In(III) by the DP-ASV method. The CPE modified with 5% (w/w) Bi<sub>2</sub>O<sub>3</sub> are not only easy to make and easy to use, but also environmentally friendly. The method has good accuracy, low detection limit, and good repeatability.

## Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

## Conflicts of Interest

The authors declare that they have no conflicts of interest regarding the publication of this paper.

## Acknowledgments

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## Research Article

# Structure and Electrochemical Properties of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ Prepared via Low-Temperature Precipitation

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This work aimed to prepare the spinel phase  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  by a combination of the low-temperature precipitation technique and assisted calcination step. X-ray diffraction (XRD) revealed that the intermediated phase was  $\text{Li}_2\text{TiO}_3$ , and the spinel phase could be evidently formed at 700°C for 12 to 20 hours. The morphology of spinel powder, determined by SEM and TEM, exhibited a good distribution at the submicrometric scale that promoted a fast kinetic of Li migration and an excellent performance at the high-rate cycling test. The stable performances were achieved in the charge-discharge test at different current densities: 80 mA/g (165 mAh/g), 320 mA (160 mAh/g), and 1600 mA (145 mAh/g) upon 100 cycles. Moreover, we observe a capacity retention of 48% (corresponding 80 mA/g) at a high rate of 5000 mA/g. The cyclic voltammetry measurement displayed a reversible system and revealed the lithium diffusion coefficient of  $1.15 \times 10^{-11} \text{ cm}^2/\text{s}$ .

## 1. Introduction

Spinel  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  has become an attractive anode material for high-power and fast-charging Li-ion battery because of its excellent cycle performance, structural stability, and little change in the unit cell volume during lithium intercalation/deintercalation. The spinel structure of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  provides a three-dimensional network for Li migration [1, 2]. The process of lithium insertion/extraction occurs as the two-phase mechanism at 1.55 V (vs.  $\text{Li}^+/\text{Li}$ ), characterized by a long flat plateau in the voltage profile. The voltage plateau happens to be much above the reduction potentials of most common electrolyte solvents mitigating the formation of the solid electrolyte interface (SEI). In spite of these beneficial properties,  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  does not yet meet all the requirements for successful use in fast-charging applications caused by its

poor electrical conductivity and sluggish diffusion of lithium ions. [3, 4].

In the literature, many efforts have been aimed to overcome these disadvantages by doping or carbon coating of particles [5, 6] to enhance the conductivity of LTO particles; or alternative synthesis methods fabricate the nano-size LTO with controlled and regular morphologies aiming to shorten the lithium diffusion pathway. It has been reported that nanocrystalline  $\text{Li}_5\text{Ti}_5\text{O}_{12}$  electrode materials have excellent performance even at high charging rate and high temperature; therefore, they are useful when applied in high-rate charge/discharge Li-ion batteries. Different synthesis methods have been investigated such as sol-gel processes, high-temperature annealing treatment, solution-combustion, and hydrothermal to improve the phase purity and electrochemical performance. Hao et al. [7] synthesized

$\text{Li}_4\text{Ti}_5\text{O}_{12}$  particles by a sol-gel method with citric acid as a chelating agent and  $\text{Li}_2\text{CO}_3$  and tetrabutyl titanate as starting materials. Mixtures of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  and rutile- $\text{TiO}_2$  were observed after heating at  $800^\circ\text{C}$  for 20 hours in air, while the pure  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  phase with an average particle size of 500 nm was obtained at  $850^\circ\text{C}$  for 24 hours. Li et al. [8] prepared  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  with nanotubes and nanowires morphology by a hydrothermal lithium exchange processing. XRD analysis showed a trace of anatase- $\text{TiO}_2$  in spinel  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  nanotubes calcinated at  $350^\circ\text{C}$  for 2 hours. The  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  spinel was synthesized by a sol-gel method using titanium isopropoxide,  $\text{LiOH}$ , and 2-methoxy ethanol and subsequent treatment with high ball milling by Kim et al. [9] It was also notified that a trace of rutile- $\text{TiO}_2$  was observed for the powder annealed at  $850^\circ\text{C}$  for 5 hours. According to previous studies, the heat treatment at high temperature in synthesizing the  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  spinel obviously led to the formation of rutile or anatase- $\text{TiO}_2$ , and these impurities are detrimental to the electrochemical performance of the spinel phase. Consequently, low-temperature synthesis or minimum heat treatment by employing a suitable aqueous particulate sol-gel route or intermediate precipitate phase has been recently suggested. Chui and coworker [10, 11] utilized the extreme excess ratio of Ti versus Li (Ti:Li = 6:1) to prepare the spinel phase  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  through the intermediated phase lithium titanate hydrate  $\text{Li}_{1.81}\text{H}_{0.19}\text{Ti}_2\text{O}_5\cdot 2\text{H}_2\text{O}$  (LTH).

Our work aimed to prepare the nanosized spinel  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  powder from the intermediated cubic phase  $\text{Li}_2\text{TiO}_3$  which was obtained from a low-temperature precipitation. The effect of temperature and duration of calcination on the formation of the spinel phase was regarded. The structural and morphological properties were characterized by powder X-ray diffraction, Raman spectroscopy, and scanning/transmission electronic microscopy (SEM/TEM). The high-rate performance through galvanostatic charge-discharge and the diffusion coefficient of lithium ions ( $D_{\text{Li}}$ ) in the host  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  were measured and compared with the bulk material.

## 2. Experimental

**2.1. Synthesis of Nanostructured  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ .** Spinel-type  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  was prepared via a low-temperature precipitation method combining with the calcining process from 600 to  $800^\circ\text{C}$ . Titanium butoxide  $\text{Ti}(\text{O}i\text{Bu})_4$  with a normal purity of 97% (Sigma Aldrich,  $d = 1.491$  g/mL at  $20^\circ\text{C}$ ,  $M = 340.39$  g/mole) and lithium hydroxide monohydrate  $\text{LiOH}\cdot\text{H}_2\text{O}$  with a normal purity of 99.95% (Sigma Aldrich) were used as titanium and lithium precursors. 10.50 mg  $\text{Ti}(\text{O}i\text{Bu})_4$  was dropped into 25 mL solution of 1 M  $\text{LiOH}$  solution under vigorous stirring at  $5^\circ\text{C}$  with the molar ratio Li:Ti of 1:1.33. Then, the produced powder was collected by centrifugation and washed several times with deionized water to neutral pH to eliminate the excess of  $\text{LiOH}$  and dried at  $120^\circ\text{C}$  for overnight. The as-prepared powder was annealed at 600– $800^\circ\text{C}$  for 12 hours.

**2.2. Structural Characterizations.** The structure of samples was identified by X-ray diffraction (XRD) in D8-Advance (Bruker) diffractometer using  $\text{CuK}\alpha$  radiation ( $\lambda = 1.5406$  Å). XRD patterns were collected in the range  $10^\circ$ – $70^\circ$  with a step of  $0.029^\circ$  per second. Lattice parameters were calculated by software CelRef. Raman spectra were measured with a XploRA Raman microspectrometer (Jobin-Yvon-Horiba), using a He:Ne laser (632.8 nm) as the excitation source. The morphologies and the distribution of grain size were determined by using scanning electron microscope (FE-SEM S4800 Hitachi, Japan) and transmission electronic microscopy (TEM, JEOL 1400, Japan).

**2.3. Electrochemical Characterizations.** The electrochemical performance, including rate capability and charge/discharge capacity of spinel  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ , was evaluated at room temperature with the coin-cell type CR-2025 in which a metallic lithium foil was used as the counterelectrode. The composite electrodes were made of the active material (80 wt.%), conducting acetylene black (7.5 wt.%), carbon graphite (7.5 wt.%), and polyvinylidene fluoride (PVdF) binder (5 wt.%) homogeneously dispersed in *N*-methyl-2-pyrrolidone (NMP) solvent. The slurry was coated on an aluminum foil and cut to pieces with diameter of 10 mm (an area surface of  $0.785$  cm<sup>2</sup>) and then dried at  $120^\circ\text{C}$  in vacuum for 12 hours. The coin cell was assembled in an argon-filled glove box (M. Braun Co.,  $[\text{O}_2] < 1$  ppm and  $[\text{H}_2\text{O}] < 1$  ppm). The employed organic electrolyte was a mixture of 1 M  $\text{LiPF}_6$  with ethylene carbonate (EC) and dimethyl carbonate (DMC) at volumetric ratio 2:1.

A constant current protocol in the range of 20 mA/g to 5000 mA/g was used for formation cycles in a potential range of 1–2.5 V (vs.  $\text{Li}^+/\text{Li}$ ). The cyclic voltammetry (CV) was performed at different scan rates between the voltage of 10 and  $120$   $\mu\text{V}/\text{s}$  to evaluate the lithium coefficient diffusion related to the charge/discharge process.

## 3. Results and Discussion

**3.1. Structure and Morphology.** Considering the structure of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ , the previous studies [1, 2, 4] demonstrated a cubic spinel (unit cell  $a = 8.3557$  Å) with a space group of F3dm. The three ions  $\text{Li}^+$  are situated at the tetrahedral 8a site, the other ions  $\text{Li}^+$  and ions  $\text{Ti}^+$  randomly locate in the octahedral 16d sites with a ratio of 1:5, and the oxygen atoms totally are located at the 32e site; this suggests that  $[\text{Li}_3]^{8a}[\text{Li}_1\text{Ti}_5]^{16d}[\text{O}_{12}]^{32e}$  is the probable structure. Figure 1 compares the XRD patterns of the intermediated phase and final samples calcinated at different temperatures from  $500^\circ\text{C}$  to  $800^\circ\text{C}$  for 12 hours. The intermediate phase can be indexed in the orthorhombic phase  $\text{Li}_2\text{TiO}_3$  (JSPDS: 00-003-1024). At  $500^\circ\text{C}$ , the spinel  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  phase was apparently formed, but the transformation was uncompleted; the remaining of the intermediate phase was still observed in the XRD diagram. At  $600^\circ\text{C}$ , XRD patterns provided the main peaks of the  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  phase (JSPDS: 000-049-0207) [12], indicating the

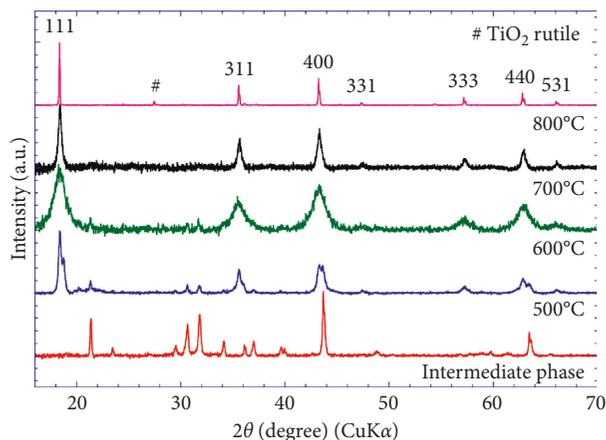


FIGURE 1: XRD patterns of samples at different calcination temperatures.

complete transformation from the intermediated phase to  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  phase. However, it was noticed in the samples thermally treated, and  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  presents wide peaks, which indicated the formation of the small crystalline material. The pure spinel phase  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  was obtained at 700°C and 800°C, and it could be obviously observed that the crystallinity degree of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  improved with increase in calcination temperature. In contrast, the calcination at 800°C led a trace of rutile- $\text{TiO}_2$ . When the calcinating temperature was raised from 600°C to 700°C, the lattice parameter  $a$  slightly increased: 8.3477 Å (600°C) to 8.3599 Å (700°C). Colbow et al. [1] reported  $a = 8.357$  Å, and Harisson et al. [13] also reported  $a = 8.358$  Å which is in good agreement with our value at 700°C. The sample calcinated at 800°C exhibited unexpectedly the high value of the lattice parameter and 8.3716 Å due to the emergence of the  $\text{TiO}_2$  rutile phase, respectively.

In order to examine the impact of calcination time, the sample at 700°C was treated at variable scheduling (Figure 2). The remaining intermediate phase was still observed for 4 hours and 8 hours, while the pure phase  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  only appeared at the duration from 12 hours to 20 hours. However, with 24 hours of calcination, the  $\text{TiO}_2$  anatase phase was merged in the LTO phase. XRD patterns of samples at 12, 16, and 20 hours are identical and indexed to the pure spinel phase. The lattice parameter  $a$  can be determined to be 8.3595 Å which is in good agreement with the reported standard values even though the wide XRD peaks indicated the small crystallite of LTO. The crystallite size of the LTO phase was, respectively, calculated from their reflections using the Scherrer equation based on the full width at half maximum (FWHM) of diffraction peaks:

$$d_{hkl} = \frac{k\lambda}{\beta \cos \theta} \quad (1)$$

where  $d_{hkl}$  is the average crystallite size,  $k$  is the constant depending on the crystalline shape (0.9),  $\lambda$  is the radiation X-ray wavelength of Cu (1.5406 Å),  $\beta$  is the FWHM of the most intense peak, and  $2\theta$  is the diffraction angle. The rough estimation of crystallite size is around 40 nm for all three

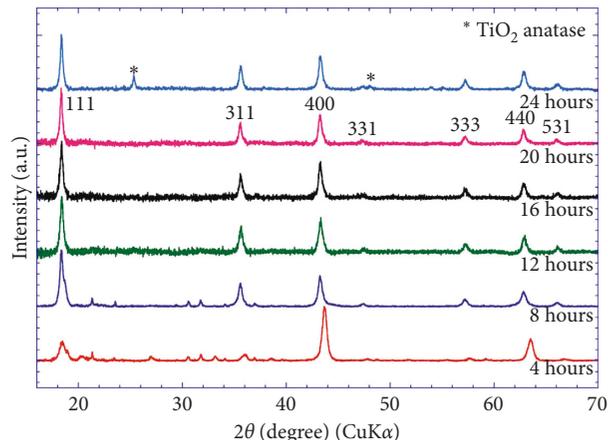


FIGURE 2: XRD patterns of samples at different calcination times at 700°C.

samples. The submicrometric LTO could suggest a fast kinetic of lithium insertion due to shortening of the lithium pathway diffusion.

Raman active modes of spinel  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  involve  $F_{2g}$ ,  $E_g$ , and  $A_{1g}$  following the calculation of symmetry group  $O_h^2$ , which represented the stretching and bending vibration of Ti-O bonds in  $[\text{TiO}_6]$  octahedra and Li-O bonds in  $[\text{LiO}_4]$  and  $[\text{LiO}_6]$  polyhedra. [14, 15] At high frequency, two vibration modes  $A_{1g}$  at 671  $\text{cm}^{-1}$  and 740  $\text{cm}^{-1}$  were assigned to the vibrations of Ti-O bonds, while the stretching vibrations of the Li-O bonds were attributed by two modes in region medium frequency 430  $\text{cm}^{-1}$  and 374  $\text{cm}^{-1}$ . The last modes in low frequency (235  $\text{cm}^{-1}$ ) were attributed to the bending vibrations of O-Ti-O bonds. In brief, we succeeded to produce the pure phase  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  treated at 700°C for three schedules (12, 16, and 20 hours) without structural difference.

Figure 3 shows the SEM and TEM morphology of the sample  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  treated at 700°C for 16 hours. It can be seen that the sample consists of submicro-scaled primary particles with a homogeneous size distribution, which are in turn composed of larger particles of 100  $\mu\text{m}$ . From the TEM image, the primary particles consist of nanorods of 10 nm in length (Figure 4).

**3.2. Electrochemical Performance.** The electrochemical performance of the spinel nanosized  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  as anode materials for lithium ion batteries has been investigated. Figure 5(a) illustrates the voltage profiles at low current density 20 mA/g of three samples  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  calcinated at 700°C for 12, 16, and 20 hours. The samples delivered a first discharge capacity of 178 mAh/g with a cutoff value of 1.0 (vs.  $\text{Li}^+/\text{Li}$ ). This is in line with the theoretical capacity of 175  $\text{mAh}\cdot\text{g}^{-1}$  meaning that the excess lithium ions were intercalated into LTO, and no SEI film formed during the first charge which is usually formed in the range 0.2–0.8 V vs.  $\text{Li}^+/\text{Li}$  [8]. In the subsequent cycles, the capacity discharge was stabilized at 167 mAh/g without obvious capacity fading. A flat plateau at 1.65 V vs.  $\text{Li}^+/\text{Li}$  precisely corresponding to the  $\text{Ti}^{3+}/\text{Ti}^{4+}$  redox reaction means that is the insertion/

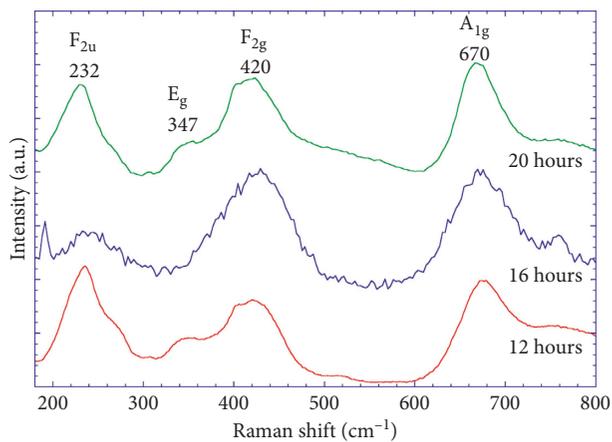


FIGURE 3: Raman spectroscopy of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ .

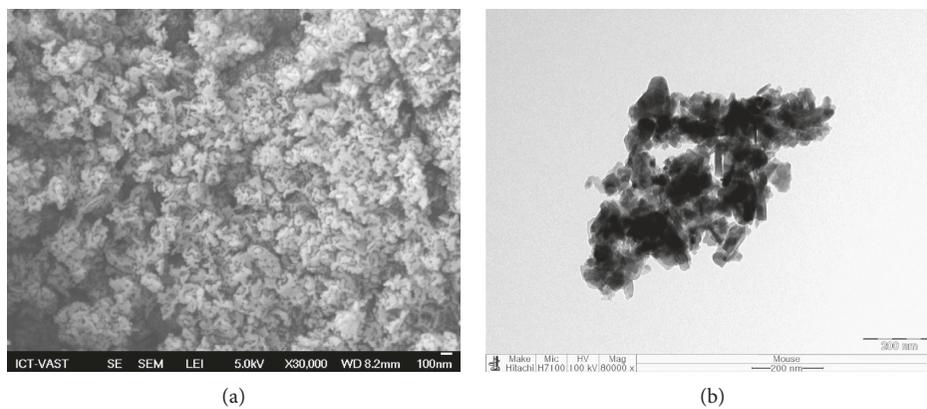


FIGURE 4: SEM images (a) and TEM image (b) of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  treated at  $700^\circ\text{C}$  for 16 hours.

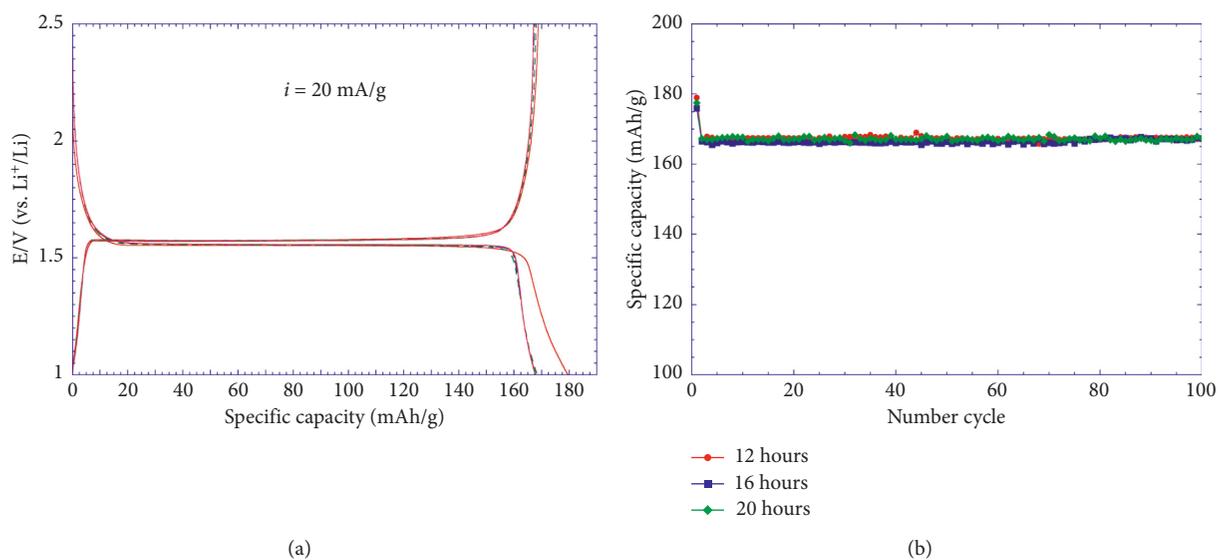


FIGURE 5: (a) Typical charge-discharge curves at current density of  $20 \text{ mA/g}$  and (b) cycling performance of samples  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  calcinated at  $700^\circ\text{C}$  for 12 hours, 16 hours, and 20 hours.

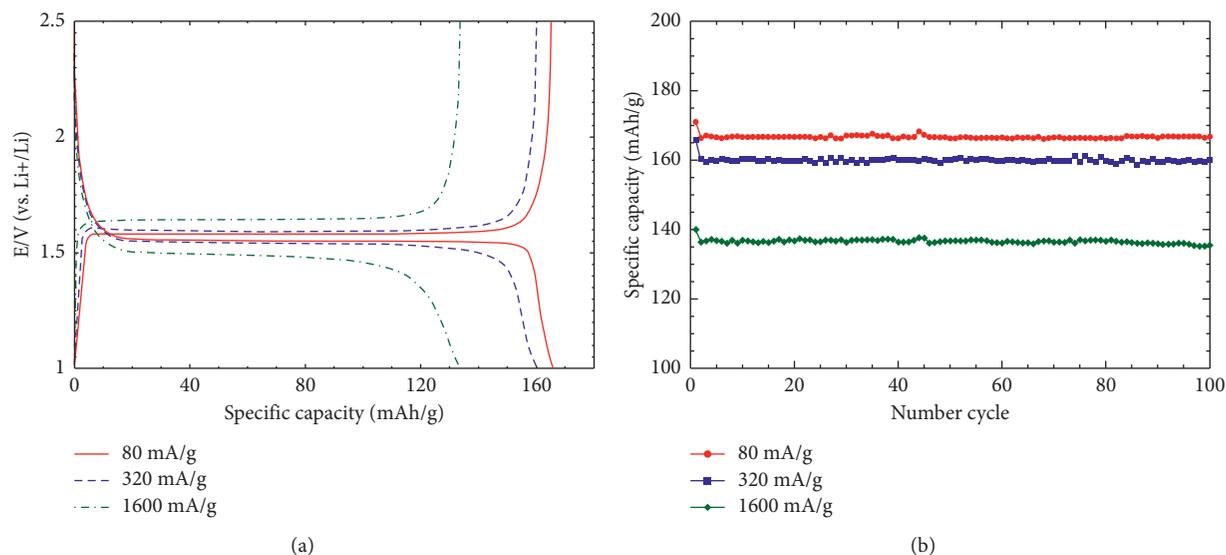


FIGURE 6: (a) Typical charge-discharge curves at current density: 80, 320, and 1600 mA/g and (b) cycling performance of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ .

extraction of lithium ions during the charge/discharge process. In addition, a small electrode polarization of about 0.02 V (below 20 mV) is observed between charge and discharge curves indicating the existence of good interparticle electrical contacts and better ion transport owing to the  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  nanoparticles and good stability of the spinel structure during Li migration. Furthermore, all three spinel samples exhibited excellent cycling stability with a capacity retention of 100% upon 100 cycles (Figure 5(b)).

Spinel  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  is subjected to cycling at different charge-discharge rates such as 80 mA/g, 320 mA/g, and 1600 mA/g to evaluate the capacity-rate relationship (Figure 6(a)). The charge-discharge curve at current 320 mA/g seems to quasi-superimpose on the one at current 80 mA/g without potential difference. The sample exhibited a capacity value of 165 mAh/g (80 mA/g) and 160 mAh/g (320 mA/g), a value close to the theoretical value of 175 mAh/g. At extremely high current of 1600 mA/g, there is a slight drop in capacity values (12.5% decrease) together with a drop in the discharge voltage plateau at 1.5 V (vs.  $\text{Li}^+/\text{Li}$ ) which causes high electrode polarization (140 mV). However, the cycling performance upon 100 cycles at all three constant current show an excellent Coulombic efficiency; typically, the capacity retention remained 100% after 100 cycles with the capacity of 165 mAh/g, 160 mAh/g, and 135 mAh/g, respectively.

The rate capability is also important parameter for evaluating an electrode material addressed to the battery as well as supercapacitor application. A constant current discharge test was performed on  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  electrodes varying the rate from 20 mA/g to 5000 mA/g during discharge in the voltage range of 1.0–2.5 V, with the voltage profiles visible in Figures 7(a)–7(c). The charge-discharge profiles at rates below 1000 mA/g (Figure 7(a)) show a low polarization from 20 mV (40 mA/g) to 90 mV (960 mA/g) indicating the electron transfer efficiency and lithium diffusion pathway.

Our spinels exhibit the better rate capability than those reported in the literature [16]. A capacity of 145 mAh/g was achieved at current 400 mA/g, and this capacity amounts to 85% of capacity at the low current of 20 mA/g. From the current density above 1200 mA/g, we observe the critical impact of rates on the voltage profiles and the specific capacity. The more the current density applied, the more the discharge plateau shortened. Traditionally, the lithium insertion/extraction into host  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  occurred via a two-phase mechanism; herein, it showed a sloping voltage curve similar to that of a one-phase reaction due to the large electrode polarization.

Figure 7(d) illustrates the electrode polarization and specific capacity as function of the C-rate, and the highest current 5000 mA/g corresponds to rate 30°C. In the high current density performance, the electrochemical profiles significantly depended on the electronic conduction, which served as the electrode polarization. The drastic increase of polarization voltage from 100 mV to 350 mV was observed when the currents applied varied from 1200 mA/g to 5000 mA/g. Our spinel  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  still shows an impressive performance at such high current densities. At three highest currents 4500 mA/g (26°C), 4750 mA/g (28°C), and 5000 mA/g (30°C), the capacities 90 mAh/g, 85 mAh/g, and 80 mAh/g were achieved, respectively. It is noteworthy that the capacity (80 mAh/g) obtained with nanosized LTO at 30°C rate is much higher than that obtained at the 5°C rate (95 mAh/g) with bulk LTO. Indeed, the morphology of mesoporous and nanoparticle LTO powders provide a short diffusion path for Li and pore fill of electrolytes ensuring a high flux of Li.

Cyclic voltammetry analysis has been carried out to further investigate the electrochemical properties of spinel  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ . Figure 8(a) shows the cyclic voltammetry curve at different scan rates to determine the kinetic of Li-migration process. The pair of anodic/cathodic peaks of spinel  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ,

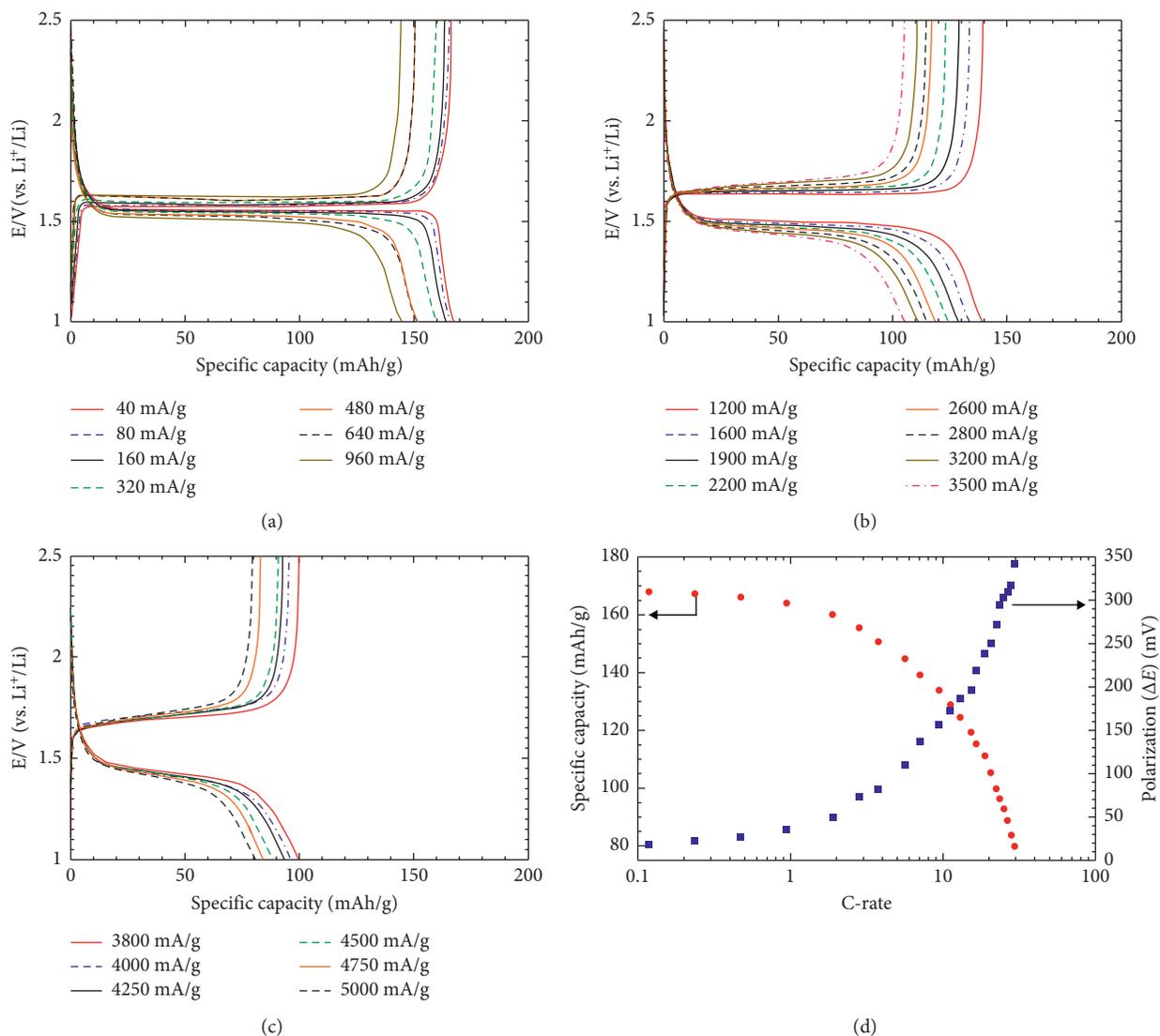


FIGURE 7: (a–c) Charge-discharge profile of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  at various current densities from 40 mA/g to 5000 mA/g and (d) electrode polarization and specific capacity as the function of C-rate.

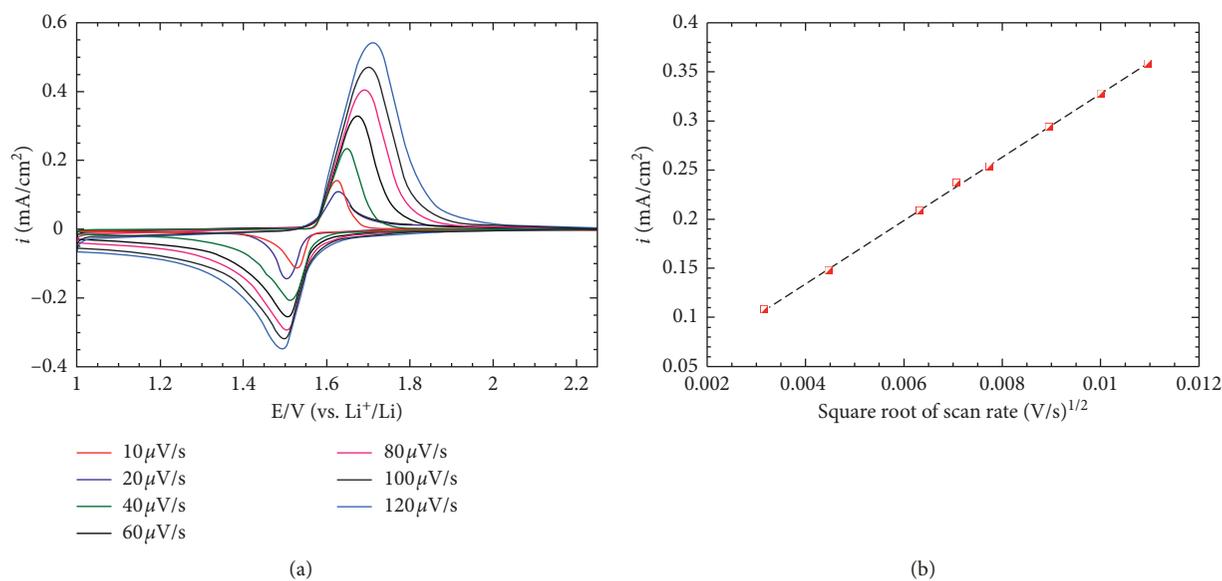


FIGURE 8: (a) CV curves under various scan rates from 10  $\mu\text{V/s}$  to 120  $\mu\text{V/s}$  and (b) current density as a function of the square root of the scan rate  $v^{1/2}$ .

located at 1.62 V/1.55 V at the scan rate of  $10 \mu\text{V/s}$ , demonstrate reversible lithium intercalation and deintercalation of host  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ , respectively. The peak separation increases with the increasing scan rate that indicated the effect of electrode polarization owing to the limited diffusion process. The plot of cathodic peak current density ( $i_{pc}$ ) as a function of the square root of the scan rate ( $v^{1/2}$ ) in Figure 8(b) shows a good linear relation between  $i_{pc}$  and  $v^{1/2}$  ( $R = 0.9999$ ). Herein, the equation Randles–Sevcik [17] can be applied to determine the diffusion coefficient of lithium ions ( $D_{Li}$ ), characterized as the kinetics of the lithium insertion process. The diffusion coefficient of lithium ions was calculated to be  $1.15 \times 10^{-11} \text{ cm}^2/\text{s}$ .

#### 4. Conclusion

In summary, spinel  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  has been successfully prepared through a low temperature precipitation process to obtain a particle-size distribution at the submicrometric scale. The electrochemical measurements show that spinel LTO exhibited the discharge capacity of 178 mAh/g at  $0.1^\circ\text{C}$  in the first discharge and favorable cyclic reversibility at different current rates of 20, 80, 320, and 1600 mA/g with a capacity of 167, 165, 160, and 135 mAh/g upon 100 cycles. Furthermore, the spinel samples show an excellent performance at extremely high rate, which is capable of delivering a capacity of 80 mAh/g at current 5000 mA/g.

#### Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

#### Conflicts of Interest

The authors declare that they have no conflicts of interest.

#### Acknowledgments

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## Research Article

# Cellulose Conversion to 5-Hydroxymethyl Furfural (5-HMF) Using Al-Incorporated SBA-15 as Highly Efficient Catalyst

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Al-incorporated SBA-15 samples (xAl/SBA-15) were successfully prepared by “atomic implantation” method. The samples were characterized by X-ray diffraction spectroscopy (XRD), transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDX), N<sub>2</sub> adsorption-desorption isotherms (BET), and temperature-programmed desorption (NH<sub>3</sub>-TPD). In this catalyst, metal oxide species were highly dispersed on the SBA-15 surface and existed as isolated atoms. It was shown that the Al incorporation lead to the formation of medium and strong acid sites. The catalytic activity and selectivity were tested in a mild hydrothermal process for degradation of cotton cellulose to 5-hydroxymethyl furfural (5-HMF). A cellulose conversion of 68.5% and 5-HMF selectivity of 62.1% after 2 h of reaction at 170°C were achieved. The very high 5-HMF yield (42.57%) obtained in this paper is much higher than that was reported in the literature.

## 1. Introduction

In recent years, the process of biomass conversion to hydrocarbon fuels has received much attention due to the limited fossil fuels resource, demanding the alternatives to obtain biofuels. Biomass is as well known as carbon renewable energy resources for the production of bio-oil by the fast pyrolysis technology. However, bio-oil is composed of different compounds with high oxygen content and low chemical stability and, therefore, cannot be used as biofuels. Recently, great efforts have been made to develop practical pathways to transform biomass-derived carbohydrates into chemicals and fuels. 5-Hydroxymethyl furfural (5-HMF) has a versatile range of applications and can be obtained from the chemical conversion of C<sub>6</sub> carbohydrates. The

conversion of cellulosic biomass to valuable chemicals such as 5-hydroxymethyl furfural, which is often termed the “sleeping giants,” is currently one of the most interests of worldwide research and developments to foster a biobased economy [1]. Therefore, considerable efforts devoted to the depolymerization of cellulose to obtain 5-HMF as a promising bio-oil.

Due to its high degree of crystallinity and stability, hydrolysis of cellulose was often carried out in acidic medium using acids like H<sub>2</sub>SO<sub>4</sub>, HCl, and HF. In the rigorous reaction condition, the experimental equipment must have high corrosion resistance. Besides, high concentration of inorganic acid used in the reaction can cause extremely negative impacts on surrounding environment. Conversion of cellulose to 5-HMF by using solid acid catalysts under

hydrothermal conditions is an environment-friendly chemical process, and it is easy to separate products by filtration. Interestingly, after the reaction, the catalyst can be easily recovered and reused. The  $\text{SO}_4^{2-}/\text{ZrO}_2\text{-Al}_2\text{O}_3$  catalysts were employed in glucose hydrolysis in hot water which led to a 5-HMF conversion 39% [2]. Zhang et al. stated the preparation of  $\text{SO}_4^{2-}/\text{ZrO}_2$  on  $\text{TiO}_2$  and showed high conversion of glucose into 5-HMF [3]. The combined yield of 5-HMF and levulinic acid reached 28.8% in the presence of  $\text{SO}_4^{2-}/\text{ZrO}_2\text{-TiO}_2$  when the Zr:Ti molar ratio was 5:5 after 2 h of reaction at 170°C.

The advantage of the use of SBA-15 material as catalyst support includes its well-ordered hexagonal mesoporous silica structure with high surface-to-volume ratio, high permeability, variable framework compositions, and high thermal stability [4–6]. However, the electrically neutral framework of purely siliceous SBA-15 gives a rise to its lack of functionality. As a result, it normally plays a role of adsorbent, not acidic or redox catalysts [7, 8]. In order to be used as acidic or redox catalysts, SBA-15 should be modified by incorporation of transition metals into framework using direct and/or postsynthesis [9–17]. Aluminium ions ( $\text{Al}^{3+}$ ) insertion into the SBA-15 creates acid sites in the structure which is extremely important for acid-catalyzed reaction. However, the incorporation of aluminium into Al/SBA-15 is difficult because of the difference in hydrolysis rates of Al and Si in low pH medium during the SBA-15 synthesis process [18]. Various synthetic methods have been devoted for the incorporation of higher amounts of aluminium to achieve higher acid sites [14, 16, 17].

In this paper, we report a novel method to incorporate aluminium ion into the SBA-15 framework by atomic implantation and use it as an efficient catalyst for conversion of cellulose to HMF. Effects of reaction temperature and catalyst dosage were also investigated.

## 2. Experimental Methods

**2.1. Preparation of SBA-15.** Synthesis of SBA-15 material was done as follows: 1 g of poly (ethylene glycol)-block-poly (propylene glycol)-block-poly (ethylene glycol) (P123) was dissolved in 60 mL of HCl (2 M) and stirred for few hours until a clearly surfactant solution was obtained. Sodium silicate solution ~27%  $\text{SiO}_2$  (Sigma-aldrich) was added dropwise into the surfactant solution with vigorous stirring for 2 hours; then, the mixture was further stirred for 24 hours at 45°C, and the obtained mixture was poured into Teflon lined and autoclave hydrothermal treatment was performed in an oven at 100°C for 24 h. Finally, the white solid product was washed, dried at 80°C overnight, and calcined at 550°C for 6 h in air.

**2.2. Preparation of xAl/SBA-15.** Al incorporate was carried out by atomic implantation method using  $\text{AlCl}_3$  (99.99%, Sigma-aldrich) as Al source [19]. In order to obtain 1Al/SBA-15 with different Al loading, we deposited Al by repeating the Al deposition time.  $\text{AlCl}_3$  first deposited on SBA-15 which was prepared previously (denoted 1Al/SBA-15 sample). Use of 1Al/SBA-15 as starting material, we

deposited the second Al layer on 1Al/SBA-15 to obtain 2Al/SBA-15 and use of 2Al/SBA-15 as starting material we deposited the third Al layer (denoted 3Al/SBA-15 sample). The reactor was a quartz tube (2 cm × 25 cm) in which amount of  $\text{AlCl}_3$  was introduced on one side and an opposite side placed a determined amount of SBA-15.

Reactor was heated to 350°C, and  $\text{AlCl}_3$  evaporated and passed through substrate of SBA-15 by flowing carrier gas ( $\text{N}_2$ ). The reaction time was varied between 0.5 h to 1 h. Then the sample was calcined at 500°C to remove chloride.

**2.3. Characterization of Materials and Membrane.** The morphology characteristics of the materials were analyzed by transmission electron microscopy (HITACHI-H-7500). The pore structure of all resulting solids was determined by nitrogen adsorption-desorption isotherms at 77 K using TriStar Plus II. The powder X-ray diffraction patterns of the samples were recorded on a D8 Advance analyzer with  $\text{Cu K}\alpha$  radiation ( $l = 1.5417 \text{ \AA}$ ). The chemical composition of the samples was analyzed by EDX, on JED-2300 analysis Station (JEOL) machine. The acid sites were measured by using  $\text{NH}_3\text{-TPD}$  (model: Autochem II). The ammonia concentration in the effluent gases was determined by a thermal conductivity detector.

**2.4. Catalytic Test.** The investigation of catalytic degradation of cotton cellulose was carried out in a high-pressure batch stainless-steel reactor equipped with a liner of polytetrafluoroethylene (PTFE). The cotton cellulose, solid acid catalysts, and water were thoroughly mixed in the reactor; then, the mixture was heated in the oven. Some effects of operation parameters were mainly investigated such as catalyst type and dosage, reaction temperature, and time on the cellulose saccharification to glucose and the monosaccharide dehydration to 5-HMF. After the reaction, the mixture of solution and solid reactants were separated by filtration.

The cellulose conversion, selectivity, and yield 5-HMF were calculated by the following equation:

$$\text{cellulose conversion (C\%)} = \frac{\text{reacted cellulose}}{\text{initial cellulose}} \times 100\%, \quad (1)$$

$$\text{5-HMF selectivity (S\%)} = \frac{\text{5-HMF}}{\text{reacted cellulose}} \times 100\%, \quad (2)$$

$$\text{5-HMF - Yield (Y\%)} = \text{C(\%)} \times \text{S(\%)}. \quad (3)$$

## 3. Results and Discussion

**3.1. X-Ray Diffraction Spectroscopy (XRD).** Figure 1(a) shows the low-angle X-ray diffraction patterns of xAl/SBA-15. In the XRD pattern, the one peak with strong intensity in the  $2\theta$  angle of ~1.02°, two peaks with weak intensity at  $2\theta$  angle of ~1.6° and  $2\theta$  ~1.8°, corresponding to the diffraction of (100), (110), and (200) reflection, respectively, which are characteristic for the structure of 2D hexagonal  $p6mm$  symmetry of mesoporous SBA-15 structure [19, 20]. In the

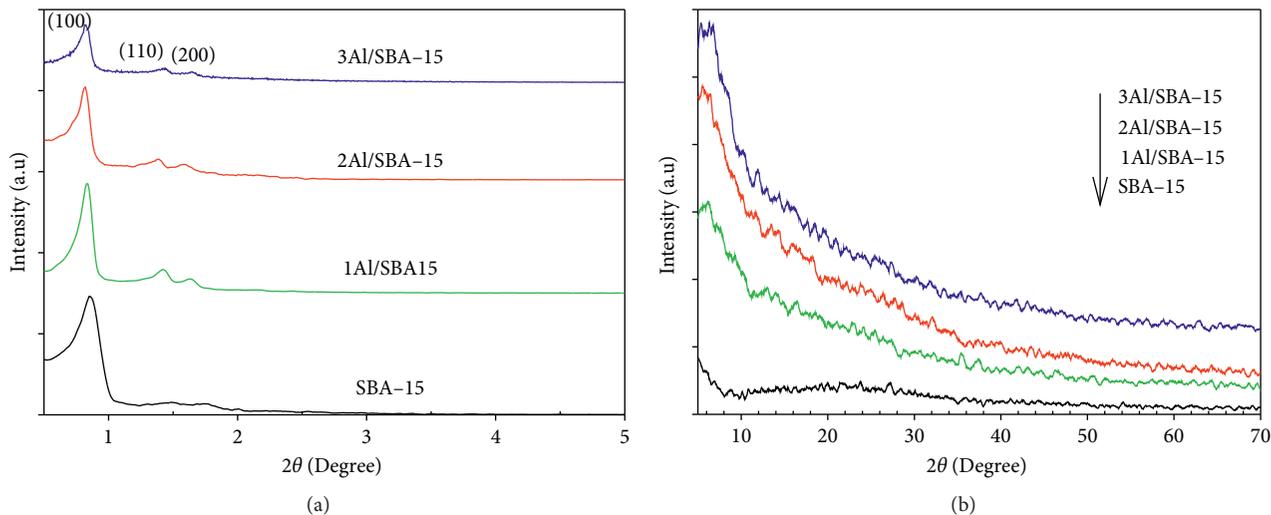


FIGURE 1: Small angle (a) and wide angle (b) XRD patterns of SBA-15 and xAl/SBA-15.

wide angle (Figure 1(b)) XRD pattern of the xAl/SBA-15, no diffraction lines of crystalline Al oxide in xAl/SBA-15 samples were observed. This can be explained by the fact that almost all Al incorporated into SBA-15 framework; therefore, the phase of Al<sub>2</sub>O<sub>3</sub> could not be detected by [5].

As shown in Table 1, the Rietveld refined parameter of the crystal structure of these samples was slightly changed with different Al incorporated into SBA-15 framework. This is related to the substitution of metal ions (Al) for Si in the SBA-15 framework. Because the ionic radius of Al<sup>3+</sup> (0.51 Å) is greater than Si<sup>4+</sup> (0.41 Å), the Al-O bond lengths are longer than Si-O bond, leading to increase in  $d_{100}$  and  $a_0$  parameters [7, 17, 21]. This result strongly confirms that Al incorporation into SBA-15 framework.

**3.2. N<sub>2</sub> Adsorption-Desorption Isotherms (BET).** Figure 2 shows the N<sub>2</sub> isotherms and pore size distribution of calcined SBA-15 and xAl/SBA-15. It can be seen from N<sub>2</sub> isotherms of these samples that the hysteresis loops indicated the typical feature of mesoporous materials owing to the capillary condensation. The increase in N<sub>2</sub> amount adsorbing on the material is clearly observed which is resulted from the multilayer adsorption in the formed mesopore [16, 19]. This indicates that the samples have a large pore size (5.5 nm for SBA-15 and 5.5–5.8 nm for xAl/SBA-15). The high degree of mesopore ordering leads a sharp inflection at relative pressures ( $P/P_0$ ) between 0.6 and 0.8 which is consistent with well-defined 3 nm mesopores. The BET surface areas of SBA-15 and xAl/SBA-15 (Table 2) were strongly decreased from 668 m<sup>2</sup>/g to 143 m<sup>2</sup>/g, respectively. This result can be explained that the new small Al oxides particles were formed and located along to the channels, causing the decrease of surface area. As seen in Table 2, the SBA-15 sample had a pore diameter of 5.50 nm and a wall thickness of 5.51 nm, while xAl/SBA-15 samples showed a slight increase of pore diameter and wall thickness. This result clearly indicated that the new mesopore system

TABLE 1: Characterization of the crystal structure of all samples.

Samples	$D_{100}$ (Å)	$a_0$ (nm) ( $a_0 = 2 \cdot d_{100} / \sqrt{3}$ )
SBA-15	95.419	11.01
1Al/SBA-15	100.356	11.58
2Al/SBA-15	101.276	11.69
3Al/SBA-15	102.542	11.84

was formed and located along to the pore SBA-15 system [11, 22].

**3.3. Transmission Electron Microscopy (TEM) and Energy-Dispersive X-Ray Spectroscopy (EDX).** The transmission electron microscopy (TEM) images of SBA-15 and xAl/SBA-15 samples are illustrated in Figure 3. The TEM image of SBA-15 display well-ordered hexagonal arrays of mesopore with one-dimensional channels, indicating a 2D hexagonal ( $p6mm$ ) mesostructure. The average wall thickness was ~5-6 nm, with similar width pore diameters determined by BET. As seen in Figures 3(b)–3(d), the pore and wall thickness of Al incorporated SBA-15 were not uniform as compared to those of pure SBA-15. Especially, for the Al-incorporated SBA-15 sample with high Al content (3Al/SBA-15), Al oxide particles covered the surface, no pores and wall of SBA-15 were observed.

The results of EDX in Figure 4 and Table 3 show that the Al element contents (5.6, 9.7, and 12.5%) deposited on the xAl/SBA-15 were approximately equal to the value calculated. From Figure 4, it was noted that the Al loading was increasing. Thus, at high Al loading (3Al/SBA-15), the intensity of Al peak was higher than that of medium loading sample (2Al/SBA-15). However, when Al content was too high, Al content determined by EDX is lower than calculated amount. This due to the saturation of Al deposited on SBA-15 surface. The 3Al/SBA-15 sample was prepared by deposition the third Al layer on 2Al/SBA-15 sample. In this case, penetration of Al into SBA-15 is hindered by the two Al

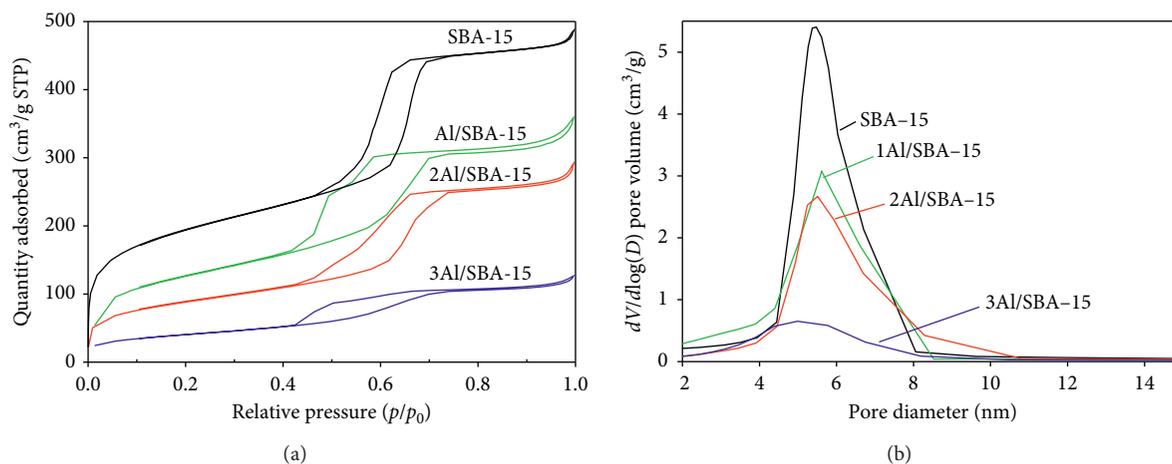


FIGURE 2: BET specific surface area of SBA-15 and xAl/SBA-15 samples (a) and pore size distribution (b).

TABLE 2: Textual characteristics of SBA-15 and xAl/SBA-15 samples.

Samples	$S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ )	$S_{\text{micro}}$ ( $\text{m}^2/\text{g}$ )	$V_{\text{pore}}$ ( $\text{cm}^3/\text{g}$ )	$D_{\text{BJH}}$ (nm)	$W_t$ (nm) $W = a_0 - D_{\text{BJH}}$
SBA-15	668.52	182.93	0.70	5.50	5.51
1Al/SBA-15	443.05	127.61	0.55	5.54	5.90
2Al/SBA-15	309.16	87.07	0.44	5.76	5.93
3Al/SBA-15	143.39	43.75	0.19	5.80	6.04

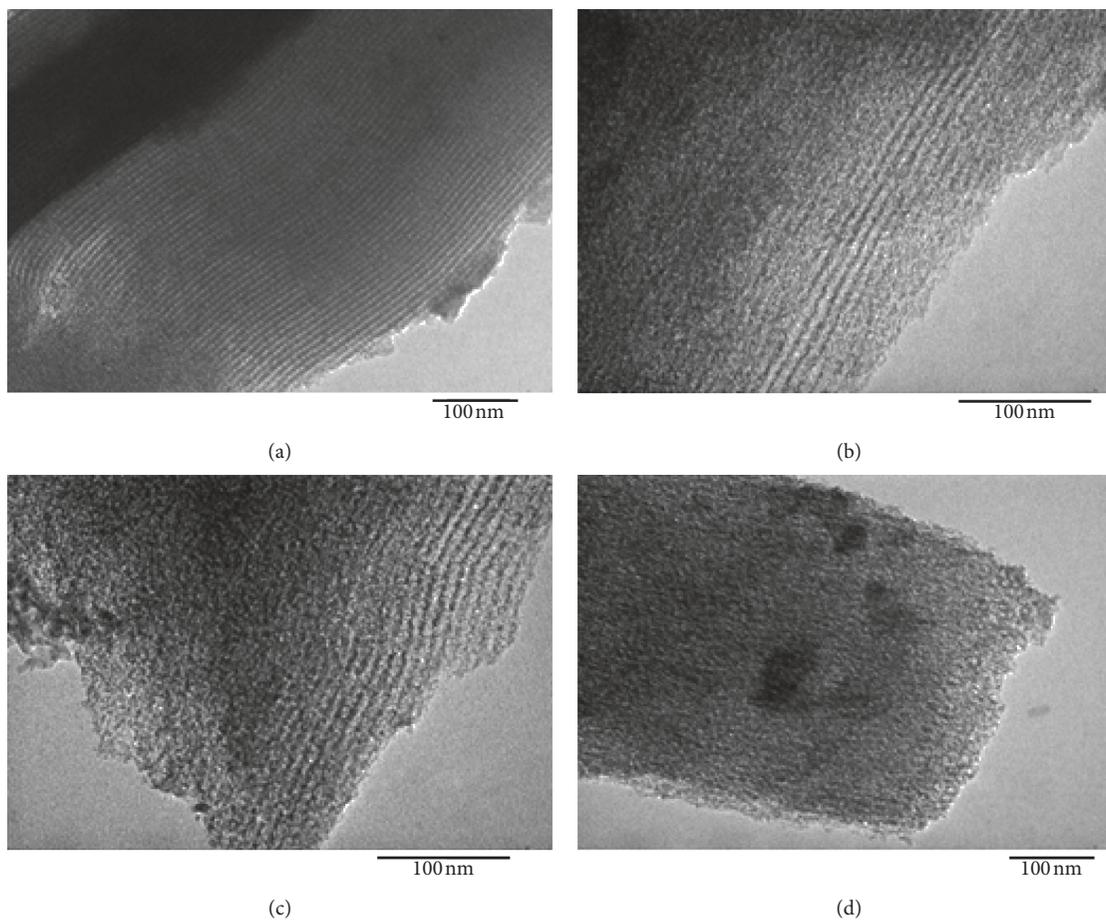


FIGURE 3: TEM images of (a) SBA-15 and (b) xAl/SBA-15, (c) xAl/SBA-15, and (d) xAl/SBA-15.

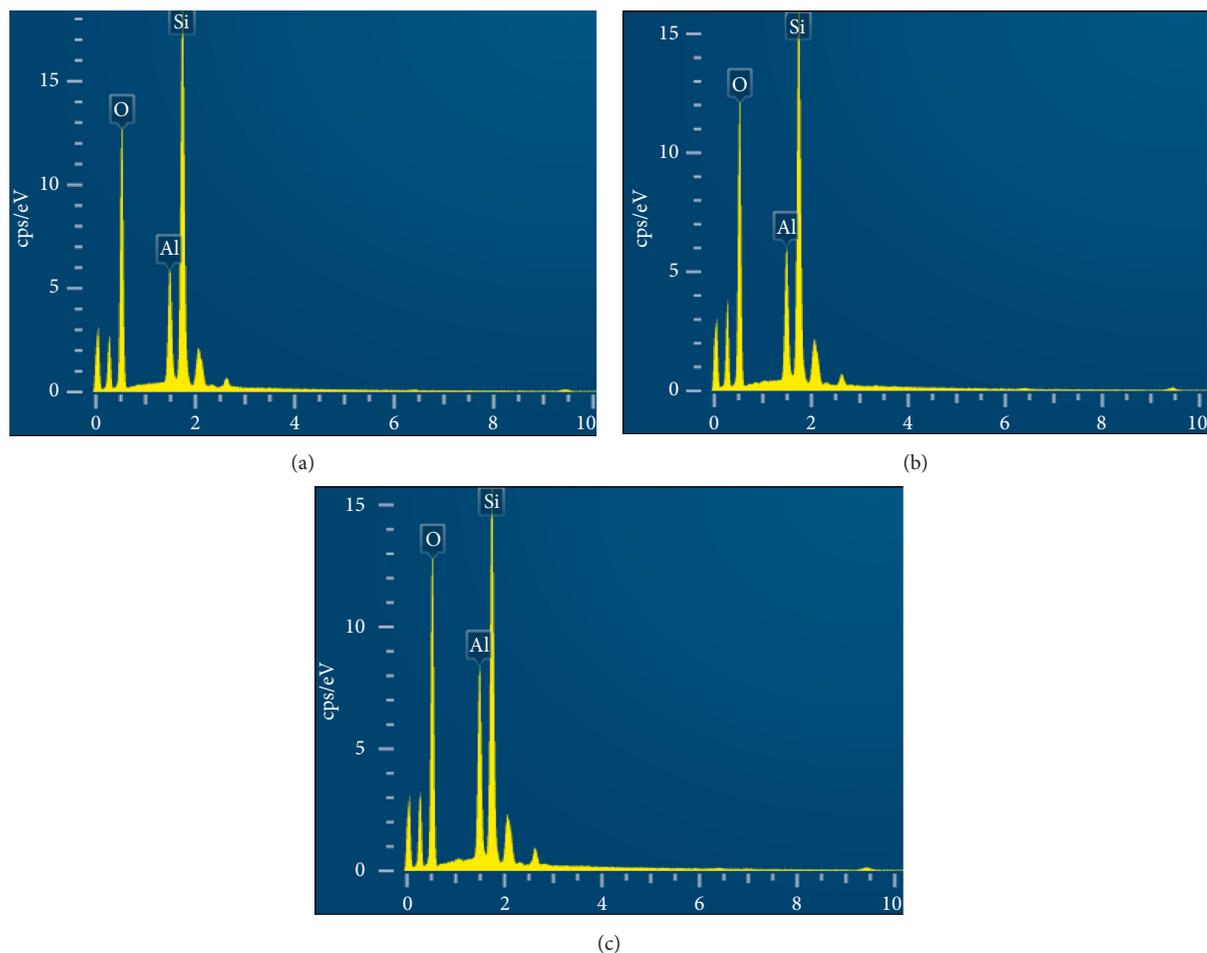


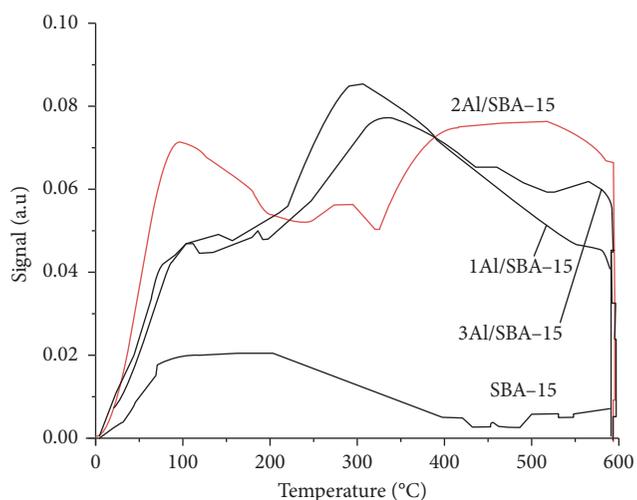
FIGURE 4: EDX of Al/SBA-15 (a), 2Al/SBA-15 (b), and 3Al/SBA (c).

TABLE 3: EDX result Si, O, and Al content in xAl/SBA-15.

Samples	Weight (%)		
	O	Si	Al
SBA-15	63.19	36.81	—
1Al/SBA-15	63.44	30.91	5.66
2Al/SBA-15	61.39	28.92	9.70
3Al/SBA-15	60.67	26.78	12.56

layers which previously deposited on SBA-15, leading to the saturation.

**3.4. Temperature-Programmed Desorption ( $\text{NH}_3$ -TPD).** It is well known that cellulose hydrolysis is catalyzed by acid catalyst. The cellulose conversion is strongly dependent on the acidity of the catalysts. To determine the acidity of Al incorporated SBA-15, we used the  $\text{NH}_3$ -TPD method [14]. Figure 5 shows  $\text{NH}_3$ -TPD profiles of Al incorporated SBA-15. Amounts of weak ( $<200^\circ\text{C}$ ), medium ( $250\text{--}300^\circ\text{C}$ ), and strong ( $500\text{--}550^\circ\text{C}$ ) acid sites are listed in Table 4. As observed in Figure 5 and Table 4, the pure SBA-15 possessed only weak acid sites (max desorption temperature  $<200^\circ\text{C}$ ), while Al incorporated SBA-15 samples showed large amount of medium and strong acid sites (Table 4). Among them,

FIGURE 5:  $\text{NH}_3$ -TPD pattern of SBA-15 and xAl/SBA-15 catalyst.

2Al/SBA-15 had the highest amount of medium acid sites ( $T_{\text{max}} \sim 250\text{--}300^\circ\text{C}$ ). This may be due to the Al amount incorporated into SBA-15 is suitable, favoring to form medium and strong acid sites (isolated Al sites formation). In the case of 3Al/SBA-15, amount of acid sites is lower than that of

TABLE 4: NH<sub>3</sub> amount of weak, medium, and strong acid sites of SBA-15 and xAl/SBA-15.

Samples	mol NH <sub>3</sub> /g cat			Total
	<200°C	250–300°C	500–550°C	
SBA-15	0.23	—	—	0.23
1Al/SBA-15	0.23	0.22	0.04	0.49
2Al/SBA-15	0.43	0.19	0.56	1.18
3Al/SBA-15	0.14	0.17	0.12	0.43

TABLE 5: Conversion and selectivity of 5-HMF over xAl/SBA-15 catalyst.

Catalysts	C <sub>5-HMF</sub> (ppm)	S (%)	C (%)	Y (%)
1Al/SBA-15	4001.24	23.15	63.27	14.64
2Al/SBA-15	10740	62.14	68.51	42.57
3Al/SBA-15	7956.02	46.03	64.49	29.68
SBA-15	662.6	2.92	40.15	1.17

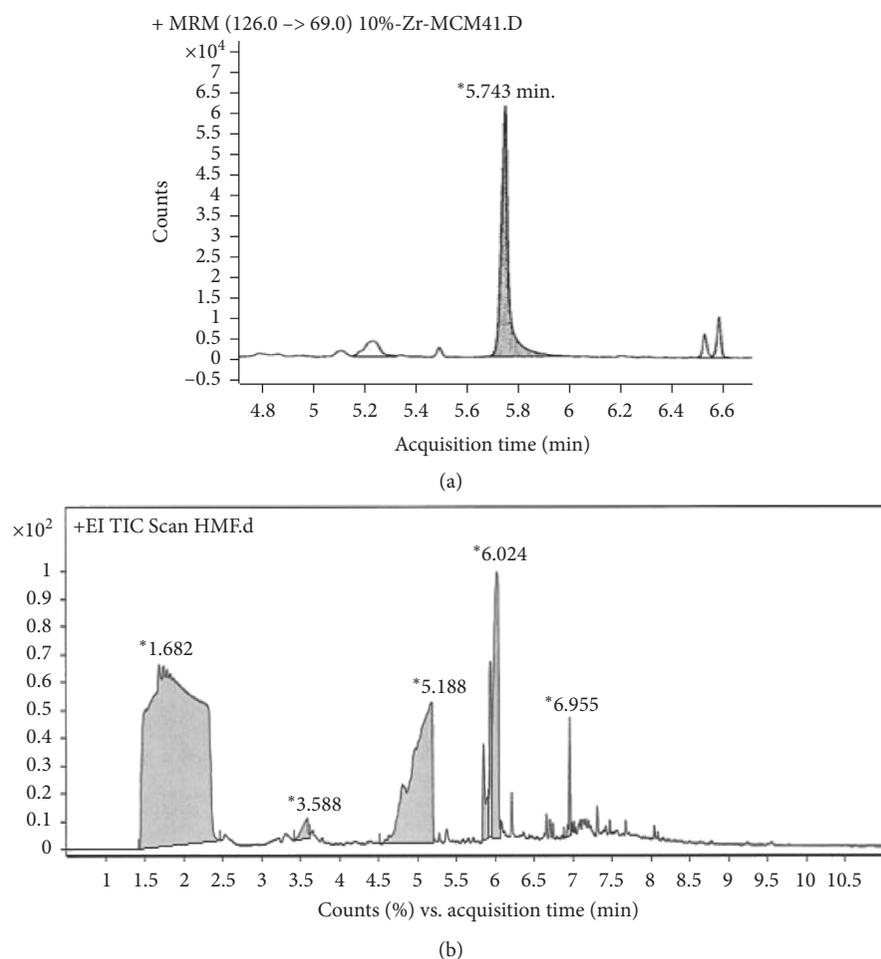


FIGURE 6: 5-HMF (a) and by-products (b) in the cellulose conversion over Al-incorporated SBA-15 samples.

2Al/SBA-15. This can be explained the formation of Al<sub>2</sub>O<sub>3</sub> particles which cover the acid sites created after the second Al layer deposition (2Al/SBA-15 sample).

**3.5. Catalytic Activity.** Table 5 shows that the conversion, selectivity, and yield of 5 HMF over SBA-15 and xAl/SBA-15

catalysts. We have tested the SBA-15 and this showed almost no catalytic activity. Conversion of cellulose to 5-HMF is catalyzed by acid sites since only small amount of weak acid sites in SBA-15 was noted (Table 4). Among Al-incorporated SBA-15 samples, 2Al/SBA-15 catalyst exhibited the highest yield of 5-HMF (42%). This value was higher than that reported in the literature [23–26]. Some previous works

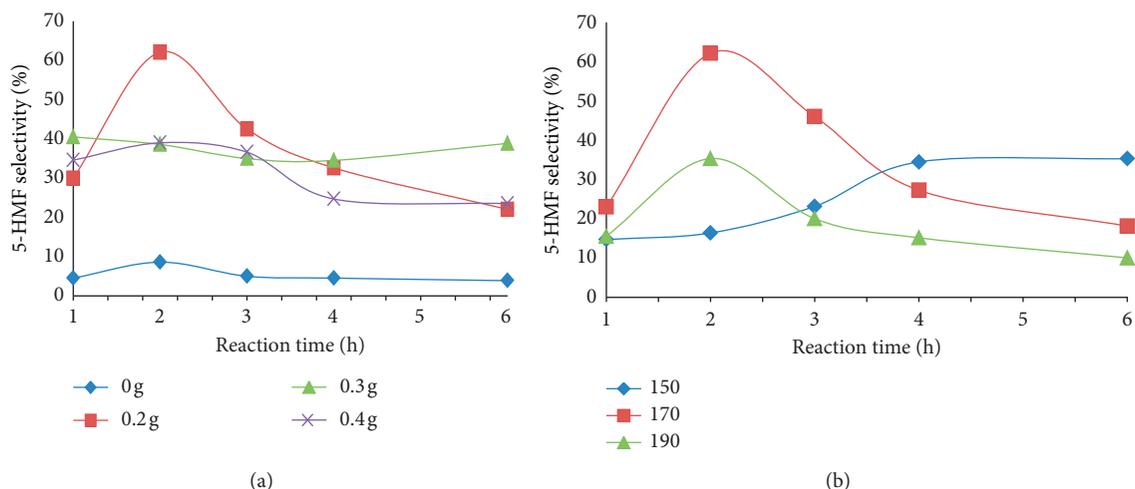


FIGURE 7: Effect of catalyst dosage (a) and reaction temperature (b) on the catalytic conversion of cellulose.

stated the low 5-HMF yield (10–20%). According to the proposed mechanism, cellulose hydrolyzed under the action of a catalyst will be converted into glucose and then isomerized to fructose and fructose followed the hydration converted into 5-HMF [27, 28]. The process of converting cellulose into glucose requires strong acidic centers, while the isomerization and dehydration process requires medium acidic centers. Therefore, in order to obtain the high 5-HMF from cellulose hydrolysis it needs both the medium and strong acid sites. However, for the sample contained high amount of very strong acid sites like  $ZrO_2$  sulfated SBA-15, the cellulose conversion was very high but the 5-HMF selectivity was low due to the formation of intermediate products (result unpublished). This also occurred for Al-incorporated SBA-15. Thus, Figures 6(a) and 6(b) illustrate the formation of by-products such as pentanoic acid ( $C_5H_8O_3$ ), 1,2,4-cyclopentanetriol ( $C_5H_{10}O_3$ ); cyclo-trisiloxane, and octamethyl ( $C_8H_{24}O_4Si_4$ ).

To investigate the effect of catalyst dosage and reaction temperature on cellulose conversion, catalyst dosage ranging from 0.2 g to 0.4 g and reaction temperature ranging from 150°C to 190°C were tested. As seen in Figure 7, catalyst dosage of 0.2 g (Figure 7(a)) and reaction temperature at 170°C (Figure 7(b)) are optimal condition for cellulose conversion. The dosage of 0.2 g is sufficient for converting cellulose to 5-HMF, introduction of high dosage of 0.3 g–0.4 g leads to the catalyst excess which cause the further conversion of 5-HMF to the by product like levulinic, formic acid. The 4-HMF yield in the cellulose conversion to 5-HMF at 150°C increased with increasing reaction time from 0 to 4 h and then maintained unchanged for prolongation time to 6 h. At higher temperature (170°C), 5-HMF yield increased because the reaction is thermodynamically favored at a high temperature. Further increase of temperature (190°C) did not lead to the increase of 5-HMF yield but it decreased. This can be explained at very high temperature, glucose formed from cellulose hydrolysis is dehydrated forward the anhydroglucose which is thermodynamically favored at very high reaction temperature [29]. Moreover, prolongation of

reaction time favored the formation of by-products including formic, acetic, levulinic, and glycollic acid [27].

#### 4. Conclusions

Al-incorporated SBA-15 samples were successfully prepared by atomic implantation method. From XRD result, it revealed the mesoporous structure of Al-incorporated SBA-15. TEM images showed that aluminium oxide species were well dispersed and located along the SBA-15 channels. Al incorporation into SBA-15 framework created the weak, medium, and strong acid sites.

Among Al-incorporated SBA-15 samples, 2Al/SBA-15 exhibited the highest yield of 5-HMF (yield 42%). The yield obtained in this study is much higher to that reported in the literature.

#### Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

#### Conflicts of Interest

The authors declare that they have no conflicts of interest.

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## Research Article

# Synthesis of SAPO-34 Using Different Combinations of Organic Structure-Directing Agents

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The effects of different mixtures of organic structure-directing agents (OSDAs) on the formation of SAPO-34 structure have been investigated. Different OSDAs, namely, triethylamine (TEA), tetraethylammonium hydroxide (TEAOH), and morpholine (Mor) and their combinations were used to synthesize SAPO-34 by a hydrothermal method. The template concentration was optimized by eliminating the competing phases to obtain the purest form of SAPO-34 phase. The as-synthesized samples were analyzed by XRD, FE-SEM/EDS, FT-IR, surface area/pore volume measurements, NH<sub>3</sub>-TPD, TG/DTA, and <sup>29</sup>Si NMR MAS. The selection of template notably impacts the crystal size and physicochemical characteristics of as-synthesized SAPO-34. The sample prepared with 3 Mor:3 TEA:1 TEAOH exhibited the highest total acidity, smallest crystal size below 3 μm, and high surface area up to 697 m<sup>2</sup>/g.

## 1. Introduction

Silicoaluminophosphate (SAPO) is a related grade of microporous material applied mostly in the scope of catalysis of processes such as hydro-isomerization of *n*-hexane, gas separations, methanol conversion to light olefins (MTO), pyrolysis reaction, or removal of NO<sub>x</sub> by selective catalytic reduction with ammonia (NH<sub>3</sub>-SCR). SAPO-34 is such an exciting catalyst in the SAPO generation. Since being discovered in the 1980s, large chabazite (CHA) with small channel systems, eight-membered rings (3.8 Å × 3.8 Å), and 9.4 Å in diameter cage called SAPO-34 has received significant attention, thanks to its high selectivity to light gases separation [1, 2].

Normally, SAPO-34 is prepared from a gel containing sources of an alumina source, a phosphorus source, a silica source, and leastwise one template source by using a hydrothermal method [3, 4]. The OSDA leads an essential duty in the synthesis of SAPO materials. Therefore, suitable OSDAs perform an indispensable role in the preparation of SAPO-34 involving in structure-directing, charge-compensating, and space-filling. Several organic amine compounds

are used as a/an OSDA(s) in SAPO-34 syntheses, for example, tetraethylammonium hydroxide (TEAOH), morpholine (Mor), triethyl amine (TEA), dipropyl amine (DPA), and diethyl amine (DEA) [5–10]. The combination of OSDA surveyed in the preparation of SAPO-34 aims to increase the qualities as well as the catalytic performance of SAPO-34 [11, 12]. Between these OSDAs, the nanoparticle size of SAPO-34 can be achieved by using the quaternary ammonium compound TEAOH as a template, so TEAOH is the most commonly used compound to synthesize SAPO-34. Reducing the particle size of SAPO-34 enhanced its catalytic behavior in many previous reports. Hirota et al. [13] increased the catalyst lifespan in the methanol-to-olefin reaction by using the SAPO-34 material, which synthesized nanocrystals with particle sizes of 75 nm compared to that with bigger sizes of 800 nm. Using the sonochemical method with TEAOH as OSDA, Askari et al. [14] also observed 50 nm-sized SAPO-34 nanocrystals, which were active for a long time in the same reaction. However, the high cost of TEAOH limits its industrial applications [15, 16]. Compared to TEAOH, Mor is much cheaper. However, the use of Mor as an OSDA leads to the creation of materials which have large particle sizes and

bad catalytic behavior in conversion reactions such as MTO [7, 15]. When TEOAH and Mor were combined as the binary OSDAs for the synthesis of SAPO-34, the obtained catalyst had a smaller crystal size and a larger surface area, thereby improving the performance of SAPO-34 catalyst in the methanol conversion reaction [17]. A similar behavior was reported by Sedighi et al. [18] who used different combinations of TEOAH and Mor to synthesize SAPO-34 and obtained the catalyst with the most extended lifetime with optimal crystal size and acidity for MTO reaction. TEA is reported to favor the formation of a SAPO-5 impurity phase, although it costs considerably lower compared to TEOAH. However, until now, synthesizing SAPO-34 with a combination of templates containing TEA in the previous reports is relatively rare. Applying combined OSDAs, for instance, adding more than one directing agent into the initial solution to lead the creation of molecular sieve, has demonstrated to be an effective and cost-down method to synthesize SAPO-34 catalysts with nanoparticle size [12].

Furthermore, SAPO-34 with nanoparticle size and higher acid properties also was the most favorite parent zeolite of copper ion-exchanged SAPO-34 catalysts for  $\text{NH}_3$ -SCR of  $\text{NO}_x$  since their Brønsted acid sites represent a coordinate role with the  $\text{Cu}^{2+}$  active sites in this reaction [19]. In SAPO-34, the substitution of aluminum and phosphorus atoms in the neutral aluminophosphate (AlPO-34) structural framework by silicon atoms will appear in Brønsted acid sites [2]. Therefore, the interactions between OSDAs and the structure of SAPO materials and the Si content in the initial mixture influence the Si contribution, resulting in the alteration of the acid properties.

The purpose of this research is the preparation at the optimal TEOAH/Mor/TEA molar ratio of the SAPO-34 material with smaller particle size and high acid properties for further catalytic application in  $\text{NH}_3$ -SCR of  $\text{NO}_x$  reaction. In this study, the combination of OSDAs between TEA, Mor, and TEOAH was applied to prepare SAPO-34, and the influences of the molar ratio of TEA/Mor/TEAOH on the element composition, morphology, topology, and SAPO-34 zeolite were investigated in detail.

## 2. Materials and Methods

**2.1. Synthesis of SAPO-34 Molecular Sieve.** SAPO-34 molecular sieves were synthesized via the regular hydrothermal method. The material was prepared from a mixture gel with a molar composition of  $1 \text{ Al}_2\text{O}_3 : 0.6 \text{ SiO}_2 : 1 \text{ P}_2\text{O}_5 : X \text{ OSDA(s)} : 110 \text{ H}_2\text{O}$ , wherein X is shown in Table 1. Firstly, aluminum isopropoxide (98%, Merck) was mixed with distilled water, and phosphoric acid (85%, aqueous solution, Merck) was added dropwise. The mixture was stirred for one hour until completely dissolved, then tetraethyl orthosilicate TEOS (98%, Sigma) was added and stirred. After one hour, the templates including morpholine (99%w/w, ACS Reagent, Sigma), tetraethylammonium hydroxide (25%w/w, Sigma), and triethylamine (98%, Merck) were added to the solution. The resulting synthesis gel was further stirred for 6 hours until a uniform reaction mixture was formed and then aged for 12 hours. The obtained gel was crystallized at  $200^\circ\text{C}$  for

TABLE 1: The composition of OSDAs for SAPO-34 preparation.

Name	Organic structure-directing agents (X)		
	Mor	TEA	TEAOH
M1	—	3	—
M2	3	—	—
M3	—	—	3
M4	3	—	1
M5	—	3	1
M6	3	1	—
M7	1	3	—
M8	3	3	1

48 hours in a Teflon-lined autoclave. The as-synthesized sample was filtered, washed, and then dried at  $120^\circ\text{C}$  for 6 hours. The obtained sample was heated at  $1^\circ\text{C}/\text{min}$  and calcinated at  $550^\circ\text{C}$  for 6 h to remove the organic compound from template agents.

**2.2. Characterization of Samples.** The power X-ray diffraction (XRD) data of catalysts were procured by a powder X-ray diffractometer Bruker D8 at room temperature using Cu anode and  $K\alpha$  radiation at  $\lambda = 1.54 \text{ \AA}$  in the angular scale of  $5\text{--}90^\circ$  and scanning mode at  $0.02^\circ$  per step.

The morphology of the samples was observed by the field emission scanning electron microscope (FE-SEM) on a Hitachi S-4800 (Japan). The chemical composition of the catalysts was determined by the Hitachi system (S-4800 model) scanning electron microscope equipped with a dispersive energy X-ray (EDX) spectrometer.

Fourier transform infrared (FT-IR) experiments were carried out with a JASCO FT/IR-4600 (Japan) infrared spectroscopy. For the identification of the functional groups or organic compounds in the catalyst, the sample and the KBr powder were mixed and milled in a mortar, with the component ratio of KBr and the catalyst at 100:1.

The nitrogen adsorption-desorption isotherms measurements were performed on a Micromeritics 2020 analyzer. Firstly, the as-synthesized catalyst was degassed under vacuum at  $300^\circ\text{C}$  and then measured at the boiling point of nitrogen ( $-195^\circ\text{C}$ ). The total surface area was determined based on the Brunauer-Emmett-Teller (BET) theory. The external surface area, micropore surface area, and micropore volume were analyzed by using the t-plot method.

The surface acidity determination was performed on temperature-programmed desorption with ammonia ( $\text{NH}_3$ -TPD) experiments by using the Micromeritics Auto Chem 2920 instrument. In all of the analyses, 0.1 g of the catalyst sample was placed on a quartz fixed-bed U-shaped micro-reactor and degassed in a continuous-flow nitrogen gas of  $50 \text{ mL}/\text{min}$  for 1 hour at  $300^\circ\text{C}$ . The sample was then cooled down to  $100^\circ\text{C}$  and then exposed to  $\text{NH}_3$  (helium-ammonia 10%) for 1 hour and thereafter fluxed with helium air at  $100^\circ\text{C}$  for 1 hour to remove any physisorbed ammonia. The progress is continued until a stable baseline is acquired. Then, the  $\text{NH}_3$ -TPD measurements were carried out from  $100^\circ\text{C}$  to  $550^\circ\text{C}$  at a fixed heating rate of  $10^\circ\text{C}/\text{min}$ . Finally, the spectrum through desorption of  $\text{NH}_3$  was recorded.

The detection of thermal amine compound decomposition of as-synthesized samples was performed by the thermal analysis method by using the thermogravimetric analysis (TGA) and differential scanning calorimeter/thermal analysis (DSC/DTA) instruments (PerkinElmer Pyris-1 TGA and DTA-7) under an airflow of 100 mL/min at a heating rate of 20°C/min from room temperature up to 800°C.

The solid state of  $^{29}\text{Si}$  NMR (nuclear magnetic resonance) spectroscopy with MAS (magic-angle spinning) experiments were carried out on a Bruker AV-300 NMR spectrometer (Ettlingen, Germany). To be more specific, the spinning rate was 6 kHz at the magic angle while the recycling rate was 5 s. For the chemical shift,  $\text{C}_6\text{H}_{15}\text{NaO}_3\text{SSi}$  sodium salt (DSS) was used as the reference material.

### 3. Results and Discussion

In the preparation of the SAPO-34 material, the crystallization process depends importantly on the type of organic structure-directing agents because of their interaction with inorganic species and the alkalinity, which have influence on both the nucleation and crystal growth rates.

Figure 1 shows the structure parameters and phase purity of the as-synthesized catalysts prepared by different component ratios of templates through X-ray diffraction spectroscopy. The XRD patterns of all the prepared samples match well with SAPO-34 structures, except for sample M1, which was synthesized with only TEA as a template. That means both single Mor and TEOAH and a mixture with different OSDAs can be used to synthesize SAPO-34. The template TEA was preferable to synthesize SAPO-5 molecular sieves at  $2\theta = 7.5, 11.1, 14.9, 19.8, 21.1,$  and  $22.5$ . The template Mor, TEOAH, or mixture with TEA/Mor/TEAOH was the most appropriate template for SAPO-34 which is characterized by diffraction peaks at  $2\theta = 9.6, 15.9, 19.2, 21.7,$  and  $27.6$ . In Figure 1, all the as-synthesized samples obtained typical diffraction peaks of the trigonal phase, respectively, for the chabazite structure of SAPO-34 as OSDAs. However, the reflection intensity and the width of peaks were different and depended on the templates. The peaks of the as-synthesized samples with a single template, especially with TEOAH, were sharp and strong, indicating its better crystallinity and phase purity compared to those of the mixed template-prepared samples. The higher intensity and broader width of peaks from the sample prepared with Mor suggest the larger crystallite size of this sample. The least intense reflection of sample M8 indicates a loss of crystallinity and the decrease of crystal size due to the incorporation of Mor with TEOAH and TEA.

Figure 2 illustrates the FE-SEM photographs of synthesized samples prepared by different components of template agents. FE-SEM images clearly show different morphologies and crystal sizes of these samples (as seen in Figure S1, supplementary data). SAPO-5 crystals were obtained when using TEA as a template (M1 sample) which had hexagonal and plate-like morphology, a variation of the particle size from 10–20  $\mu\text{m}$ . Using Mor, TEOAH could observe SAPO-34 which had cube-like rhombohedra morphology with different

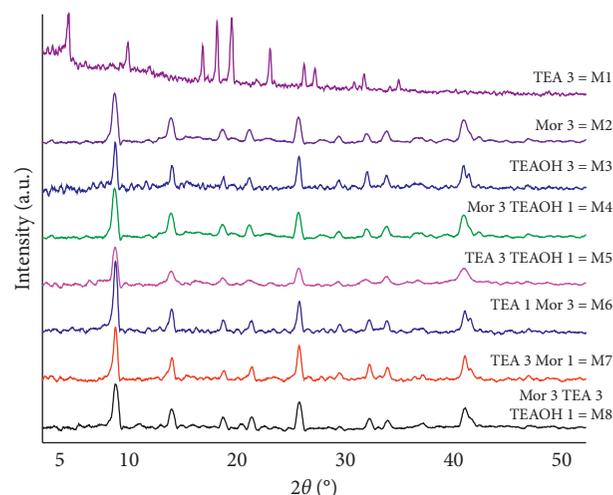


FIGURE 1: X-ray powder diffraction pattern of the as-synthesized sample.

crystal sizes. M2 and M3 samples obtained perfect crystallization and could be very similar to natural chabazite with, respectively, crystal size varying from 20–45  $\mu\text{m}$  and from 3–8  $\mu\text{m}$  as well. These results are in agreement with their crystallinity and phase purity from XRD.

A mixture of Mor or TEA with TEOAH has shown the cube-like morphology which is the specific characteristic of SAPO-34 with impurities. FE-SEM photographs of M4 and M5 samples exhibited that SAPO-34 crystallization by TEA/TEAOH caused the presence of more impurity and larger particles about 5  $\mu\text{m}$ , whereas using Mor/TEAOH as a templating agent resulted in good material purity with mean crystallite size less than 9  $\mu\text{m}$ . The use of TEA or TEOAH as a sample in the initial synthetic gel may have a favorable effect in reducing the crystal size. The presence of TEOAH compared to TEA in preparation gel caused significant particle size reduction. Besides, using Mor as a subtemplate probably supports the formation of the purity phase of SAPO-34. The results are in complete agreement with the previous publications [20, 21].

The formation of SAPO-34 morphology could be determined by using different kind of templates. M6 and M7 samples have not only same crystallinity which can be seen on XRD pattern but also similar crystal shape of cube-like agglomerating to sphere. This means that TEA and Mor can cause the agglomeration of cubic particles to form a bigger sphere-like particle. The extent of the agglomeration depends on the ratio between templates. The morphology of M6 and M7 suggests that increasing the amount of TEA in the original gel results in the aggregation of cubic crystal into spherical particles. Moreover, combinations of TEA and the other templates lead to the formation of impurity phases [22]. TEOAH template seems to be stronger than morpholine in competition with TEA and directing structure. While the particles synthesized with the mixture of TEOAH and TEA (M5 sample) only contain fewer impurities on the surface but not agglomerated, the crystals of M6 with cube-like morphology appear in competition with the cubic crystals of SAPO-34 including some impurities from the AFI

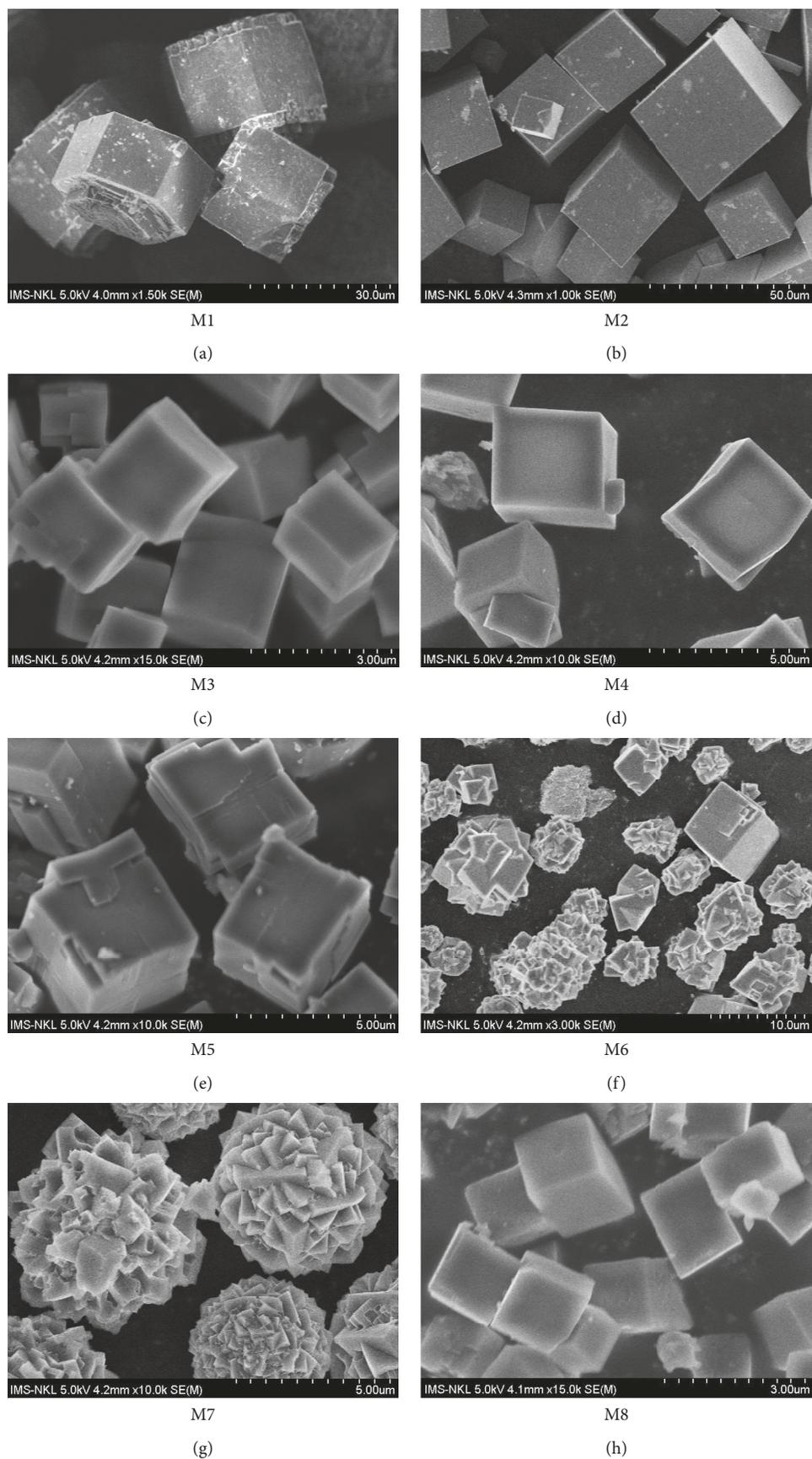


FIGURE 2: Field emission scanning electron microscope images of as-synthesized samples. (a) M1. (b) M2. (c) M3. (d) M4. (e) M5. (f) M6. (g) M7. (h) M8.

structure. Sample M7 synthesized with a higher amount of TEA than that of Mor has a dominant spherical morphology. In the formation of SAPO-34 catalysts, with the combination of TEA and morpholine, the morphology evolves from spherical agglomerates consisting of micrometer-sized cubic crystals to self-assemblies of spherical nanosheets spliced by nanosquare pieces [23].

Compared to a single and binary template(s), the mixture of tri-templating provides smaller particles of SAPO-34 below  $3\ \mu\text{m}$ . Three templates, including both TEOH and TEA as agents for monitoring the crystal size, result in a decrease in particle size.

Therefore, nucleation enhancement is probably liable for crystal size reduction [24]. Mixing different OSDAs leads to the reduction in particle size as well as proper arrangement in size distribution and formation of a pure SAPO-34 structure. They can be enhanced by the presence of TEOH even in little amount. This fact can be explained by the role of structure-directing substances to fill the space and impact between three different types of OSDA, including TEA, Mor, and TEOH. Furthermore, using more than one OSDA could narrow space-filling around the molecule templates, leading to a rise in the number of small crystal seeds in the nucleation process.

Table 2 shows the final elemental composition of production evaluated by the EDS analysis. The final SAPO-34 compositions concerning aluminum, silicon, and phosphorous elementals based on  $(\text{Al}_x\text{P}_y\text{Si}_z)\text{O}_2$  formula were achieved by the mole percentage of each atom. Compared to all starting gel ratio  $\text{Si}/(\text{Al} + \text{P} + \text{Si})$  of 0.13 (the Si content is 13%), this proportion in products was higher than 13% after crystallization. The samples synthesized by a single template showed the highest composition of Si element. The composition of Si element in samples synthesized by a single template was the highest, while that of samples prepared by mixture of OSDAs were lower. This could be attributable to alkaline environment coming from structure-directing agents and the fundamental interactions between templates and structure of SAPO materials. The influence of Si distribution by the number of framework charges are due to not only Si atoms introduced into SAPO-34 channels but also the number of OSDA molecules inserted into cages [25]. It means that if there are an additional content of silicon integrating within the structure of SAPO-34 materials, they could exist as amorphous phase in extra-framework [15, 26].

FT-IR spectroscopy is a well-known technique for identifying zeolite materials' framework structures and their acidity due to the appearance of some typical vibrations in IR spectra, which could come from the charge-balancing cations, the framework, or the relatively isolated groups [27]. Figure 3 shows the IR spectra of SAPO-34 with differing OSDA type of the samples, and the transmission bands of the as-synthesized samples are in good agreement with the published data [28–30]. In the fingerprint region ( $400\text{--}1150\ \text{cm}^{-1}$ ), the bands collected around  $500\ \text{cm}^{-1}$  and  $620\ \text{cm}^{-1}$  are mainly referred to the T-O tetrahedra bending bands of  $\text{SiO}_4$  and double-6 rings. The double-6 ring is a basic structural unit of CHA framework; hence, an appearance of this peak corresponds to the successful synthesis of SAPO-34. The vibration band at  $850\ \text{cm}^{-1}$  is assigned to the symmetric stretching vibration of

TABLE 2: Elemental compositions and relative crystallinity of the products.

Sample name	Composition (mol%)		
	%Al	%P	%Si
M2	50.75	34.02	15.23
M3	49.77	34.44	15.79
M4	47.34	38.43	14.23
M5	47.16	39.23	13.61
M6	48.77	37.76	13.47
M7	49.79	37.16	13.05
M8	49.25	36.70	14.05

P-O (or Al-O), while that at  $1150\ \text{cm}^{-1}$  is credited for the asymmetric stretching vibration of O-P-O. The band at  $1600\ \text{cm}^{-1}$  corresponds to the vibrational bending mode of H-O-H weakly adsorbed in the SAPO-34 channels and assigned to  $\text{CH}_3$  bending vibrational frequencies of the template molecule [31, 32]. The asymmetric stretching vibration of physically adsorbed  $\text{CO}_2$  from the environment shows weak absorbance at  $2360\ \text{cm}^{-1}$  [27, 28]. All spectra of as-synthesized samples show a broad adsorption band between  $3400\ \text{cm}^{-1}$  and  $3600\ \text{cm}^{-1}$ , which could be allocated to the hydroxyl groups from the Si-OH-Al bond. This hydroxyl bonding evidences that the production of Brønsted acidity of SAPO-34 improves [28]. The intensity of this peak was almost similar for samples M3, M4, M5, and M8, except for M6 sample, which is lower. It could be assumed that the OH peak in FT-IR spectra of M6 sample is assigned for the formation of hydroxyl groups in the defect structure.

The nitrogen adsorption-desorption isotherms of the as-synthesized SAPO-34 samples are displayed in Figure 4, and Table 3 shows the crystal size and surface area of these samples. As seen in Figure 4, M3, M4, M5, and M8 samples displayed the curve at low relative pressures which referred to type I isotherm microporous solids. And, absorption near the saturation pressure in the isotherm lines of the as-synthesized samples can be detected due to the intercrystalline porosity, which is common in the nanostructures and microporosity of SAPO-34 [33]. As illustrated in this table, the average sizes of these samples vary from  $3\ \mu\text{m}$  to  $38\ \mu\text{m}$  depending on the type of templates. It is significant that the surface area of SAPO-5 material was smaller than that of the SAPO-34 molecular sieve. The surface area of pure SAPO-34 reached up to  $650\ \text{m}^2/\text{g}$  in several previous reports [34–36]. Our prepared SAPO-34 samples also have a high surface area in the range from  $440\ \text{m}^2/\text{g}$  to  $725\ \text{m}^2/\text{g}$  depending on the type of templates. The highest surface area belonged to the sample prepared by using TEA/TEAOH as OSDAs, which is even higher than that of pure reported SAPO-34. The differences in the surface area are attributable to specific changes in channel dimensions and crystal network caused by each OSDAs.

$\text{NH}_3$ -TPD descriptions exhibited two desorption profiles of ammonia peaks corresponding to the weak and strong acid sites of as-synthesized SAPO-34 materials (Figure 5). The desorption of  $\text{NH}_3$  molecules on weak acidic centers, which are mostly Lewis acid sites and/or the Brønsted acid sites produced by either P-OH hydroxyl groups not

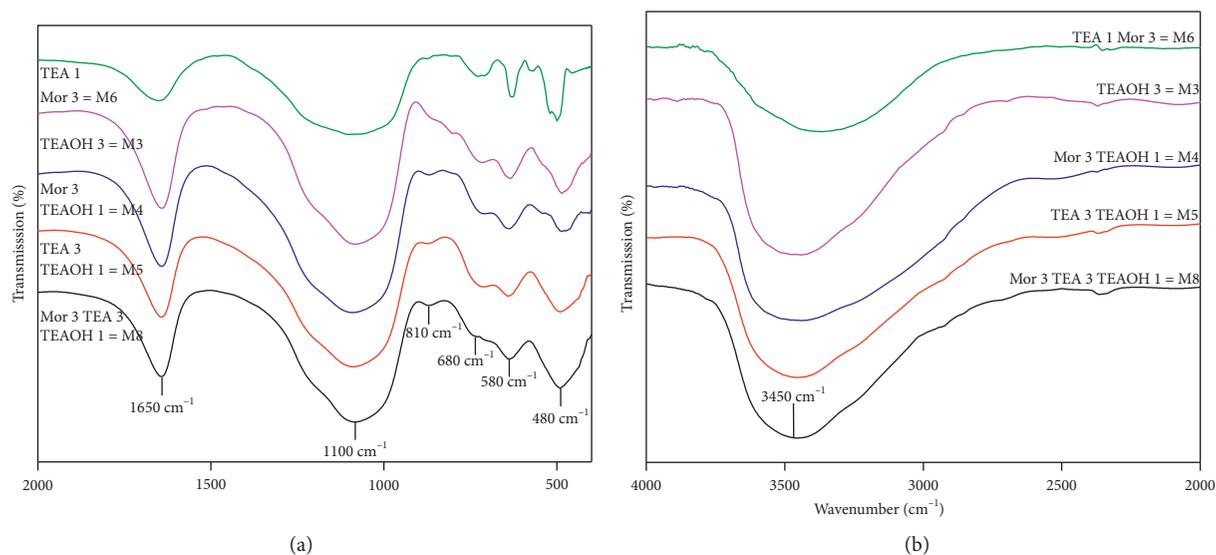


FIGURE 3: FT-IR spectra of as-synthesized samples with a range of wavelengths: (a) 2000–400  $\text{cm}^{-1}$ ; (b) 4000–2000  $\text{cm}^{-1}$ .

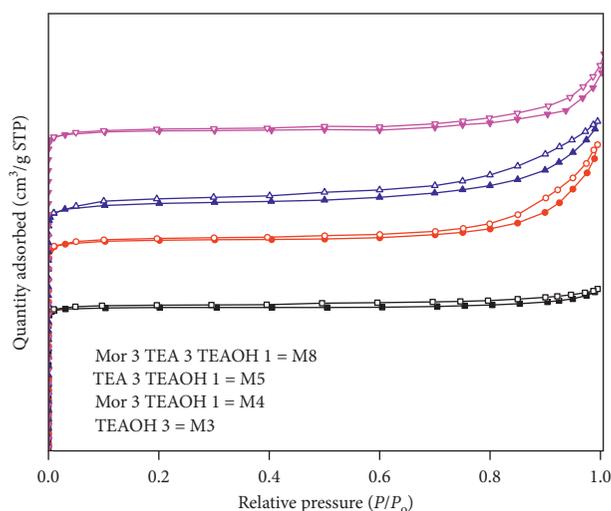


FIGURE 4:  $\text{N}_2$  adsorption (filled symbols) and desorption isotherms (open symbols) of as-synthesized samples.

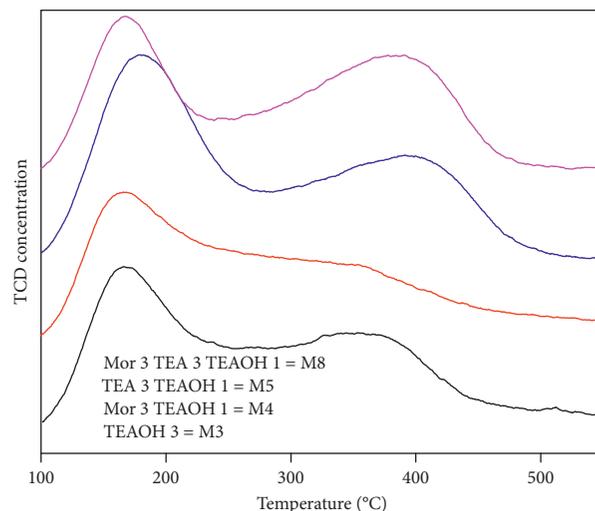


FIGURE 5:  $\text{NH}_3$ -TPD profiles of as-synthesized samples.

TABLE 3: Physicochemical properties of synthesized samples.

Sample Name	Average Size ( $\mu\text{m}$ ) <sup>a</sup>	BET Surface ( $\text{m}^2/\text{g}$ ) <sup>b</sup>	Type of SAPO sample
M1	16	210	SAPO-5
M2	38	480	
M3	5	707	
M4	5	725	
M5	9	683	SAPO-34
M6	10	440	
M7	12	466	
M8	3	697	

<sup>a</sup>Determined by the FE-SEM image; <sup>b</sup>calculated from  $\text{N}_2$  adsorption data.

sufficiently linked to the  $[\text{AlO}_4]$  tetrahedra or Al-OH and Si-OH groups or other zeolitic defects, causes the appearance of the first peak at a low temperature of 150–250°F [37].

The desorption peak shown at a higher temperature of 350–450°C is ascribed to the stronger acid sites, formed by the substitution of P by Si atoms in the framework of the SAPO-34. These sites are related to Si-OH-Al hydroxyl groups as strong Brønsted acid sites, which should be operated for MTO or deNO<sub>x</sub> reaction [37, 38].

The amount of  $\text{NH}_3$  desorption of four samples is different, which depends on the amount of Si contents. The M3 sample with the highest Si content has the highest Brønsted acid sites since these sites (Si-OH-Al) are generated by the proton produced by the template(s) for balancing the negative charges which originated from the incorporation of Si into the neutral AlPOs framework. The origin of the formation of the acid centers of SAPO-34 molecular sieves is consistent with the previous report [39], in which acid sites were produced by the incorporation of Si into the aluminophosphate channel. Although Si content of M8 was lower

than that of the M4 sample (Table 2), the M8 sample exhibited higher total acid sites due to a higher concentration of hydroxyl groups, indicating that the formation of Si islands in M4 samples might decrease its acid content. Moreover, the combination of TEA/Mor and TEOAH benefits for the Si incorporation into the SAPO-34 framework, leading to an increase in strong acid amounts of the M8 sample. There is an agreement between the ammoniac adsorption-desorption curve with the FT-IR spectrum of the samples in terms of band region of the OH vibration. The replacement of Si for other atoms (Si and P) in the AlPO framework plays an essential role in acid site production [39].

Figure 6 depicts the TG/DTA curves of the prepared samples under different templating agents burning in the air. Three weight losses (I, II, and III) in the range of 25–800°C are observed in the TG analysis. The first weight loss (I) occurring from 25 to 200°C is assigned to the desorption progress of physically adsorbed water from the as-synthesized samples. A strongly exothermic process arising between 200°C and 450°C caused the second weight loss (II) which represented combustion decomposition of the templates. The third weight loss (III) with an exothermic process at a temperature greater than 450°C is likely due to the removal of the residual templating agents in the channel molecular sieve of SAPO-34 [40]. The TGA results show that there was a competition among the decomposition of templates at temperatures higher than 500°C. Three absorption peaks were observed in all differently templating samples. Water decomposition occurred at a low temperature (70°C) with a weak signal, demonstrating the modest capacity in the molecule and the weak interactions between water molecules and the molecular sieve. The second absorption peak represents the intensity of the removal of the templates. In particular, sample M8, obtained with the tri-template TEA/Mor/TEAOH, had a sharp and strong removal peak while double-template with several structure-directing agents, namely, TEA/TEAOH and Mor/TEAOH, had different elevation peaks at this point. The results show that the interaction between the TEOAH agent and the framework of SAPO-34 was the most powerful.

The TGA results of M4, M5, and M8 samples are shown in Table 4. According to the molecular weight loss research, the reduced weight of water was quite small, and the primary reason for weight loss was caused by the removal of the templates. Besides, the weight loss of the different samples was distinct. The moles of templates located in the molecular sieves prepared with the different templates were directly calculated by using the thermogravimetric analysis results. The average number of templating agents per cage in the sample molecular sieve was 1.48, 1.25, and 1.36 with M4, M5, and M8, respectively. For sample M5, which used the dual template of Mor and TEOAH, more favorably entered the cage structure due to the presence of negative charges of morpholine in the SAPO-34 framework. Marchese et al. [41] reported that on average, 1.5 molecules of morpholine present within the chabazite channels of SAPO-34. Meanwhile, the molecular volume of cyclic morpholine is significantly lower than that of TEA, which contains three ethyl

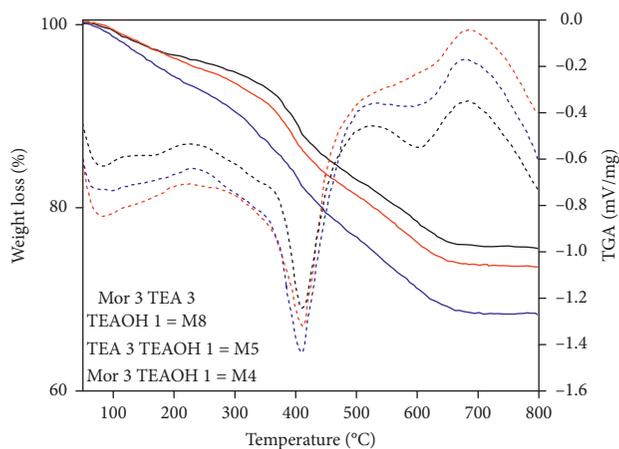


FIGURE 6: The TG (straight line) and DTA (dot line) curves for as-synthesized samples with different templates.

TABLE 4: The TGA results for as-synthesized samples.

Sample	Weight loss (%)		A mole of templates per unit cell
	200°C	200–700°C	
M4	5.62	25.815	1.48
M5	3.64	19.91	1.25
M8	4.33	22.62	1.36

branches [42]. In the case of Mor/TEA/TEAOH mixture, because the material framework and TEOAH templating agent had the most potent force and easily linked with the aluminum atoms, silicon atoms, and phosphorus atoms at the precursor process of crystallization, adding TEOAH enhances the medium number of OSDAs in the material cage.

The silicon situation in the framework of SAPO-34 was analyzed by  $^{29}\text{Si}$  MAS NMR. In Figure 7, several peaks exhibited in the spectrum of samples M4, M5, and M8 are shown. According to [43], the strong peak at  $\delta = -90.3$  ppm should be due to Si(4Al) species; the small peaks formants shown at  $\delta = -93.2$  ppm and  $-98.9$  ppm were attributed to Si(3Al) and Si(2Al) species, respectively, and the peak appeared at  $\delta = -108.9$  ppm resulting from the Si(0Al) environment. The presence of different silicon situations is suitable for the silicone replacement theory [44], in which SM2 (the substitution of P atoms by Si atoms alone) and SM3 (a pair Si atoms substituted by a pair of Al + P). A silicon-island region surrounded by the SM2 method was created, and the center was substituted by SM3. Compared to the dual template of Mor/TEAOH and TEA/TEAOH, increasing the relative contents of Si(3Al), Si(2Al), Si(1Al), and Si(0Al) structures is the result of using a combination of three templates. Based on Table 5 which shows the distribution of the acid properties of as-synthesized catalysts with different template agents, it can be concluded that the creation of silicon islands enhances the acidity of the silicoaluminophosphate zeolite SAPO-34 synonymous with the acid strength of the molecular sieves SAPO-34 which gradually grew up by increasing the size of the silicon islands [45]. The strongest acid sites were located on the borders of the silicon islands.

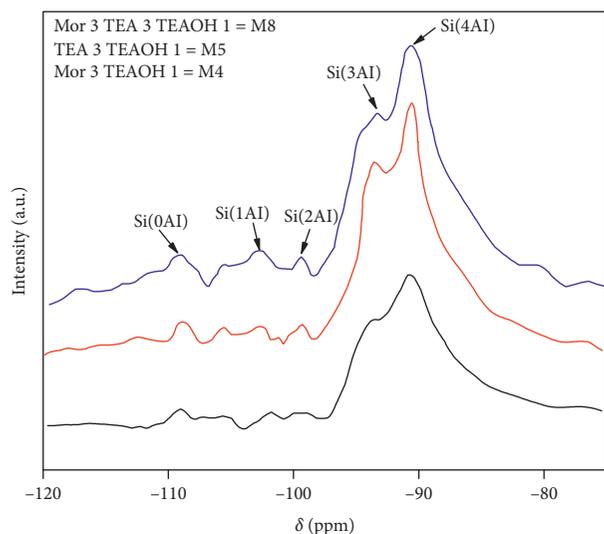


FIGURE 7:  $^{29}\text{Si}$  MAS NMR spectrum of M4, M5, and M8 samples.

TABLE 5: Acid properties of the as-synthesized catalyst.

Samples	Peak (mmol/g)		Total (mmol/g)
	Peak 1	Peak 2	
M3	1.34	0.91	2.25
M4	1.15	0.90	2.05
M5	0.99	0.96	1.95
M8	1.25	1.19	2.34

## 4. Conclusions

By using the hydrothermal method, SAPO-34 molecular sieves were prepared with various combinations of Mor/TEA/TEAOH as organic structure-directing agents showed different physicochemical characteristics. The single-template TEA was preferable to synthesize SAPO-5 molecular sieves, while TEOAH and Mor favored SAPO-34 formation. The morphology of all samples was the same to the uniform cube-shaped particles of the standard SAPO-34 material, except as-synthesized samples using Mor/TEA as OSDAs, which additionally includes sphere-shaped particles consisting of cubic agglomerates. Combination of tri-templates in the initial gel led to decrease in the particle size of the samples. The morphology of spherical particles can be created by a coherence of nanosized crystals, and the crystal size will be reduced to submicrometer size. The catalyst with molar ratios of Mor:TEA:TEAOH = 3:3:1 increased the surface area, decreased the crystal size of the samples to nanosize, improved the crystallinity, and enhanced the acid content. The preparation of SAPO-34 catalysts with mixture template synthesis was proven to be effective and has economic advantages.

## Data Availability

The X-ray diffraction, field emission scanning electron microscope, Fourier-transform infrared method,  $\text{N}_2$  adsorption-desorption, magic-angle spinning nuclear magnetic resonance,

thermogravimetric analysis, differential scanning calorimeter/thermal analysis, and temperature-programmed desorption of ammonia data used to support the findings of this study are included within the article. The field emission scanning electron microscope data used to support the findings of this study are included within the supplementary information file for more details with images of increased resolution.

## Conflicts of Interest

The authors declare that they have no conflicts of interest.

## Acknowledgments

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## Supplementary Materials

Supplementary Figure S1. field emission scanning electron microscope images of as-synthesized SAPO-34 from different organic structure-directing agents. FE-SEM images clearly show different morphologies and crystal sizes of these samples on a larger scale. (*Supplementary Materials*)

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## Research Article

# Sonochemical Synthesis and Properties of $\text{YVO}_4:\text{Eu}^{3+}$ Nanocrystals for Luminescent Security Ink Applications

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Solutions and redispersible powders of nanocrystalline, europium-doped  $\text{YVO}_4$ , are prepared via a wet chemical method using the ultrasonic processor (sonochemical) and microwave and thermal stirring. From X-ray diffraction (XRD) results,  $\text{YVO}_4:\text{Eu}^{3+}$  nanoparticles synthesized using sonochemical method have better crystallinity than those prepared using thermal stirring and microwave methods exhibiting the tetragonal structure known for bulk material. From field-emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM) results, it is found that the size of nanoparticles is around 25 nm and increasing after annealing at 900°C. From UV-Vis result, there is a peak at 270 nm corresponding to the absorption of  $\text{VO}_4^{3-}$  groups. The photoluminescence (PL) results clearly show the strongest red emission peak at the wavelength around 618 nm. The highest luminescent intensity is obtained for the sample prepared by the sonochemical method at pH = 12 and annealing temperature at 900°C for 4 h. The average lifetimes of the  $\text{Eu}^{3+}$  ions in the samples annealed at 300, 600, and 900°C for 1 h at 618 nm emission under 275 nm excitation are 0.36, 0.62, and 0.64 ms, whereas sample annealed at 900°C for 4 h has lifetime of 0.70 ms. The security ink, containing synthesized  $\text{YVO}_4:\text{Eu}^{3+}$  nanoparticles, is dispersed in glycerol and other necessary solvents. The experimental security labels are printed by inkjet using the electrohydrodynamic printing technique. The resulting lines represented to the security labels are analyzed by the 3D microscope equipment and UV 20 W mercury lamp with a wavelength of ~254 nm. The seamless line of the printed security label has the value of the width at ~230  $\mu\text{m}$ , thickness at ~0.68  $\mu\text{m}$ , and distance between two adjacent lines at 800  $\mu\text{m}$ . This result is compatible for producing security labels in small size (millimeter) in order to increase security property.

## 1. Introduction

The study of rare earth doped luminescence materials has been largely motivated by the prospect of original specific applications such as electroluminescent techniques, biological labels, and integrated optics [1–6].

Moreover, rare earth nanoparticles are interesting due to their marked improvement in lumen output, color rendering index, energy efficiency, and greater radiation stability [6–11].

$\text{YVO}_4:\text{Eu}^{3+}$  has large application in color television cathode ray tube displays [12] and high-pressure mercury

lamps [13] as a red phosphor. The photoluminescence quantum yield of the europium emission is as high as 70% in  $\text{YVO}_4$  with the excitation by UV light [14]. It is also applied in biology [15–17] and specially in producing security ink. The vanadate group ( $\text{V}^{5+}-\text{O}^{2-}$  charge transfer band) in  $\text{YVO}_4:\text{Eu}^{3+}$  phosphor is excited by ultraviolet radiation, and this provides efficient energy transfer to  $\text{Eu}^{3+}$  [18].

$\text{YVO}_4:\text{Eu}^{3+}$  phosphor can be prepared by different methods, for example, high-temperature solid state method [19], combination method [20], microwave rapid heating method [21–23], sol-gel method [24], and hydrothermal reaction method [25]. Recent studies have shown that there

is a tremendous potential in nanoscale rare earth doped luminescence materials in abovementioned fields.

In recent years, the inkjet technique has been in research to make spare parts such as electric circuits and biosensor [26–35]. The advantage of this technique is having fewer steps in preparation and ability to print in many different bases such as conductive base, uncondutive base, solid base, and flexible base. This inkjet technique requires research in the printing process and inkjet ink. In 2012, Meruga et al. investigated security ink from the rare earth nanoparticles  $\beta$ - $\text{NaYF}_4$ -doped  $\text{Yb}^{3+}/\text{Er}^{3+}$  and  $\text{Yb}^{3+}/\text{Tm}^{3+}$  to print security QR code on paper and PET by Optomec direct-write aerosol jetting [36]. According to the work of Gupta et al. in 2010, they evaluated the security ink made of rare earth nanoparticle  $\text{Y}_2\text{O}_3$  doped  $\text{Eu}^{3+}$  ( $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ ), and the samples in this research were printed by screen printing techniques [37]. The purpose of our security inkjet technique is making products with high security. With inkjet technology and this security ink, we study printing the labels with the demand of high security on money, visa, certificate, and military products. The high security characteristic of the product is determined by two factors—the first is small size and delicacy of the printed label (related to the printing technique) and second is the strong emissivity of printed label under UV (related to optical emission of  $\text{YVO}_4:\text{Eu}^{3+}$  nanoparticles in the ink). The emissivity of  $\text{YVO}_4:\text{Eu}^{3+}$  nanoparticles is affected by many factors such as particle size and crystallinity, doping level of  $\text{Eu}^{3+}$  ions into  $\text{YVO}_4$ , etc. All these parameters are affected by the production method applied for nanoparticles [38–42].

In this study, we use the wet chemical method to synthesize  $\text{YVO}_4:\text{Eu}^{3+}$ . Our purpose is to apply  $\text{YVO}_4:\text{Eu}^{3+}$  as phosphor in security ink. Hence, performing research in producing the  $\text{YVO}_4:\text{Eu}^{3+}$  nanoparticles with strong luminescent intensity is crucial along with the research in inkjet process. Regarding the references on synthesis of  $\text{YVO}_4:\text{Eu}^{3+}$  nanoparticles by wet-chemical method [12–21, 38–42], we use three different routes to synthesize  $\text{YVO}_4:\text{Eu}^{3+}$  nanoparticles, which are thermal stirring, microwave methods, and ultrasonic methods, in order to compare the luminescent level of the nanoparticles. According to the published results, the best doping level of  $\text{Eu}^{3+}$  in  $\text{YVO}_4$  for luminescence properties is 5 mol% [38, 43–55]. We use  $\text{YVO}_4:\text{Eu}^{3+}$  nanoparticles to produce ink for PS JET 300 V inkjet printer. This printer is operated by the electrohydrodynamic (EHD) inkjet technique. The advantage of EHD inkjet technique is the ability to print labels in small size (in micrometers) on various material substrates.

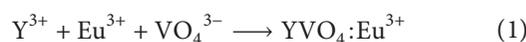
## 2. Materials and Methods

**2.1. Materials.**  $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (99.8%, Aldrich),  $\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  (99.9%, Aldrich), and  $\text{Na}_3\text{VO}_4$  (99.98%, Aldrich) are used as starting materials.  $\text{NaOH}$  (99%, Merck) is used to control pH.

$\text{C}_3\text{H}_8\text{O}_3$  (99.5%, Merck),  $\text{C}_2\text{H}_6\text{O}$  (99.5%),  $\text{C}_4\text{H}_8\text{O}_2$  (99.8%, Merck), and  $\text{C}_2\text{H}_6\text{O}_2$  (99.5%, Merck) are solvents and binding agents used in the synthesis of security ink.

**2.2. Synthesis of  $\text{YVO}_4:\text{Eu}^{3+}$  Nanoparticles and Security Ink.**  $\text{YVO}_4:\text{Eu}^{3+}$  nanoparticles are synthesized by the wet chemical method. Dissolving 0.88 g of  $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (2.3 mmol) and 0.05 g of  $\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  (0.12 mmol) into 15 ml DI water ( $\text{Eu}^{3+}$  doping molar concentration is 5%) in 15 min leads to the formation of solution A, whereas 0.44 g of  $\text{Na}_3\text{VO}_4$  (2.4 mmol) in 15 ml DI water is solution B. Mixing solution A with solution B dropwise leads to white precipitation in the mixture. The pH value of mixture is adjusted to 12 by using 5 M of  $\text{NaOH}$ .

This mixture is heat-treated by three different ways for comparison, which are thermal stirring at  $\sim 150^\circ\text{C}$  in 1 h, microwave in 15 min by Mars 6 (CEM Corporation) [21–23], and sonochemical by ultrasonic liquid processors VCX 750 (Sonics and Materials) with electrical frequency 20 kHz in 15 min. Synthesized  $\text{YVO}_4:\text{Eu}^{3+}$  nanoparticles are dried at  $60^\circ\text{C}$  and annealed at 300, 600, and  $900^\circ\text{C}$  in an oven (Carbolite Gero, Max. temp. up to  $1100^\circ\text{C}$ ) for 1 h. The formation of  $\text{YVO}_4:\text{Eu}^{3+}$  nanoparticles follows equation (1):



The security ink using  $\text{YVO}_4:\text{Eu}^{3+}$  nanoparticles is synthesized by mixing  $\text{YVO}_4:\text{Eu}^{3+}$  nanoparticles in such solvents as glycerin, ethanol, ethyl acetate, and ethylene glycol at appropriate ratios.

**2.3. Security Printing.** The test patterns are printed onto glass substrate by a commercial printer (PS JET 300 V). This printer is operated by the electrohydrodynamic (EHD) inkjet technique.

**2.4. Characterization.** The prepared  $\text{YVO}_4:\text{Eu}^{3+}$  nanoparticle samples are studied by UV-Vis absorption spectroscopy by using a double-beam spectrophotometer in the wavelength range from 200 to 900 nm. Particle size is determined by transmission electron microscopy (TEM) and field emission scanning electron microscopy (FE-SEM). Samples for TEM measurements are suspended in ethanol and ultrasonically dispersed. The suspension drops are placed on a copper grid coated with carbon. The crystallite structure of  $\text{YVO}_4:\text{Eu}^{3+}$  is analyzed by X-ray diffraction spectroscopy. The emission spectra are recorded at room temperature using a Hitachi F-4500 spectrophotometer. The decay of luminescence is measured by a Horiba Deltaflex™ with 275 nm SpectraLED excitation source.

The security ink viscosity is analyzed by an m-VROC™ VISCOMETER. The samples after printed by inkjet printer are synthesized by a 3D microscope (Sensofar Metrology) and UV 20 W mercury lamps (Germicidal lamp, Sankyo Denki Co.) having a wavelength of around 254 nm.

## 3. Results and Discussion

**3.1. Effect of Different Synthesis Methods on the Formation of  $\text{YVO}_4:\text{Eu}^{3+}$  Nanoparticles.** The wet chemical method is applied in all experiments; however, there is difference in the

heating method during synthesis process as mentioned above. Three synthesized samples correspond to three different methods with the same chemical components and ratios. The doping concentration of  $\text{Eu}^{3+}$  is 5 mol% in  $\text{YVO}_4$  host ( $\text{Y}_{0.95}\text{Eu}_{0.05}\text{VO}_4$ ), which had been optimized previously by Georgescu et al. [43], Kumar et al. [44], and He et al. [45]. Each heating method has different effect to  $\text{YVO}_4$  particles crystallinity and doped ability of ion  $\text{Eu}^{3+}$  to host matrix. The crystallization and doped ability have crucial effect to luminescent intensity of  $\text{YVO}_4:\text{Eu}^{3+}$  nanoparticles. The XRD patterns recorded for the  $\text{YVO}_4:\text{Eu}^{3+}$  samples are shown in Figure 1. All diffraction peaks were successfully attributed to known tetragonal phase of  $\text{YVO}_4$  (JCPDS, No. 17-0341) [41, 42, 46].

Among three preparation methods, the highest peak intensity is observed for the sample fabricated by the sonochemical treatment, that reveals the best crystallinity level of  $\text{YVO}_4:\text{Eu}^{3+}$  nanoparticles in this sample. According to theory and references of sound waves, the constitution of ultrasound region happens with sound wave frequency above 20 kHz. The ultrasound region can be divided into two parts: one where the cavitation phenomenon takes place (20–100 kHz), called power ultrasound, and the other where no cavitation occurs (5–10 MHz), used for diagnostics. Sonochemical effects depend on the cavitation phenomenon. According to the “hot spot” theory, each cavitation bubble behaves like a microreactor, which, in aqueous systems, at an ultrasonic frequency of 20 kHz each cavitation bubble collapse acts as a localized “hotspot” generating temperatures of about 4000 K and pressures in excess of 1000 atmospheres [47–51].

A series of radicals, such as  $\text{H}^*$  and  $\text{OH}^*$ , are formed, by the irradiation process of ultrasound to water, at the gas-phase interface of the cavitation bubbles, and the responsibility for the enhanced reactivity to a lesser extent, in the bulk solution [51].

These factors have positive effect to the crystalline nanoparticle formation and incorporation of  $\text{Eu}^{3+}$  ions into  $\text{YVO}_4$  lattice. These factors have effect to the luminescent intensity of  $\text{YVO}_4:\text{Eu}^{3+}$  nanoparticles.

The TEM micrographs and size distribution diagrams of  $\text{YVO}_4:\text{Eu}^{3+}$  nanoparticles prepared by sonochemical and thermal stirring methods are shown in Figure 2. The monodispersion state of  $\text{YVO}_4:\text{Eu}^{3+}$  nanoparticles is evident. In Figure 2(a), more even size distribution is observed with maximum at  $\sim 25$  nm. The wider and nonhomogeneous size distribution is seen in Figure 2(b). The TEM results agreed with the XRD results shown in Figure 1.

There are three major steps in the excitation-emission process of  $\text{YVO}_4:\text{Eu}^{3+}$  under UV radiation. Firstly, UV radiation is absorbed by  $\text{VO}_4^{3-}$  groups. However, UV radiation can be directly absorbed by  $\text{Eu}^{3+}$  ions, and this is dependent on the wavelength. Secondly, the migration of activation energy through vanadate sublattice leads to the transferring of the excited energy to  $\text{Eu}^{3+}$  ions, and the last step is the production of strong red emission by the de-excitation process of excited  $\text{Eu}^{3+}$  ions [15, 41, 52, 56]. A proposed energy transfer mechanism demonstrating the above process is shown in Figure 3.

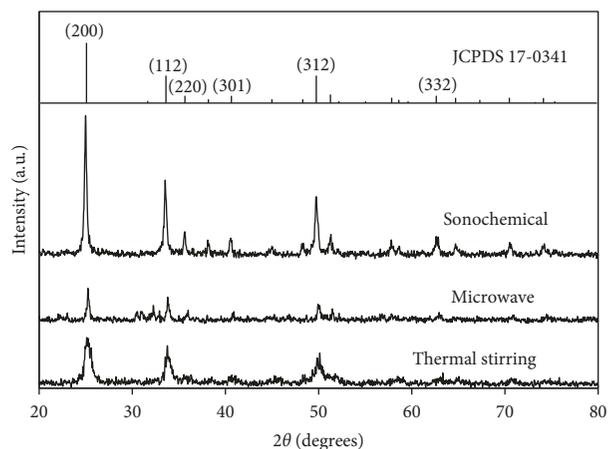


FIGURE 1: The XRD pattern of  $\text{YVO}_4:\text{Eu}^{3+}$  nanoparticles synthesized with a different method.

In Figure 4 (left inset), the UV-V is spectra of  $\text{YVO}_4:\text{Eu}^{3+}$  nanoparticles prepared by sonochemical and wavelength and thermal stirring methods are shown. The redispersed dry powder of  $\text{YVO}_4:\text{Eu}^{3+}$  in the same amount of deionized water was stirred 2-3 min, resulting in the transparent colloid representing the absorption spectrum. There is a peak at around 270 nm in these three samples that proved the existence of absorption in the  $\text{VO}_4^{3-}$  groups [39, 41, 52, 56]. According to references, it is explained as the attribution to the charge transfer from oxygen ligands to the central vanadium atom in  $\text{VO}_4^{3-}$  group [15, 40, 41]. The UV-Vis spectra in Figure 4 (left inset) are crucial regarding to the luminescence mechanism of  $\text{YVO}_4:\text{Eu}^{3+}$  nanoparticles, and it proves that there is an energy absorption and transfer from  $\text{VO}_4^{3-}$  to  $\text{Eu}^{3+}$ . The sample of the sonochemical method exhibits the strongest absorption while the one of the thermal stirring methods exhibits the weakest absorption.

In Figure 4, the photoluminescence emission spectra of  $\text{YVO}_4:\text{Eu}^{3+}$  nanoparticles prepared by three synthesis methods are shown. The samples were excited at  $\sim 275$  nm. The sharp lines in the range from 550 to 750 nm correspond to the transitions from the excited  $^5\text{D}_0 \rightarrow ^7\text{F}_j$  of  $\text{Eu}^{3+}$  ions (Figure 3) [15, 41, 57–59]. There is no obvious vanadate group emission band indicating the transfer of absorption energy of the vanadate groups to  $\text{Eu}^{3+}$  ions. There is assignment of strongest red emission peak at 618 nm to the  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  transition, emission peak at 590 nm to  $^5\text{D}_0 \rightarrow ^7\text{F}_1$  of  $\text{Eu}^{3+}$  ions, and strong emission peak at 692 nm to the  $^5\text{D}_0 \rightarrow ^7\text{F}_4$  transition [15, 40, 41].  $\text{Eu}^{3+}$  ions occupy asymmetry inversion center instead of  $\text{Y}^{3+}$  in the strongest emission from  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  transition [15, 41]. The sample produced by the sonochemical method has the strongest intensity at 618 nm, as compared to that of other samples. Regarding this result, the characteristics of the ultrasonic processor, high local temperature and pressure, are attributed to the forming of  $\text{YVO}_4:\text{Eu}^{3+}$  nanoparticles with high crystalline structure and better doping of  $\text{Eu}^{3+}$  ions to  $\text{YVO}_4$  lattice. We also assumed that sound waves with characteristic of mechanical waves affect the doping of  $\text{Eu}^{3+}$

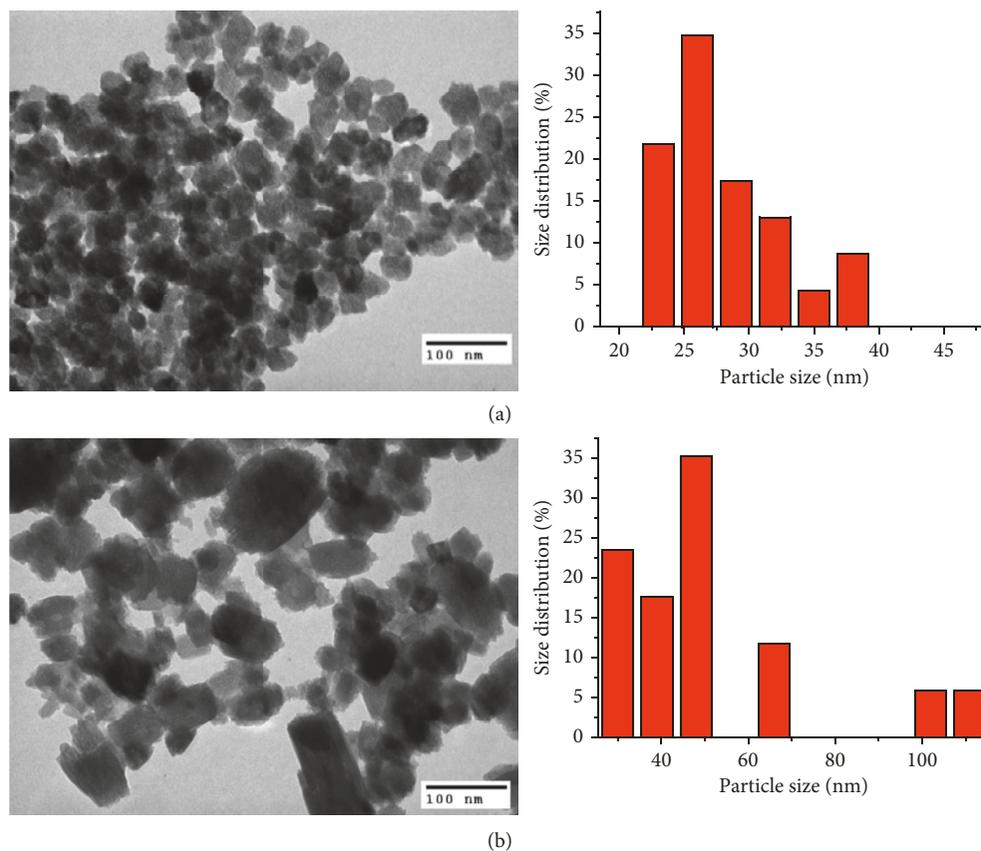


FIGURE 2: TEM micrographs and the size distribution diagram of  $\text{YVO}_4:\text{Eu}^{3+}$  nanoparticles synthesized by sonochemical (a) and thermal stirring (b).

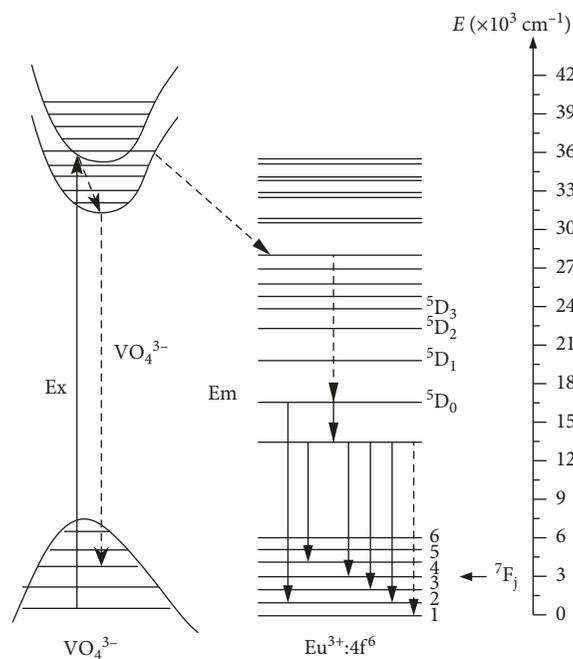


FIGURE 3: Energy levels and transitions scheme of  $\text{Eu}^{3+}$ . Vertical arrows: absorption and emission transitions.

ions to the  $\text{YVO}_4$  lattice. And, it leads to the highest intensity of emission peak [51]. Figure 4 (right inset) is the image of  $\text{YVO}_4:\text{Eu}^{3+}$  nanoparticles powder, synthesized by

sonochemical method, under excitation at 254 nm by the UV lamp. The powder turns red under the UV lamp corresponding to dominant emission at 618 nm.

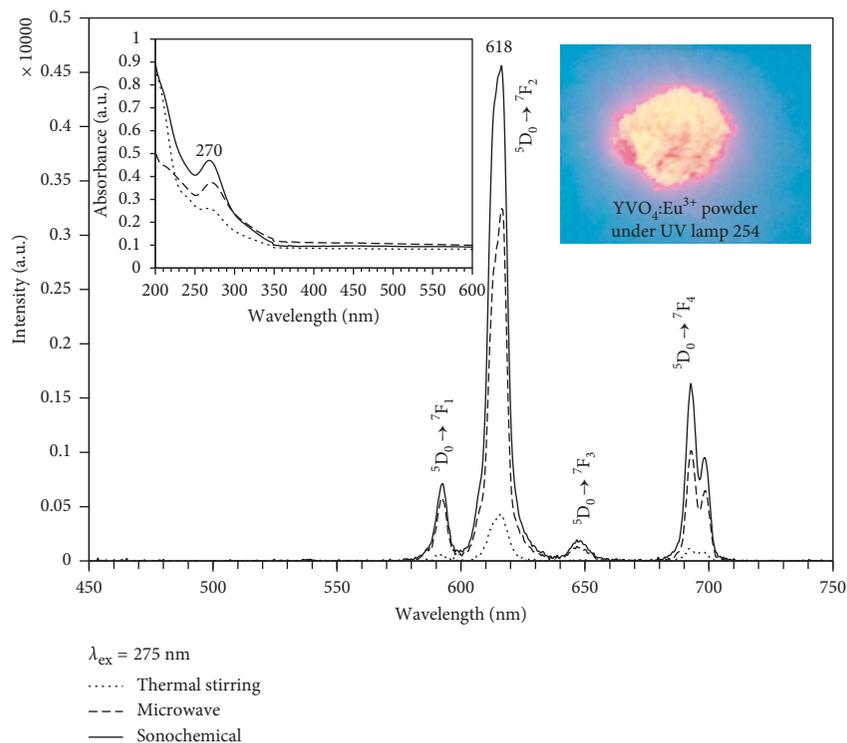


FIGURE 4: Photoluminescence spectra of  $\text{YVO}_4:\text{Eu}^{3+}$  nanoparticles synthesized with a different method. Right inset shows UV-VIS spectra of  $\text{YVO}_4:\text{Eu}^{3+}$  nanoparticles synthesized with a different method. Left inset is image of  $\text{YVO}_4:\text{Eu}^{3+}$  powder synthesized with sonochemical method under UV lamp 254 nm.

The purpose is synthesizing  $\text{YVO}_4:\text{Eu}^{3+}$  nanoparticles with strong luminescence. There are many factors which affect the light emitting of  $\text{YVO}_4:\text{Eu}^{3+}$  nanoparticles (related to the light emitting mechanism) such as the doping level of  $\text{Eu}^{3+}$  ions, particle crystalline, and nanoparticle size. Among these factors, the nanoparticle crystallinity and the incorporation of  $\text{Eu}^{3+}$  ion into the  $\text{Y}^{3+}$  positions in the lattice of  $\text{YVO}_4:\text{Eu}^{3+}$  nanoparticles play important roles in the increasing of luminescence. As to the above result, the  $\text{YVO}_4:\text{Eu}^{3+}$  nanoparticles with highest luminescent intensity are synthesized by the sonochemical method, and so, this method will be used for the future research.

$\text{YVO}_4:\text{Eu}^{3+}$  nanoparticles are synthesized by the wet chemical method with De-ion water as solvent, in which the pH parameter affects the forming of particles as well as the crystalline growth of nanoparticles. Hence, the pH of aqueous vanadate solution is an important parameter in the synthesis [22, 23, 43, 60]. The samples are synthesized with the pH value variation (adjusted by 5 M·NaOH) in the solution as follows: 8, 10, 12, and 14 (with sonochemical method and the ratio of chemical as mentioned above). The change in the luminescence intensity of  $\text{YVO}_4:\text{Eu}^{3+}$  nanoparticles is shown in Figure 5.

Figure 5 shows the main emission is at 618 nm due to  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  transition with the strongest emissivity. The samples are excited at  $\sim 275$  nm. At 618 nm, the luminescence intensity of sample with pH=12 is strongest, the second is pH=14, and the weakest is pH=8. This can be explained that the reaction does not occur when pH > 12 and

only the precipitation of very small particles of  $\text{Y}(\text{OH})_3$  takes place instead of  $\text{YVO}_4$ . When the pH is smaller than 12, the color of the solution changes slowly from light to dark yellow. This may be the attribution to the forming of polyanvanadate species [23, 43]. Hence, pH=12 is optimal for emissivity of  $\text{YVO}_4:\text{Eu}^{3+}$  nanoparticles.

**3.2. Effect of Annealing Temperature on the Characteristics of  $\text{YVO}_4:\text{Eu}^{3+}$  Nanoparticles Synthesized by Sonochemical Method.** The annealing process is carried out after nanoparticles formation, and it plays an important role in increasing the crystallinity and decreasing structure distortion of rare earth nanocrystals [38, 40, 45].  $\text{YVO}_4:\text{Eu}^{3+}$  nanoparticles are synthesized by the sonochemical method and then centrifuged at 9000 rpm. The final powder is dried at  $60^\circ\text{C}$  in 6 h and then annealed at 300, 600, and  $900^\circ\text{C}$  in 1 h.

Figure 6 shows the XRD patterns, as recorded for the  $\text{YVO}_4:\text{Eu}^{3+}$  nanoparticles prepared at 300, 600, and  $900^\circ\text{C}$ . Only the tetragonal phase of  $\text{YVO}_4$  (JCPDS, No. 17-0341) is observed in all samples. The sample annealed at  $900^\circ\text{C}$  for 1 h has better crystallinity in comparison to that of the samples annealed at 300 and  $600^\circ\text{C}$  for 1 h. This result shows that annealing at  $900^\circ\text{C}$  is preferable for the sample synthesis.

Figure 7 shows the FE-SEM patterns of the samples annealed at 300, 600, and  $900^\circ\text{C}$  for 1 h and the energy dispersive X-ray (EDX) spectra of  $\text{YVO}_4:\text{Eu}^{3+}$  nanoparticles annealed at  $900^\circ\text{C}$  for 1 h. Using ImageJ software for calculation, the correlative average particle sizes are found to be

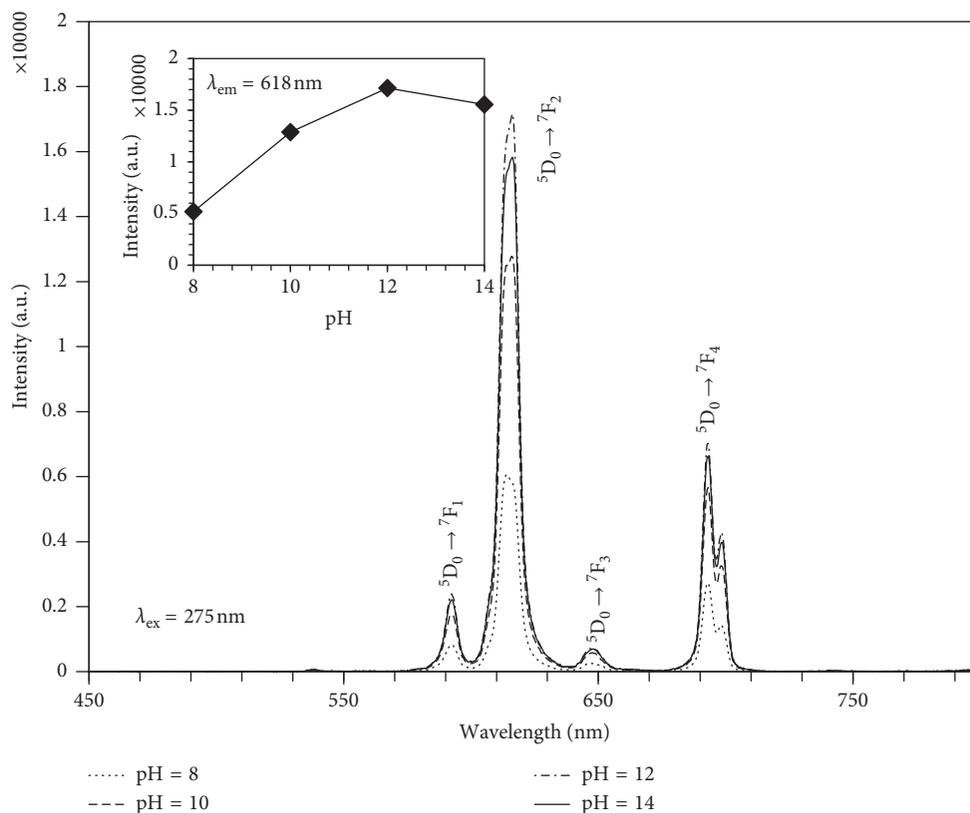


FIGURE 5: Photoluminescence spectra of samples with different pH values. Inset shows pH value dependence on  ${}^5D_0 \rightarrow {}^7F_2$  intensity.

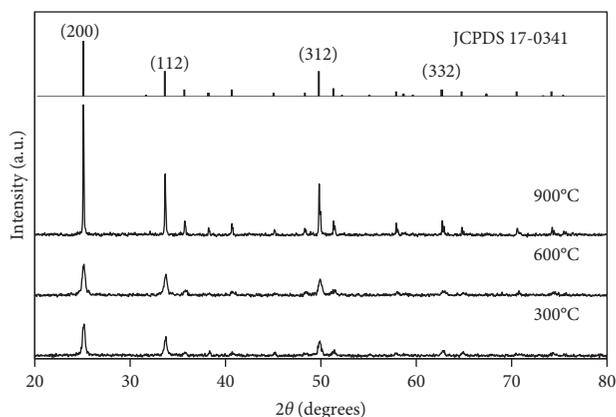


FIGURE 6: XRD samples of  $YVO_4:Eu^{3+}$  nanoparticles synthesized at different annealing temperatures.

47 nm, 78 nm, and 170 nm. Thus, when the annealing temperature increases, the particle size also increases. The increasing of  $YVO_4:Eu^{3+}$  nanoparticles size along with increasing annealing temperature has been observed by Georgescu et al. [38] and Li et al. [61]. This phenomenon can be explained by the nephelauxetic effect which is related to the metal-ligand bond covalency. Therefore, the covalency of  $Eu^{3+}-O^{2-}$  bonds in  $YVO_4:Eu^{3+}$  increases as the temperature increases in thermal treatment. There is a relation between the increase of covalency with nanoparticle size and the expansion of the cell parameters of  $YVO_4:Eu^{3+}$  nanoparticles in rapport with the bulk material.

The EDX spectrum in samples of  $YVO_4:Eu^{3+}$  nanoparticles affirms the existence of yttrium (Y), oxygen (O), vanadium (V), and europium (Eu) factors, indicating that  $Eu^{3+}$  ions are doped into the  $YVO_4$  nanocrystals.

The photoluminescence spectra which appeared under excitation at 275 nm of samples fabricated at different annealing temperatures are shown in Figure 8. Right inset is the UV-Vis spectra of  $YVO_4:Eu^{3+}$  nanoparticles with different annealing temperatures—left inset is the diagram presenting the dependence of  ${}^5D_0 \rightarrow {}^7F_2$  intensity on annealing temperature. The optical emission mechanism is the absorption of ultraviolet light by  $VO_4^{3-}$  groups and transfer of energy to  $Eu^{3+}$ , the energy which is released in the form of fluorescence [61–63]. Hence, the absorption of  $VO_4^{3-}$  is displayed in Figure 8 (right inset). There is an absorption in the  $VO_4^{3-}$  groups related to the peaks at 270 nm of three samples. In accordance with references, we can explain that the oxygen ligands attributed to the charge transfer to central vanadium atom in  $VO_4^{3-}$  group. The result of UV-Vis spectra is important because of the luminescent characteristic of  $YVO_4:Eu^{3+}$  nanoparticles resulting in the energy absorption and transfer from  $VO_4^{3-}$  to  $Eu^{3+}$  [22, 41]. All three samples have the strongest peak at 618 nm resulting from  ${}^5D_0 \rightarrow {}^7F_2$  transition. This leads to the indication of the occupying of  $Eu^{3+}$  ions to the asymmetry inversion center instead of  $Y^{3+}$ . Figure 8 (left inset) shows the dependence of luminescence intensity on annealing temperature. With the annealing at 900°C for 1 h,  $YVO_4:Eu^{3+}$  nanoparticles have the strongest luminescence intensity, which can be explained that the increase of temperature will

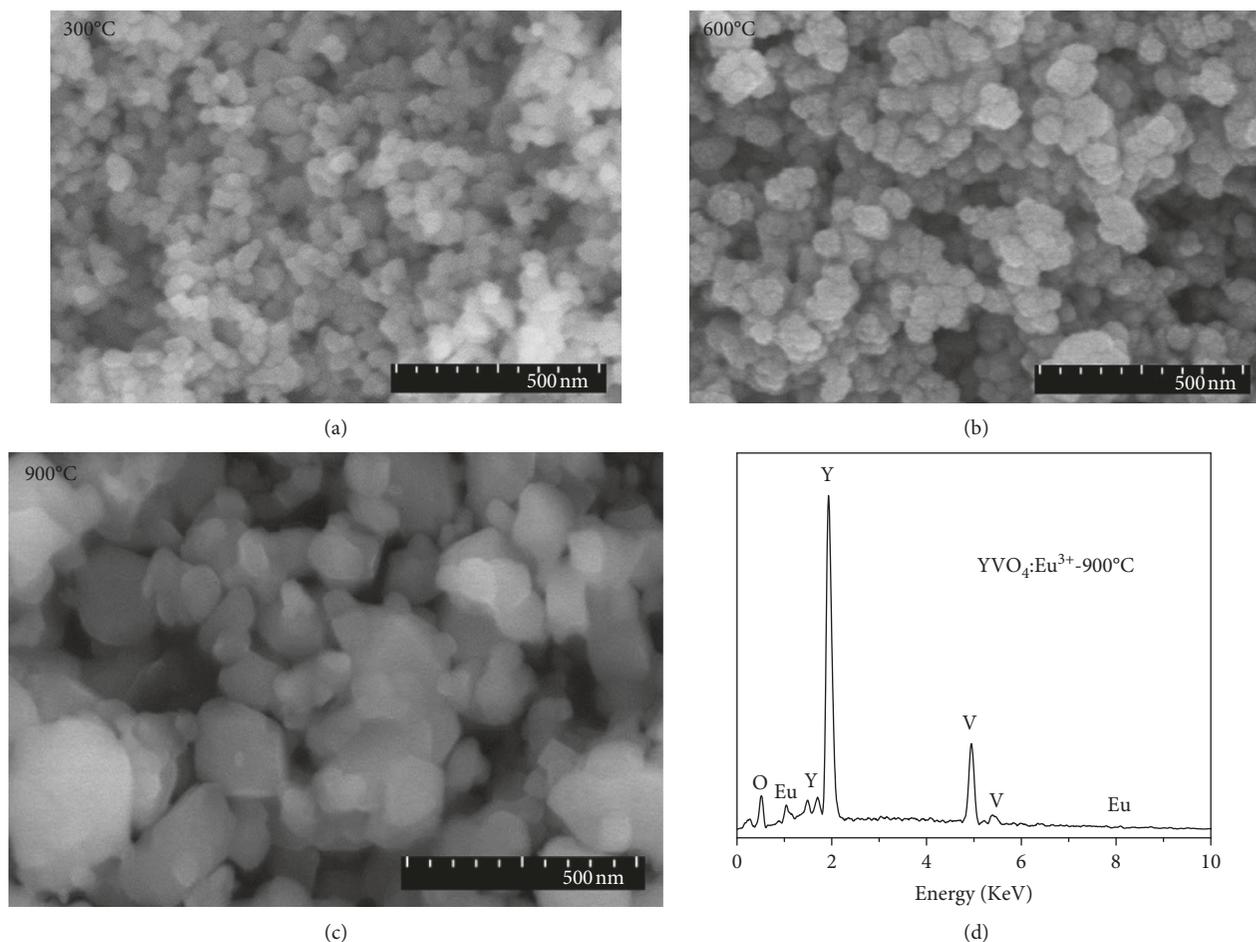


FIGURE 7: FE-SEM micrographs of  $\text{YVO}_4:\text{Eu}^{3+}$  nanoparticles at different annealing temperatures and corresponding EDX spectrum of samples annealed at 900°C (in 1 h).

decrease the number of top surface defects. However, the annealing temperature in this research remains not over 900°C in order to control the size of nanoparticles. Due to the nanoparticle size increasing, the disadvantage appeared in the preparation of security ink.

Figure 9 shows the photoluminescence spectra of samples annealed at 900°C for 2, 4, and 5 h with excitation at ~275 nm. The more increasing of  $\text{Eu}^{3+}$  local symmetry environment causes the increase of the strongest emission from  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  transition over annealing time from 2 h to 4 h. However, the annealing time of 5 h leads to the lower intensity than that at 4 h. The relative intensity ratio of  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  to  $^5\text{D}_0 \rightarrow ^7\text{F}_1$  peaks can show the symmetry rate of local environment of  $\text{Eu}^{3+}$  ions [23, 61, 64]. To reveal the influence of heat treating temperature and time on the luminescence properties, the relative intensity ratios of  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  and  $^5\text{D}_0 \rightarrow ^7\text{F}_1$  transitions in the samples are calculated, and the results are shown in Table 1.

In three samples annealed at 300, 600, and 900°C for 1 h, a tendency to decrease the intensity ratio with increasing heat treating temperature indicates the increase of symmetry of local environment of  $\text{Eu}^{3+}$  ions heat treatment temperature. The highest relative intensity ratio was obtained in the sample annealed at 300°C and the lowest in the sample at

900°C, which shows that highest  $\text{Eu}^{3+}$  local symmetry environment is in the sample treated at 900°C. These results can be explained that the low annealing temperature (at 300°C) leads to the slower crystal growth rate, the sample obtains enough energy due to increase in the annealing temperature (at 900°C) and has better crystallinity.

In four samples annealed at 900°C for 2, 3, 4, and 5 h, the relative intensity ratio decreases gradually from 2 h to 4 h sample, but this ratio in 5 h sample is higher than 4 h sample. It shows that the local symmetry of  $\text{Eu}^{3+}$  environment is the highest in the 4 h sample in comparison with other samples. The reason is that the particles have enough time and energy to have better crystallite growth [38, 40, 65]. However, increasing of the heat-treating time to 5 h leads to structure distortion and decrease of  $\text{Eu}^{3+}$  local symmetry environment.

In Figure 10, the room-temperature luminescence decay curves of  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  transition of  $\text{Eu}^{3+}$  are shown for the samples annealed at 300, 600, and 900°C for 1 h (Figures 10(a)–10(c)) and at 900°C for 4 h (Figure 10(d)). The excitation wavelength is fixed at 275 nm. The common factors affecting the decay kinetics behavior are the number of different luminescent centers, defects, energy transfer, and impurities in the host [62]. The raw data recorded for the

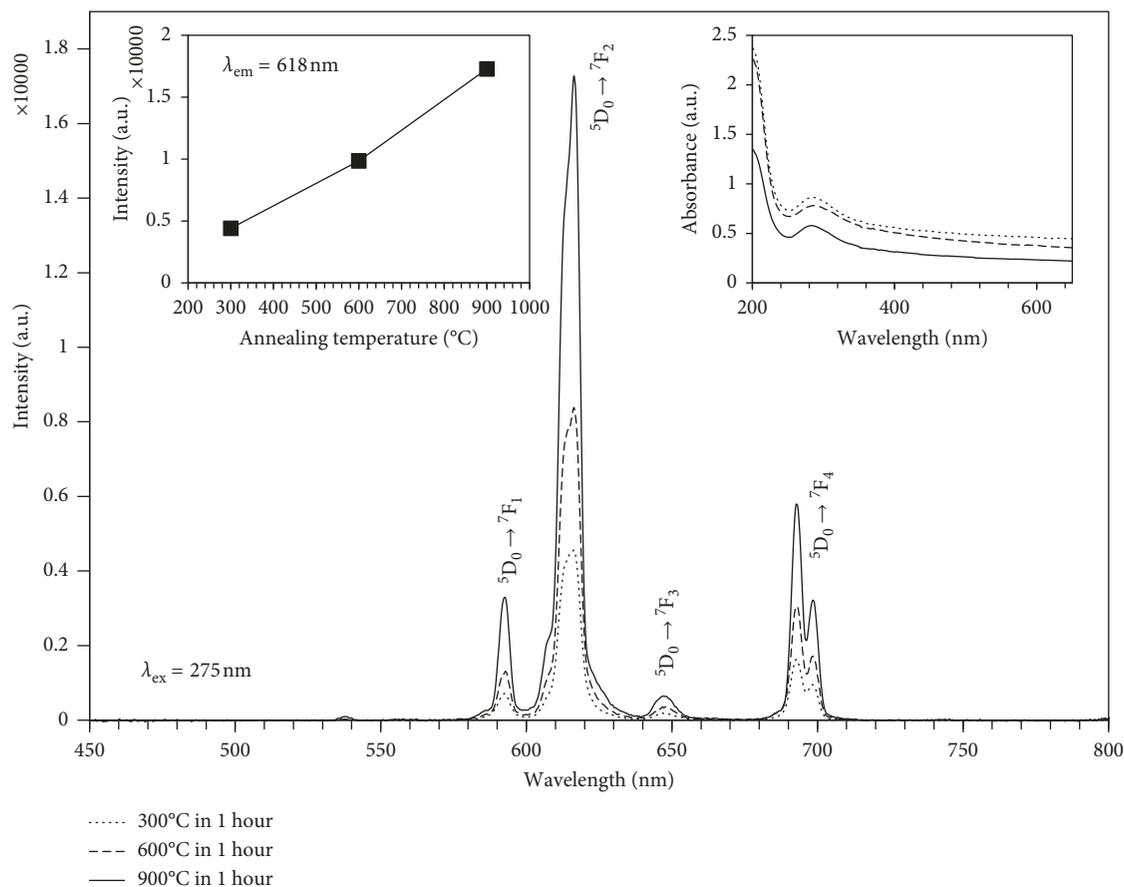


FIGURE 8: Photoluminescence spectra of samples at different annealed temperatures. Inset (right) shows the UV-V is spectra of  $\text{YVO}_4:\text{Eu}^{3+}$  nanoparticles with different annealed temperatures; left inset is the diagram of dependence of  $^5\text{D}_0\text{-}^7\text{F}_2$  intensity on annealing temperature.

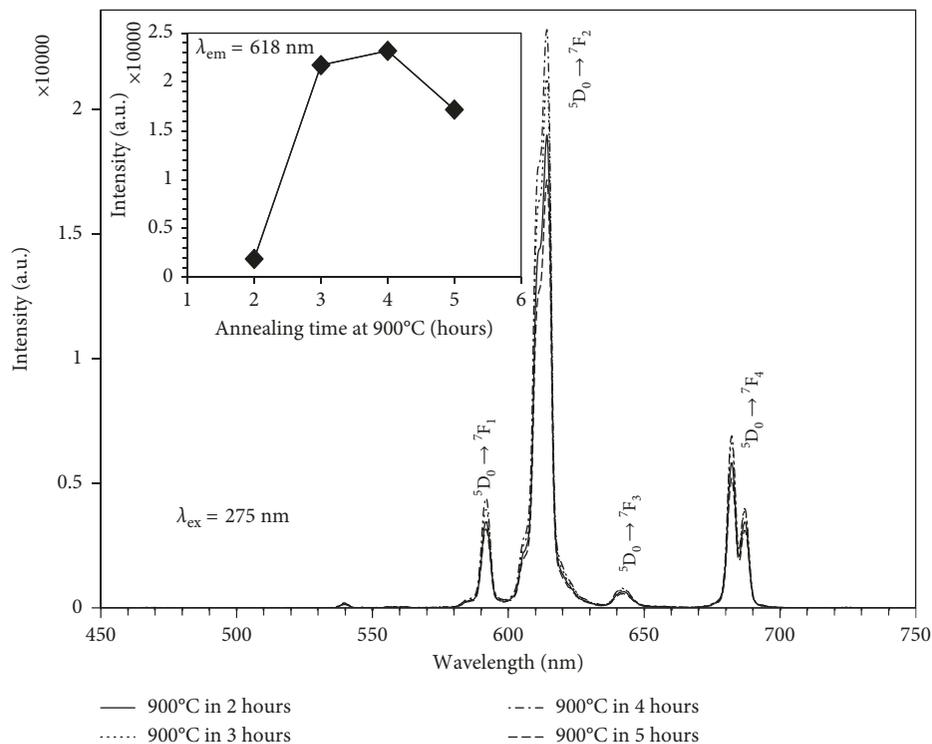
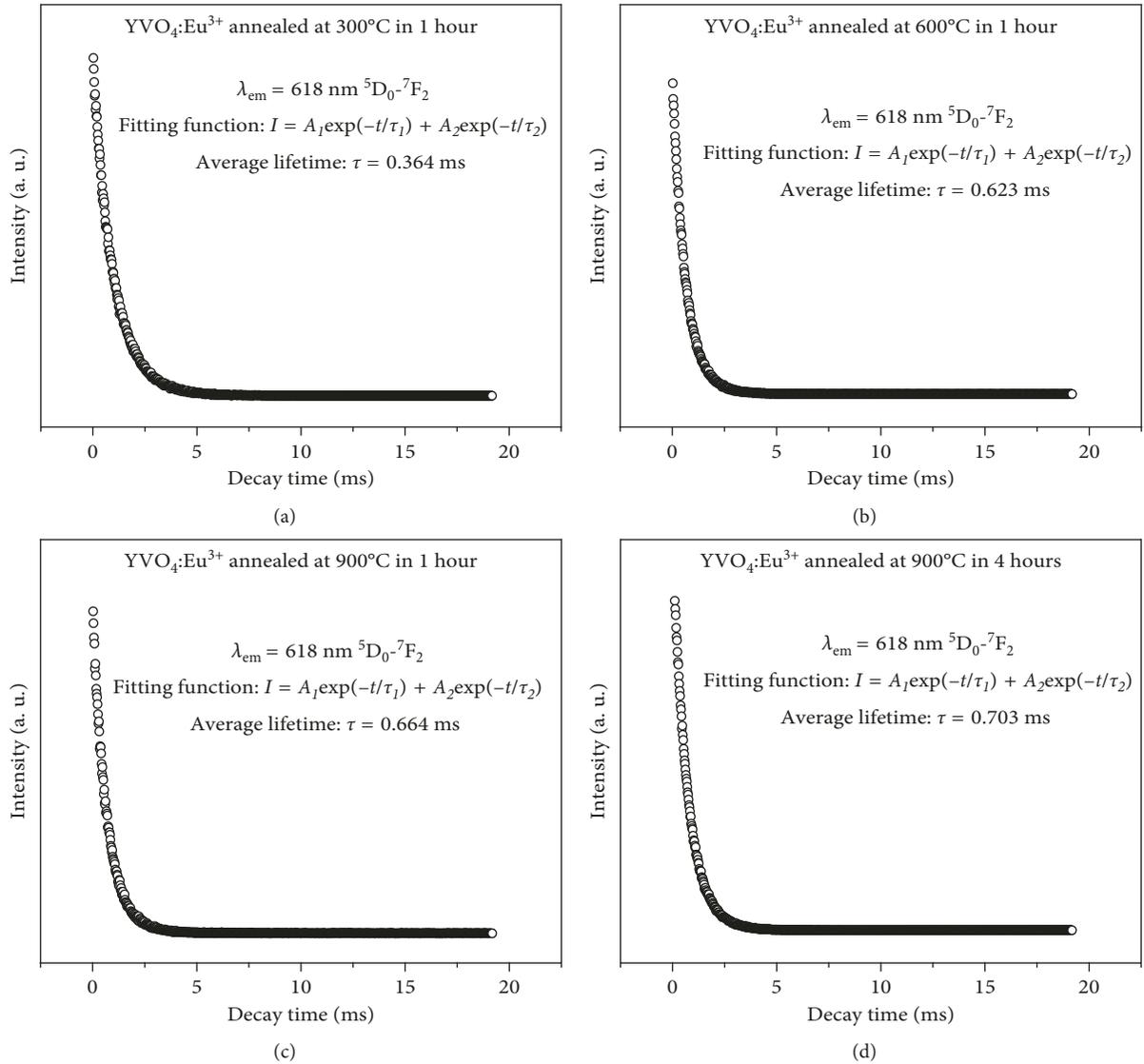


FIGURE 9: Photoluminescence spectra of samples annealed at 900°C in different durations. Inset shows diagram of dependence of  $^5\text{D}_0\text{-}^7\text{F}_2$  intensity on the annealing time at 900°C.

TABLE 1:  ${}^5D_0 \rightarrow {}^7F_2/{}^5D_0 \rightarrow {}^7F_1$  relative emission intensity ratio.

Sample	${}^5D_0 \rightarrow {}^7F_2/{}^5D_0 \rightarrow {}^7F_1$
300°C-1 h	8.80
600°C-1 h	5.58
900°C-1 h	5.26
900°C-2 h	6.38
900°C-3 h	5.97
900°C-4 h	5.71
900°C-5 h	5.87

FIGURE 10: The luminescence decay curves for the  ${}^5D_0$  excited state of  $\text{Eu}^{3+}$  under 275 nm excitation for  $\text{YVO}_4:\text{Eu}^{3+}$  samples synthesized with different annealing temperatures and durations.

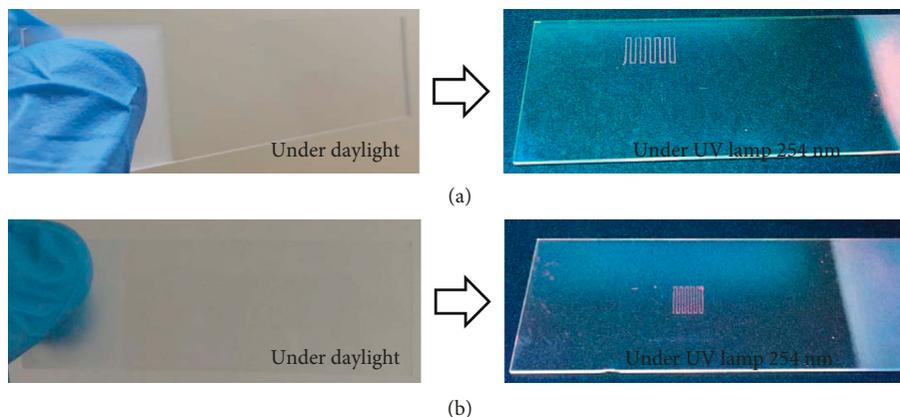
decay curves of all samples are well-fitted by a double-exponential function (equation (2)).

$$I = A_1 \exp\left(\frac{-t}{\tau_1}\right) + A_2 \exp\left(\frac{-t}{\tau_2}\right), \quad (2)$$

where  $I$  is the luminescence intensity at time  $t$ ,  $A$  is the fitting parameter, and  $\tau$  is the decay lifetime, respectively. The average lifetimes of the  $\text{Eu}^{3+}$  ions in samples annealed at 300, 600, and 900°C in 1 h at 618 nm emission under 275 nm excitation are calculated to be 0.364, 0.623, and 0.644 ms. The

TABLE 2: Formulation of  $\text{YVO}_4:\text{Eu}^{3+}$  nanoparticles ink.

Ingredient	$\text{YVO}_4:\text{Eu}^{3+}$	Glycerin	Ethanol	Ethyl acetate	Ethylene glycol
Percentage (% wt.)	8	62	16	4	10

FIGURE 11: The image of lines under daylight and UV lamp, labels with distance between two lines at  $300\ \mu\text{m}$  (a) and  $800\ \mu\text{m}$  (b).

average lifetime increases with the increase of annealing temperature from  $300^\circ\text{C}$  to  $900^\circ\text{C}$ . The decay lifetime difference may appear due to the nonradiative transition caused by the surface defects and/or crystallinity rate [42]. The higher the annealing temperature, the lower the surface effect. As shown in Figures 10(c) and 10(d) the average decay lifetime of  $\text{Eu}^{3+}$  ions in sample annealed at  $900^\circ\text{C}$  for 4 h is  $0.703\ \text{ms}$ , which is longer than that in the sample annealed at  $900^\circ\text{C}$  for 1 h. The measured decay time comprises both radiative and nonradiative transmission. The radiative decay component is dependent upon the number of light emitting activator ions in the nanoparticles [44]. We assume that  $\text{Eu}^{3+}$  ions doped in host lattice are light emitting activators, meaning that the occupancy of  $\text{Eu}^{3+}$  ions to  $\text{Y}^{3+}$  sites in the samples annealed at  $900^\circ\text{C}$  for 4 h is better than that in the sample treated for 1 h.

**3.3. Test Security Printing.** There are very few reports on the use of rare earth ions as luminescent colloids. The typical report of Gupta et al. is the usage of spherical  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  nanoparticles as security ink for screen printing technique, and Meruga et al. studied the security ink from the rare earth nanoparticles  $\beta\text{-NaYF}_4$ -doped  $\text{Yb}^{3+}/\text{Er}^{3+}$  and  $\text{Yb}^{3+}/\text{Tm}^{3+}$  to print security QR code by Optomec direct-write aerosol jetting. Our purpose is printing label at small size, from micrometer to millimeter, with high sharpness in order to increase the security ability for product. Therefore, we use  $\text{YVO}_4:\text{Eu}^{3+}$  to produce ink for the PS JET 300 V inkjet printer. This printer is operated by the electrohydrodynamic (EHD) inkjet technique. The advantage of the EHD inkjet technique is the ability to print labels at small size (in micrometer) on various material substrates.

For the preparation of security ink, the  $\text{YVO}_4:\text{Eu}^{3+}$  nanoparticles are synthesized by the sonochemical method and then redissolved into organic solvents. On the basis of the above results,  $\text{YVO}_4:\text{Eu}^{3+}$  nanoparticles, synthesized by the sonochemical method and annealed at  $900^\circ\text{C}$  for 4 h, are most appropriate to be used as security ink in inkjet printing due to

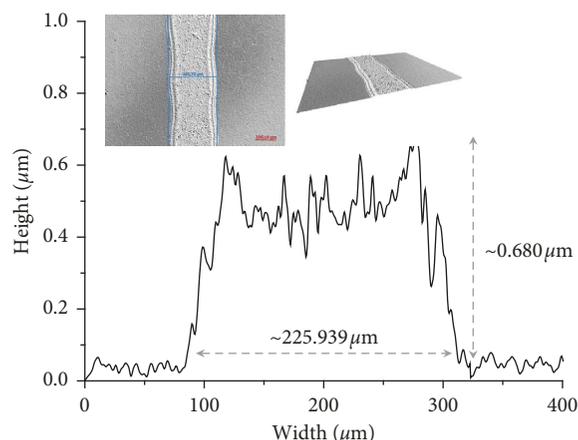


FIGURE 12: The height-width diagram of section of line after printed. Inset shows the micrograph of the respective line taken by Sensofar Metrology 3D microscope technique.

high luminescent intensity at  $618\ \text{nm}$  and proper size for not clogging the printhead. Formulation of  $\text{YVO}_4:\text{Eu}^{3+}$  nanoparticles ink is shown in Table 2 with the viscosity at  $\sim 350\ \text{cP}$ . The printhead is made of metal with diameter at  $\sim 198\ \mu\text{m}$ , DC voltage at  $1500\ \text{V}$ , frequency at  $500\ \text{Hz}$ , distance between print head and substrate at around  $150\ \mu\text{m}$ , and printing speed at  $20\ \text{mm/s}$ . We perform printing experiment with representative line security labels at small size length of  $5\ \text{mm}$  and distance between two lines set at  $300$  and  $800\ \mu\text{m}$ .

The printed line image on glass substrate under daylight and UV lamp  $254\ \text{nm}$  is shown in Figure 11. The lines printed in Figure 11(a) are with distance set at  $800\ \mu\text{m}$  apart and length at  $5\ \text{mm}$  and Figure 11(b) with length at  $5\ \text{mm}$  and distance set at  $300\ \mu\text{m}$  apart. In this experiment, the printed lines are nearly transparent under daylight and have red color luminescence under UV lamp working at  $254\ \text{nm}$ . The lines are clear, sharp, seamless, and not overlapped over each other even at small distance,  $300\ \mu\text{m}$ .

The sample with distance of 800  $\mu\text{m}$  between two lines set is analyzed by Sensofar Metrology 3D microscope technique. Figure 12 and inset present the height-width diagram of section of line after being printed and the micrograph of the respective line. The line is seamless with the width at  $\sim 230 \mu\text{m}$  and thickness at  $\sim 0.68 \mu\text{m}$ . According to this result, there is a possibility of printing small security labels with micrometer to millimeter size on glass substrate in order to enhance security property.

#### 4. Conclusion

The  $\text{YVO}_4:\text{Eu}^{3+}$  nanoparticles are synthesized by thermal stirring and microwave and sonochemical methods. According to the analyzed result, the crystallization of  $\text{YVO}_4:\text{Eu}^{3+}$  nanoparticles appears in the tetragonal structure and the phosphor has the strongest luminescence at wavelength of 618 nm due to  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  transition. The creation of the high local temperature and pressure by the sonochemical method has positive effect on the formation of crystalline  $\text{YVO}_4:\text{Eu}^{3+}$  nanoparticles and doping of  $\text{Eu}^{3+}$  ions into  $\text{Y}^{3+}$  position. As shown by TEM observation, the average size of  $\text{YVO}_4:\text{Eu}^{3+}$  nanoparticles synthesized by the sonochemical method is  $\sim 23 \text{ nm}$ .

The value of pH in the synthesized solution has influence on the emission intensity of  $\text{YVO}_4:\text{Eu}^{3+}$  nanoparticles, as pH at 12 is the most appropriate value. Concerning annealing at different temperatures,  $\text{YVO}_4:\text{Eu}^{3+}$  nanoparticles show the strongest luminescence intensity when being annealed at 900°C. The optimal luminescence intensity appears in the sample annealed at 900°C for 4 h. The size of  $\text{YVO}_4:\text{Eu}^{3+}$  nanoparticles is proportional to the annealing temperature, and the average size of  $\text{YVO}_4:\text{Eu}^{3+}$  nanoparticles is  $\sim 170 \text{ nm}$  at 900°C applied for 1 h. The average lifetimes of the  $\text{Eu}^{3+}$  ions emission at 618 nm under 275 nm excitation of the samples annealed at 300, 600, and 900°C for 1 h are 0.364, 0.623, and 0.644 ms, whereas the value in the sample annealed at 900°C for 4 h is 0.703 ms.

Analysis of the results shows that the lines printed by inkjet technique is solid and even with the width at  $\sim 230 \mu\text{m}$ , the thickness at  $\sim 0.68 \mu\text{m}$ , and the smallest distance of two adjacent lines at 300  $\mu\text{m}$ . The test lines are nearly invisible under daylight, and they are red under UV mercury lamps with wavelength of  $\sim 254 \text{ nm}$ .

#### Data Availability

No data were used to support this study.

#### Conflicts of Interest

The authors declare that they have no conflicts of interest.

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## Research Article

# Fast and Effective Route for Removing Methylene Blue from Aqueous Solution by Using Red Mud-Activated Graphite Composites

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In this work, the mixture of red mud slurry and inorganic salt ((NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>) has been used as an electrolyte for electrochemical activation of graphite. The red mud-activated graphite composite was then used as an adsorbent for removing methylene blue from aqueous solution by the batch method. The effect of pH, contact time, adsorbent dosage, and the initial concentration of methylene blue was investigated. The optimal condition was found at pH 6, contact time 120 min, and amount of adsorbent 1 mg/L. The maximum adsorption capacity was found to be 89.28 mg/g based on the Langmuir isotherm equation, suggesting that the red mud-activated graphite composite is a very potential adsorbent for removing methylene blue and is also used in other coloured wastewater treatments.

## 1. Introduction

Dyes and pigments (e.g., methylene blue (MB)) are widely used in textile, dyeing, printing, and coating industries. Their wastewater contains a high concentration of non-biodegradable organic compounds which can cause long-term health effects on human beings and animals and significantly qualitative changes in the environment [1]. Therefore, it is essential to remove the contaminants such as dyes and heavy metal ions in the wastewater before discharging into the water source. Several methods such as biodegradation, chemical treatment, the use of UV and ozone, and adsorption have been applied to get rid of MB

from wastewater [2–6]. Among them, the utilization of agricultural or industrial by-products as adsorbents for wastewater treatment has received lots of attention [7]. Recently, chemically or thermally activated seawater neutralized treated red mud (RM) has been effectively used as a promising candidate for removing heavy metal ions and dyes from aqueous solution as a result of the reaction between the hydroxyl groups and active site on red mud or through adsorption onto external surfaces [8, 9]. Besides, the application of graphene oxide (GO) or graphene nanosheets (GSs) adsorbent has been shown to be a simple and effective method for the removal of dye contaminants from wastewater [1, 10]. Moreover, the modification of graphene under

basic conditions or the combination of graphene with other metal oxides showed a great potential for removal of heavy metals ions in water [11–13]. In order to generate porosity for adsorptive purposes, the activation of graphite using alkaline hydroxides such as KOH or NaOH usually requires concentrated alkali solution, long reaction time, and high temperature [14, 15]. Therefore, finding a simple, effective, and energy-saving process for producing activated graphite materials is highly demanded.

As previously discussed, red mud with a high basic property must be activated simultaneously with other materials [16], using acidic conditions [17] or high temperature [18] before utilization. Also,  $(\text{NH}_4)_2\text{SO}_4$  solution has been demonstrated to be an effective electrolyte for one-step fast electrochemical exfoliation of graphite [19]. These works show a great possibility of using the mixture of RM slurry and  $(\text{NH}_4)_2\text{SO}_4$  as an electrolyte for activating graphite. Therefore, in this study, we combine red mud slurry with  $(\text{NH}_4)_2\text{SO}_4$  as an electrolyte for simultaneous activation and exfoliation of graphite and employ the as-product for removing MB from aqueous solution.

## 2. Materials and Methods

**2.1. Synthesis and Characterization of Materials.** 300 mL of red mud slurry (Tan Rai factory, Lam Dong Province, Vietnam) was added with 100 mL of 5% w/w  $(\text{NH}_4)_2\text{SO}_4$  solution under a magnetic stirrer to form a homogeneous electrolyte at pH 14. Graphite rod was then activated by electrochemical exfoliation using this electrolyte with the voltage of 15 V and temperature from 50–70°C for 120 min (Scheme 1). The beaker was cooled to room temperature in 1 h, and the material was filtrated and washed with DI water until natural pH is reached. The obtained material was finally put in drying oven at 150°C for 24 h and placed in a desiccator at 25°C (denoted as RMGC). The activated graphite without red mud (named as electrochemically exfoliated graphite (EEG)) was also prepared for the comparison purpose using conventional electrolytic solution at pH 14 (200 mL of 7.5% KOH and 50 mL of 5%  $(\text{NH}_4)_2\text{SO}_4$ , pH 14).

XRD patterns were characterized by using a diffractometer (D2 PHASER using Cu  $K\alpha$  radiation). RMGC and EEG structures were examined using high-resolution confocal Raman microscopy (HORIBA, Lab RAM HR 800 equipped with a 514.5 nm Ar laser source). Morphology of materials was determined by using a high-resolution transmission electron microscope (HRTEM, JEOL 2100F apparatus operated at 200 kV). Field emission scanning electron microscopy (SEM) images were collected using the JEOL JSM-6500F scanning electron microscope operated at 15 kV.

**2.2. Adsorption Studies.** The adsorption experiments for RMGC were carried out by the batch method at room temperature. Several factors including contact time (0 to 270 minutes), initial MB concentration (10, 25, 50, 75, and 100 mg/L), amount of adsorbent (0.01–0.1 g), and solution pH (2.0–12.0) were investigated. The solution of 10% HCl

and 0.1 M NaOH was used to adjust pH solution before addition of the adsorbent. After the test periods, the samples were separated by centrifugation for 15 min at 4000 rpm and the collected supernatant determined the concentration of MB by absorbance measurement using a UV-Vis spectrophotometer (Hitachi UH5300) at a wavelength of 665 nm.

$\text{pH}_{\text{pzc}}$  (the point of zero charge) of the RMGC was determined in a similar method as Faria et al. [10] At first, 25 mL of 0.01 M NaCl solution was prepared and added into conical flasks, and the pH solution was adjusted by adding NaOH and HCl solutions from 2 to 12. After that, each conical flask was added 0.1 g of the obtained material and shaken for 48 h at room temperature. After the tests, the pH solution was redetermined and denoted as the final pH. Concomitantly, the difference between the initial pH and final pH (initial pH—final pH) was plotted against the initial pH. The point at which the resulting curve intersected with abscissa was  $\text{pH}_{\text{pzc}}$  of the RMGC.

The adsorption capacity and removal efficiency of MB on RMGC was calculated by the following equation:

$$q = \frac{(C_0 - C_e)V}{M}, \quad (1)$$

$$R\% = \frac{(C_0 - C_e)}{C_0} \times 100\%,$$

where  $V$  (L) is the solvent volume and  $M$  (g) is the mass of adsorbent.  $C_0$  and  $C_e$  (mg/L) are initial and equilibrium concentrations, respectively.  $q$  (mg/g) is the adsorption capacity at equilibrium time, and  $R$  (%) is the removal efficiency of MB.

Adsorption isotherms were conducted at pH 6, contact time 120 min, and room temperature. The different initial concentrations of MB (10, 25, 50, 75, and 100 mg/L) were experimented to analyse the data. The isotherm models of Freundlich and Langmuir are expressed by the following equations:

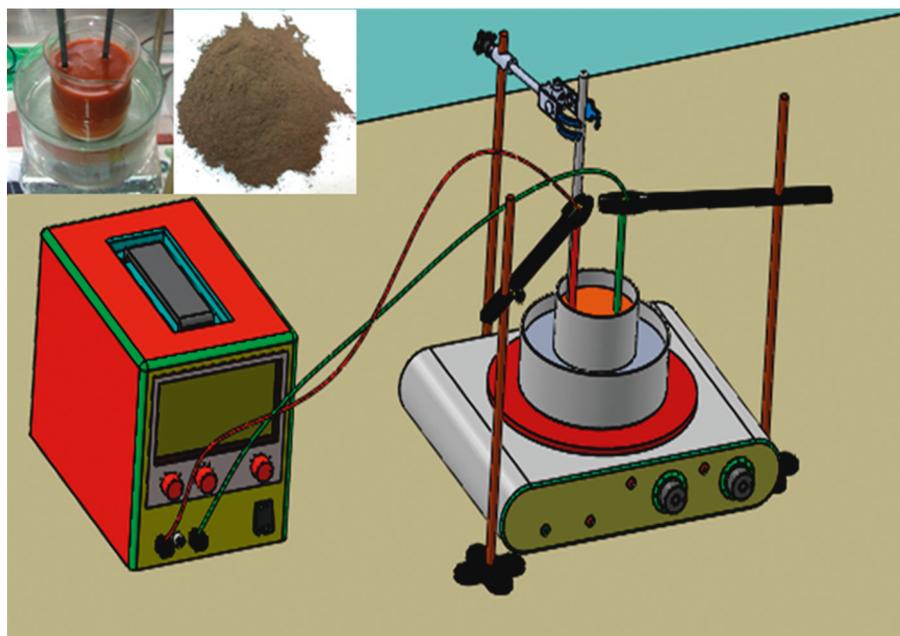
$$\text{Freundlich: } q_e = K_f C_e^{1/n}, \quad (2)$$

$$\text{Langmuir: } q_e = \frac{q_0 b C_e}{1 + b C_e},$$

where  $K_f$  and  $n$  are Freundlich constants related to sorption capacity and sorption intensity of adsorbent.  $q_e$  and  $C_e$  are the adsorption capacity and concentration at equilibrium of MB in solution, respectively.  $q_0$  and  $b$  are the monolayer adsorption capacity and the Langmuir constant.

## 3. Results and Discussion

**3.1. Structural Analysis.** To investigate the morphology of the materials, SEM micrographs are depicted in Figure 1. EEG image displayed flattened morphology and turned into a particle-on-sheet structure in RMGC after exfoliating, which can be further observed by the TEM image in Figure 2. Clearly, exfoliated graphite flakes were overlapped with nanoparticles, which were fairly uniformly distributed on its surface layer (Figure 1(c)). In situ EDS also revealed that the



SCHEME 1: Schematic of RMGC formation (the inset is the working system and as-product).

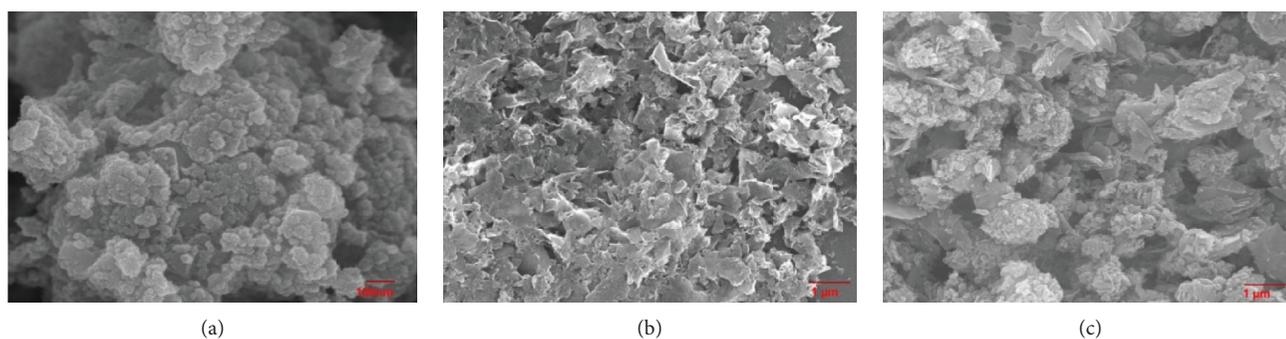


FIGURE 1: SEM images of (a) RM, (b) EEG, and (c) RMGC.

RMGC mainly consisted of C, O, Fe, Si, and Al elements (Figure 2).

The XRD patterns of all collected materials are displayed in Figure 3. The EEG pattern shows a sharp and high-intensity peak at a value of  $2\theta$  of  $26.6^\circ$ , indexing to the 002 reflection. In addition, there are three small peaks at values of  $2\theta$  of  $42.8$ ,  $21.6$ , and  $34.6^\circ$ , indexing to the 100, 101, and 004 reflections, respectively. After exfoliating, these peaks still remained, while new small peaks appeared at  $2\theta$  values of  $18.1$ ,  $21.3$ ,  $29.6$ ,  $33.1$ ,  $35.6$ ,  $37.1$ ,  $54.2$ ,  $62.2$ , and  $64.3^\circ$ . These new peaks can be assigned to the phases of quartz (Qz =  $\text{SiO}_2$ ), gibbsite (Gb =  $\gamma\text{-Al}(\text{OH})_3$ ), goethite (Gt =  $\alpha\text{-FeOOH}$ ), and hematite (Hm =  $\text{Fe}_2\text{O}_3$ ) [13]. Raman spectroscopy was used to further verify the structure of RMGC. As shown in Figure 4, the characteristic peaks of exfoliated graphite flakes were D- and G-band at  $1573\text{ cm}^{-1}$  and  $1583\text{ cm}^{-1}$ , respectively, also presented in RMGC [20]. Previously, the  $\text{OH}^-$  ions will initially oxidize graphite at the edge and/or grain boundaries and were proposed to expand the distance between graphite layers as well as for the following anion intercalation. Concretely, the sulfate ions

$\text{SO}_4^{2-}$  intercalate and facilitate in separating weakly bonded graphite layers [19]. In addition, RM is a heterogeneous mixture of fine-grained solids, mainly consisting of hematite, gibbsite, quartz, titanium oxide, carbonates, and desalination products (e.g., cancrinite and sodalite) with high alkalinity, resulted in the exits of hydrated  $\text{OH}^-$  together with  $\text{SO}_4^{2-}$  ions. We considered that applying bias voltage, oxygen evolution of  $\text{SO}_4^{2-}$  and  $\text{OH}^-$  ions could attach the edge sites and grain boundaries of graphitic layers, which eventually lead to exfoliation including activation with fine RM particles.

**3.2. Adsorption Studies.** The effect of pH on the RMGC's adsorption of MB is shown in Figure 5. In pH range of 2 to 6, it is obvious that the removal efficiency increased rapidly and was then stable when pH increased from 6 to 12. In the pH drift test (Figure 5(b)), the  $\text{pH}_{\text{pzc}}$  value of the RMGC was observed at  $8.3 \pm 0.1$ . At lower pH, a large number of  $\text{H}^+$  ions compete with cationic dye for adsorption sites on RMGC. Moreover, the presence of  $\text{H}^+$  ions could protonate the

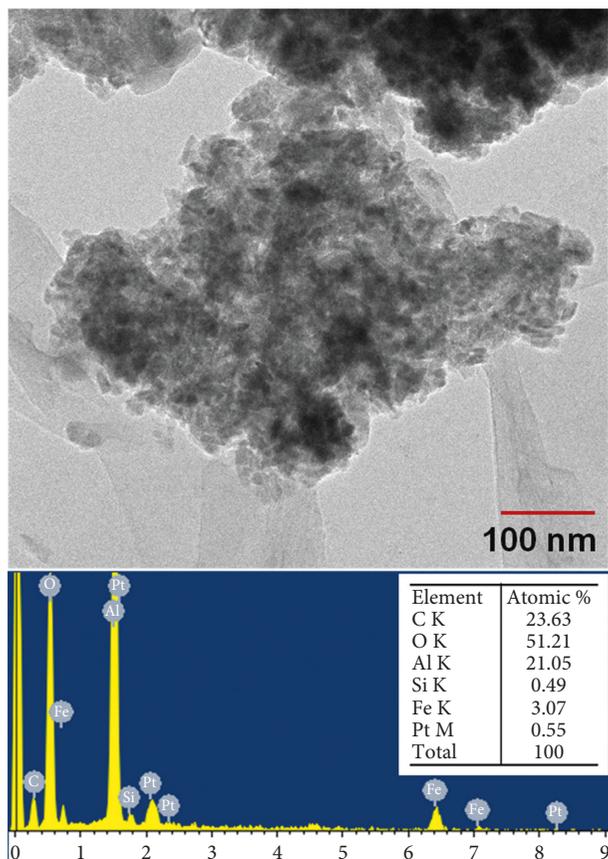
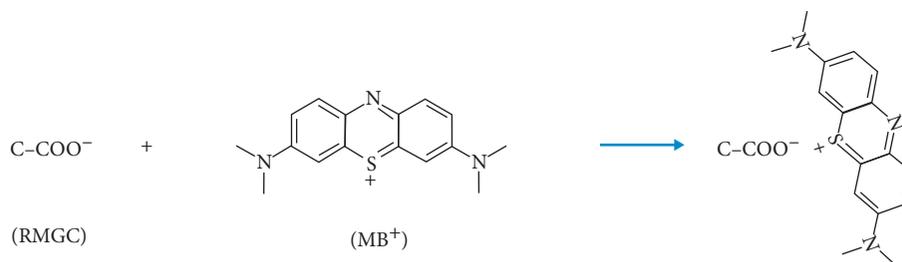


FIGURE 2: TEM image of RMGC, EDS spectrum of RMGC.

functional groups of the graphene and further decreases the adsorption amount of MB. On the contrary, the deprotonation of surface groups at a higher pH would increase the negative charges on the surface, which could result in a greater adsorption amount of MB. Therefore, the electrostatic attraction is responsible for adsorption of MB on RMGC, and the mechanism is proposed as follows:



The highest removal efficiency of MB on RMGC was at pH = 6. In the actual environment, the wastewater generally occurs at the neutral pH value. Thus, the pH value for further experiments was from 5 to 6.

To determine the equilibrium time of removal of MB on RMGC, time intervals up to 270 min of experiment were

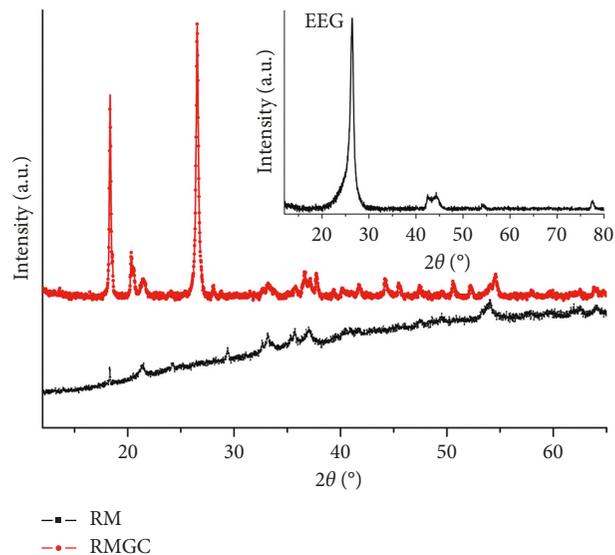


FIGURE 3: XRD patterns of RM and RMGC (inset is that of EEG).

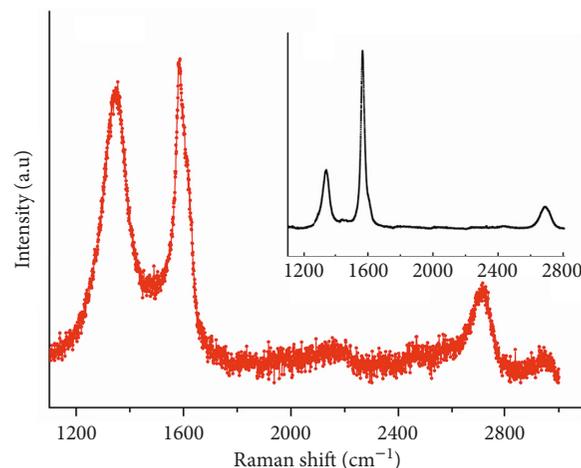


FIGURE 4: Raman spectrum of RMGC (inset is that of EEG).

conducted. As can be seen from Figure 6, MB was rapidly absorbed after 120 min at a removal efficiency of 96.02% but slowed down gradually when reached equilibrium. The reason could be explained by the availability of active sites during the adsorption process, generally in the first stage and after a certain time period of adsorption. Specifically, the active sites

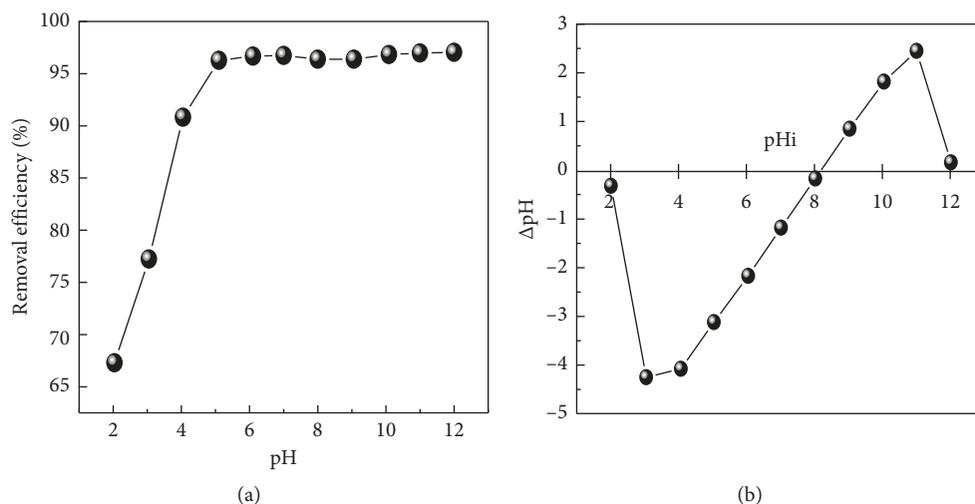


FIGURE 5: (a) Effect of pH value on MB adsorption and (b)  $\text{pH}_{\text{pzc}}$  (MB concentration: 50 mg/L; adsorbent dose: 0.05 g).

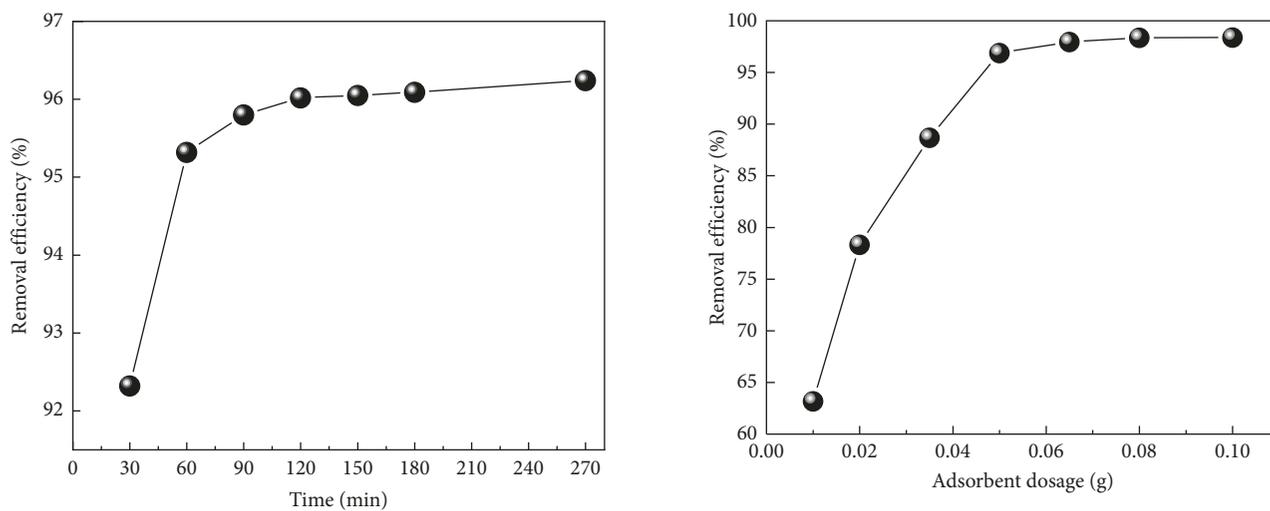


FIGURE 6: Effect of contact time on MB adsorption (MB concentration: 50 mg/L; adsorbent dose: 0.05 g).

will be settled by MB molecules when contact time is increased. At a certain time, the active sites will be fully occupied and could cause to create a repulsive force between the adsorbate on the adsorbent surface and in the bulk phase. After equilibrium conditions are attained, the removal efficiency kept was almost invariable. The contact time at 120 min was preferred as the equilibrium time for further experiments.

Figure 7 illustrates the effect of adsorbent dosage on MB removal efficiency using RMGC. It can be clear that the removal efficiency of MB gradually risen with an increase in an adsorbent dosage up to 0.05 g and thereafter remained unchanged. The more the adsorbent dosage could be added, the more the active sites are available. As a result, the more vacant surface sites were utilized at a fixed MB concentration. The amount of adsorbent was chosen to be 0.05 g for further experiments.

FIGURE 7: Effect of adsorbent dosage on MB adsorption (MB concentration: 50 mg/L; time: 120 min).

Figure 8 presents the effect of initial concentration on the adsorption of MB on RMGC, revealing that removal efficiency decreased from 98.75 to 84.16% as the MB concentration increased from 50 to 250 mg/L, as a result of the progressive increase in the electrostatic interaction between MB and RMGC active sites. Under these circumstances, the active sites were covered since MB concentration increases. Additionally, the higher initial concentrations lead to an increase in the affinity of the cationic dyes towards the active sites.

The relative isotherm parameters and correlation coefficient ( $R^2$ ) values are listed in Table 1. The analyzed data suggested that MB adsorption could be described in the Langmuir model than the Freundlich model since its  $R^2$  value was higher. This demonstrated that the adsorption of MB on RMGC was monolayer adsorption and controlled by a homogeneous process. Additionally, the maximum capacity ( $q_{\text{max}}$ ) of MB adsorbed on RMGC was predicted as 89.28 mg/g, which was similar to some other adsorbents [21, 22]. The

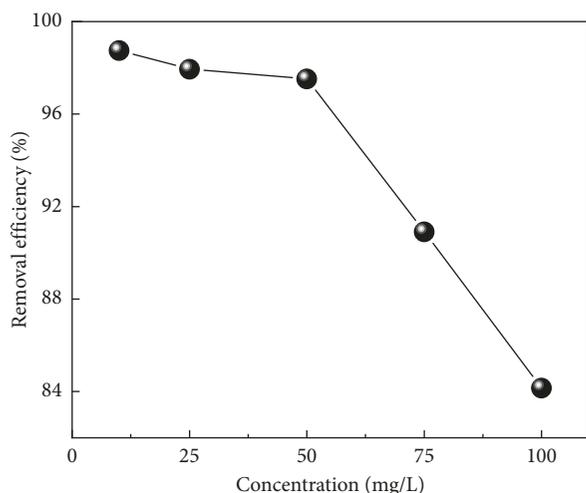


FIGURE 8: Effect of initial concentration on MB adsorption (adsorbent dose: 0.05 g; time: 120 min).

TABLE 1: Adsorption isotherm constants for the adsorption of MB by RMGC.

Model	Parameters	Value
Langmuir	$q_{\max}$ (mg/g)	89.28
	$b$ (L/mg)	0.77
	$R^2$	0.9995
Freundlich	$n$	2.315
	$K_f$ (mg/g)/(mg/L) <sup>n</sup>	30.489
	$R^2$	0.894

TABLE 2: Comparison of RMGC with other adsorbents.

Adsorbents	pH	Time	$q_{\max}$ (mg/g)	References
Charcoal	—	~6 h	67.2	[21]
Fibrous clay minerals	4	24 h	85.5	[22]
Graphene/Fe <sub>3</sub> O <sub>4</sub> composites	2–11	20 min	43.82	[23]
Graphene/carbon nanotube	6–7	180 min	81.97	[24]
RMGC	6	120 min	89.28	This work

—, no information.

comparison of  $q_{\max}$  and experimental conditions of various adsorbents is given in Table 2.

#### 4. Conclusions

The adsorbent of red mud-activated graphite composites (RMGC) was successfully prepared via electrochemical exfoliation of graphite in the mixture of RM slurry and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> as an electrolyte and applied for the adsorption of methylene blue in aqueous solution. The optimal conditions for removal of MB were at pH 6 and 120 min. According to the Langmuir model, the maximum adsorption capacity was found to be 89.28 mg/g. The RMGC has proven to be an effective low-cost adsorbent for the removal

of MB, which could be studied extensively in order to apply it for wastewater treatment in the future.

#### Data Availability

No data were used to support this study.

#### Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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## Research Article

# Enhancing Activity of Pd-Based/rGO Catalysts by Al-Si-Na Addition in Ethanol Electrooxidation in Alkaline Medium

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The article presents modified Pd-based catalysts supported on reduced graphene oxide (rGO), used in the electrooxidation reaction of ethanol in alkaline medium. When  $\text{NaBH}_4$  reducing agent was used, the random presence of Na was found out. According to this result, Na was used as a promoter of Pd-based catalyst. Consequently, the Al-Si-Na addition not only assisted active phase Pd nanoparticles to disperse homogeneously on graphene support, but also contributed to increase catalytic activity in the reaction. This value,  $16138 \text{ mA}\cdot\text{mg}^{-1}_{\text{Pd}}$ , is about 1.5 times higher than that of the catalyst modified by Al-Si. Moreover, the stability of the catalyst is enhanced more. The electrochemical stability of PASGN.N catalyst was relatively good: after 500 scanning cycles, the current density diminished 32% compared with the highest peak current density of the 15<sup>th</sup> cycle, which was chosen as a reference. These significant improvement results in electrooxidation of ethanol have opened up the high potential application of these catalysts in direct-ethanol fuel cell.

## 1. Introduction

Nowadays, the direct ethanol fuel cell (DEFC) is one of the potential options for use in portable electronic devices, storage, and small electrical appliances. DEFC has high energy efficiency, remarkable efficiency in energy conversion, low temperature in operation, and considerable poison gas emissions. Moreover, producing ethanol from agricultural products and biomass fermentation process on a large scale is widely carried out [1, 2]. However, in DEFC, noble metal-based catalysts, despite their good activity, are highly costly and easily poisoned by the adsorption process of the intermediate compounds formed during electrooxidation of ethanol. In addition, the electrode kinetics are sluggish [3, 4].

In the noble metal group, Pd and Pt had similar structure and electrochemical properties. However, for the electrooxidation of ethanol, Pd showed more advantages in comparison with Pt by the better resistance in alkaline

medium, faster anionic film exchange capacity, and higher possibility of combination with other metals or transition metal oxides.

Some Pd-based catalysts such as Pd-Co [5], Pd-Ni [6–8], Pd-Ni-Sn [9], Pd-Ru-Ni [10], Pd-Cu [11], Pd-Au [12], Pd-Ag [13], or Pt-Pb [14] have been studied to minimize Pd content and poisoning effect in high electrochemical activity of remaining Pd. According to various researches, the presence of transition metals such as Co and Ni, provided  $\text{M-ROH}_{\text{ads}}$  or formed  $\text{M-(ROH)}_x$  species (where M is the metal atom, ROH are methanol or ethanol), which changed the ethanol adsorption ability and enhanced the adsorption process of intermediate  $\text{CHO}_{\text{ads}}$ ,  $\text{CO}_{\text{ads}}$ , limiting the poisoning process and thus improving the catalytic activity [5–7, 9, 10].

On the other hand, choosing the support for Pd-based catalyst is an important factor that affects the electrochemical activity of catalyst. Carbon nanotubes (CNTs) and carbon black (Vulcan XC-72) are commonly used as support [15–18]. Recently, graphene materials have been attracting a

high attention because of their advantages of physical and chemical properties such as electrical conductivity and a very high surface area ( $\sim 2630 \text{ cm}^2\text{-g}^{-1}$ ) [19]. And, more especially, graphene enhances the dispersion of active metal particles.

In a recent research of Tan and colleagues [20], it was observed that the combination of Pd and Ni on graphene remarkably augmented catalytic activity of electrooxidation of ethanol in alkaline medium in comparison with PdNi/C and Pd-Ni catalysts. Liu et al. [21] obtained similar results at the same conditions of the catalytic test for catalyst of  $\text{MnO}_2$ -promoted Pd supported on graphene oxide (GO) and multiwalled carbon nanotubes. This was explained by the few-layer structure, a high conductivity, and the large accessible area of GO which enhanced the interaction and dispersion of the Pd-active phase on graphene surface. In addition, GO also contains oxygen-functional groups which are the combination site of metal ions, thereby increasing catalytic stability in the electrolyte medium.

In our paper [22], Si-Al was a very good bimetallic promoter phase in modified catalyst based on Pt/rGO in methanol electrooxidation. The results in this paper showed that modified Pt-rGO with 7% Si-Al was the best catalyst which had the highest activity in methanol electrooxidation with more than  $1700 \text{ mA}\cdot\text{mg}^{-1}\text{Pt}$  current density. The Al and Si compounds obtained in the catalyst exist as pseudo-boehmite ( $\text{AlOOH}$ ) and silica ( $\text{SiO}_2$ ), and they improve dispersion of the active phase on GO surface.

In this article, the preparation of Pd/rGO-based catalysts modified by promoters such as Al, Si, Al-Si, and Al-Si-Na and reduced by  $\text{NaBH}_4$  and ethylene glycol (EG) was reported. These catalysts are intended to be used as an anode catalyst for DEFC. These catalysts modified by promoters exhibited high activity in electrooxidation of ethanol in alkaline medium, and a highly improved resistance against poisoning of intermediary compounds in comparison with non-modified Pd/rGO catalysts.

## 2. Materials and Methods

**2.1. Chemicals.** Exfoliated graphite was provided by SGL Carbon GmbH (GFG). Tetraethyl orthosilicate (TEOS) 99%, aluminum tri-isopropoxide 99.9%,  $\text{CH}_3\text{COONa}$  99%, NaOH 98.8%,  $\text{H}_2\text{SO}_4$  96%, and ethanol 99.9% were purchased from Merck. And, Nafion® solution (whose mass fraction is 5%), ethylene glycol (EG), sodium borohydrite ( $\text{NaBH}_4$ ), isopropanol (IPA) 99.5%, and  $\text{PdCl}_2$  99% were purchased from Sigma Aldrich. The nitrogen gas of high purity (99.95% (Air Liquide)) and deionized water were used in all experiments.

**2.2. Catalyst Preparation and Characterization.** GO slurry synthesized by the modified Hummers' method [23] was diluted to the content of  $5 \text{ mg}\cdot\text{mL}^{-1}$ . Several catalysts based on graphene-supported palladium modified by metallic promoters were prepared in this study.

Sample of 28.57% Pd by active metal loadings (theoretically calculated, denoted as PG.E) and sample of 26.40% Pd-7.60% Na (PNG.E) made from GO, EG,  $\text{CH}_3\text{COONa}$ ,

and  $\text{PdCl}_2$  were synthesized in the similar way of preparation of 40% Pt/rGO following a procedure described in [22].

In this catalyst, theoretical total mass fraction of Al and Si was 4.76% and mass fraction of Pd was 27.21%. The PdAlSiNa/rGO catalyst was reduced by EG as PASG.E catalyst with the addition of  $\text{CH}_3\text{COONa}$  precursor (whose mass fraction of Na is 7.26%) during the synthesis (denoted as PASNG.E).

The PdAl/rGO and PdSi/rGO catalysts reduced by EG (PAG.E and PSG.E) were synthesized in the similar way of preparation of PASG.EG catalysts but in absence of Si or Al precursors during synthesis, respectively. The theoretical elemental composition is 4.76 wt% of Al and 27.21 wt% of Pd in PAG.E catalyst, and 4.76 wt% of Si and 27.21 wt% of Pd in PSG.E catalyst.

All catalysts reduced by  $\text{NaBH}_4$  are Pd/rGO, PdNa/rGO, PdAlSi/rGO, and PdAlSiNa/rGO, respectively, were denoted as PG.N, PNG.N, PASG.N, and PASGN.N. The PASGN.N catalyst synthesis process was performed as follows: a precursor mixture of 18.8 mL of  $\text{PdCl}_2$  0.01 M and 10 mL of the solution GO  $5 \text{ mg}\cdot\text{mL}^{-1}$  was mixed and ultrasonicated for 2 min before adding 8.2 mg Al-isopropoxide, 2 mL IPA, 20  $\mu\text{L}$  TEOS, and 34 mg  $\text{CH}_3\text{COONa}$ . The obtained mixture was sonicated by probe ultrasonic for 2 min. Then, 20 mL of  $\text{NaBH}_4$  0.15 M was slowly added into the mixture for 15 min. The reaction mixture was continuously stirred for 15 h before being washed with distilled water. The final product was dried by using a vacuum oven at  $80^\circ\text{C}$  for 2 h. The PG.N, PNG.N, and PASG.N catalysts were synthesized by the same method as above with the addition of corresponding precursors.

Transmission electron microscope (TEM) JEOL JEM 2010 and scanning electron microscope (SEM) in a S-4800 microscope (Hitachi, Japan) were used to investigate the morphology and microstructure of catalysts. A LabRam HR (Horiba Jobin Yvon) spectrometer was operated to record Raman spectra. A KRATOS Axis Ultra DLD spectrometer was applied to perform the XPS analyser. The ICP-OES analyses were performed after pretreatment of the samples, in an ICP-OES ACTIVA (Horiba Jobin Yvon). The infrared spectrum of the samples, in the wavelength range of  $400\text{--}4000 \text{ cm}^{-1}$ , was measured on a Tensor 27-Bruker FTIR spectrometer. XRD patterns of the catalysts were measured on a D8 Advance (Bruker) apparatus. The process of these measurement preparations was clearly presented in [22].

**2.3. Electrochemical Measurement.** Electrochemical measurements were performed on a PGS-ioc-HH12 Potentiostat/Galvanostat electrochemical workstation (Institute of Chemistry—Vietnam Academy of Science and Technology). All experiments were conducted in a three-electrode system at room temperature: a glassy carbon working electrode (whose diameter is 5 mm), a platinum counterelectrode, and an Ag/AgCl reference electrode. The procedure of preparing catalyst ink was similar to the one described in [22]. The catalyst ink was prepared by dispersing 2 mg of the catalyst powder in a mixture containing 0.9 mL ethanol and 0.1 mL Nafion solution 5 wt % under sonication for 30 min.

Electrochemical active surface area (EASA) measurements were carried out in 0.5 M NaOH aqueous solutions at a scan rate of  $50 \text{ mV}\cdot\text{s}^{-1}$ , in the potential range of  $-0.8 \text{ V}$  to  $0.5 \text{ V}$ .

Cyclic voltammetry was carried out in (NaOH 0.5 M +  $\text{C}_2\text{H}_5\text{OH}$  1 M) aqueous solutions at a scan rate of  $50 \text{ mV}\cdot\text{s}^{-1}$ , in the potential range of  $-0.8 \text{ V}$  to  $0.5 \text{ V}$ . The chronoamperometric curves for the catalysts were recorded in a (NaOH 0.5 M +  $\text{C}_2\text{H}_5\text{OH}$  1 M) solution at a constant potential value of  $-0.25 \text{ V}$  (vs. Ag/AgCl) for 4000 s.

### 3. Results and Discussion

Cyclic voltammograms and chronoamperometry curves in a (NaOH 0.5 M +  $\text{C}_2\text{H}_5\text{OH}$  1 M) solution at a room temperature for ethanol electrooxidation on Pd/rGO-based catalysts modified by different metals in ethylene glycol environment were introduced in Figure 1 and Table 1.

From the catalytic activity evaluation results for catalysts reduced by EG during synthesis, Pd-based catalyst that is nonmodified (PG.E) clearly showed a lower electrooxidation activity of ethanol than Pd-based catalyst modified by metal (see Figure 1(a)). Specifically, in alkaline medium, the activity of the catalysts is in ascending order as follows: PG.E ( $5369 \text{ mA}\cdot\text{mg}^{-1}_{\text{Pd}}$ ) < PAG.E ( $5374 \text{ mA}\cdot\text{mg}^{-1}_{\text{Pd}}$ )  $\approx$  PSG.E ( $5574 \text{ mA}\cdot\text{mg}^{-1}_{\text{Pd}}$ ) < PASG.E ( $7822 \text{ mA}\cdot\text{mg}^{-1}_{\text{Pd}}$ ) (see Table 1).

On the other side, the forward scanning peak current density (or called anodic current density)— $I_F$ —means current density of ethanol electrooxidation on the electrode surface. And, the reverse scanning peak current density (or called cathodic current density) means current density in reduction of the oxygen group on the electrode surface. If  $I_F/I_R$  ratio and  $I_F$  are higher, ethanol electrooxidation on electrode surface will happen more completely [24–27]. Therefore, in alkaline medium, the Pd-based catalysts modified by monometallic such as Al and Si showed only a slight improvement of catalytic activity in comparison with PG.E (see Table 1). Meanwhile, the one modified by bimetallic Al-Si (PASG.E) showed a significant increase in activity, which indicates a positive synergistic effect with Pd of two metals.

Some intermediate species such as  $\text{CHO}_{\text{ads}}$  and  $\text{CO}_{\text{ads}}$  formed during the ethanol electrooxidation poisoned the catalysts, which explained why all catalysts display an initial fast current decay in the chronoamperometry test (see Figure 1(b)). It is noted that the PASG.E catalyst exhibited better activity and resistance against poisoning by intermediate compounds in comparison with other catalysts reduced by EG during synthesis. After 4000 s of working, the current density of the PASG.E catalyst was  $104.4 \text{ mA}\cdot\text{mg}^{-1}_{\text{Pd}}$ , significantly higher than that of PG.E catalysts ( $21.6 \text{ mA}\cdot\text{mg}^{-1}_{\text{Pd}}$ ), PAG.E ( $48.1 \text{ mA}\cdot\text{mg}^{-1}_{\text{Pd}}$ ), and PSG.E ( $34.35 \text{ mA}\cdot\text{mg}^{-1}_{\text{Pd}}$ ). These remarkable results may be explained by the presence of pseudoboehmite ( $\text{AlOOH}$ ) and silica ( $\text{SiO}_2$ ) that preferentially prevented the adsorption of toxic intermediate and/or formed products on the surface of catalyst, leading to the increase in the number of available catalytic site for reactants.

Thus, the addition of the metal as promoter phase in general, and the bimetallic phase Al-Si in particular, increased the electrochemical activity and also significantly improved resistance against poisoning of intermediate compounds of Pd/rGO catalysts reduced by EG agent.

The content of noble metals and other elements in the catalysts was determined by the ICP-OES characterization and shown in Table 2. It is interesting to note that the mass fraction of Pd found in most catalysts is approximately 10%, compared to the theoretical value of Pd ranging from 25% to 28%. The mass fraction of other metals was measured from 0.2% to 2.7%. The Pd loading of the catalysts reduced by  $\text{NaBH}_4$  is higher than that reduced by EG. Especially, the ICP-OES measurement showed the presence of Na in all catalysts reduced by  $\text{NaBH}_4$ .

The valence state and surface composition of PASG.N catalyst were determined by X-ray photoelectron spectroscopy (XPS) measurements (see Figure 2). Figure 2(a) presents the XPS spectrum included the characteristic peaks of C 1s, O 1s, Al 2s, Al 2p, Si 2s, and Si 2p. Accordingly, Al and Si existing at the Al and Si compounds obtained in the catalysts exist as pseudoboehmite ( $\text{AlOOH}$ ) and amorphous silica ( $\text{SiO}_2$ ) [22]. In addition, a characteristic peak of Pd 3d is also observed on the spectrum. Especially, the random appearance of Na 1s and Na KLL that corresponds with the ICP results may be an important factor to augment activity of PASG.N catalyst.

Moreover, an intense peak of the C 1s core level was observed in the XPS spectrum of rGO (see Figure 2(c)). After the deconvolution, two major peaks were identified and assigned as  $\text{sp}^2 \text{ C}=\text{C}$  at 284.4 eV (due to the graphitic carbon),  $\text{sp}^3 \text{ C}-\text{O}$  at 285.8 eV and 289.4 eV (due to the hydroxyl and epoxy groups with graphene framework) [28].

Figure 2(b) shows the Pd 3d core level XPS spectrum of PASG.N catalyst which is resolved into  $3d_{5/2}$  and  $3d_{3/2}$  doublets caused by spin-orbital coupling [28]. The Pd 3d signals for catalysts can be deconvoluted into two pairs of doublets, which can be attributed to metallic Pd (0) and Pd (II). The deconvolution energies for Pd (0) and Pd (II) were at 335.7 and 340.9 eV, and 336.7 eV and 342.6 eV, respectively. Metallic Pd phase was proved to be the major contribution as the intensities of Pd (II) were quite lower than those of Pd (0). It means that reducing from Pd (II) to Pd (0) reaction has happened successfully.

Besides, the relative signal intensities of Pd (0) and Pd (II) of PASG.N catalyst were different, 53.56% and 37.81%, respectively. In addition, the Pd weight density on the catalyst surface was 8.23%, while that of Al, Si, and Na was 2.38%, 3.44%, and 2.19%, respectively, which are similar to ICP results. It means that Pd nanoparticles were dispersed evenly both inside and outside of the catalyst. Moreover, the ratio between Pd (0) and Pd (II) PASG.N in XPS result of PASG.N, approximately 1.41, is higher than that of PASG.E, approximately 1.01. This may be a cause of the different electrochemical activity of these catalysts.

In fact, when the agent  $\text{NaBH}_4$  was used instead of EG, the catalyst presented more catalytic activity and resistance against poisoning of intermediate compounds. Specifically, with the bimetallic Al-Si promoter phase, catalyst reduced by

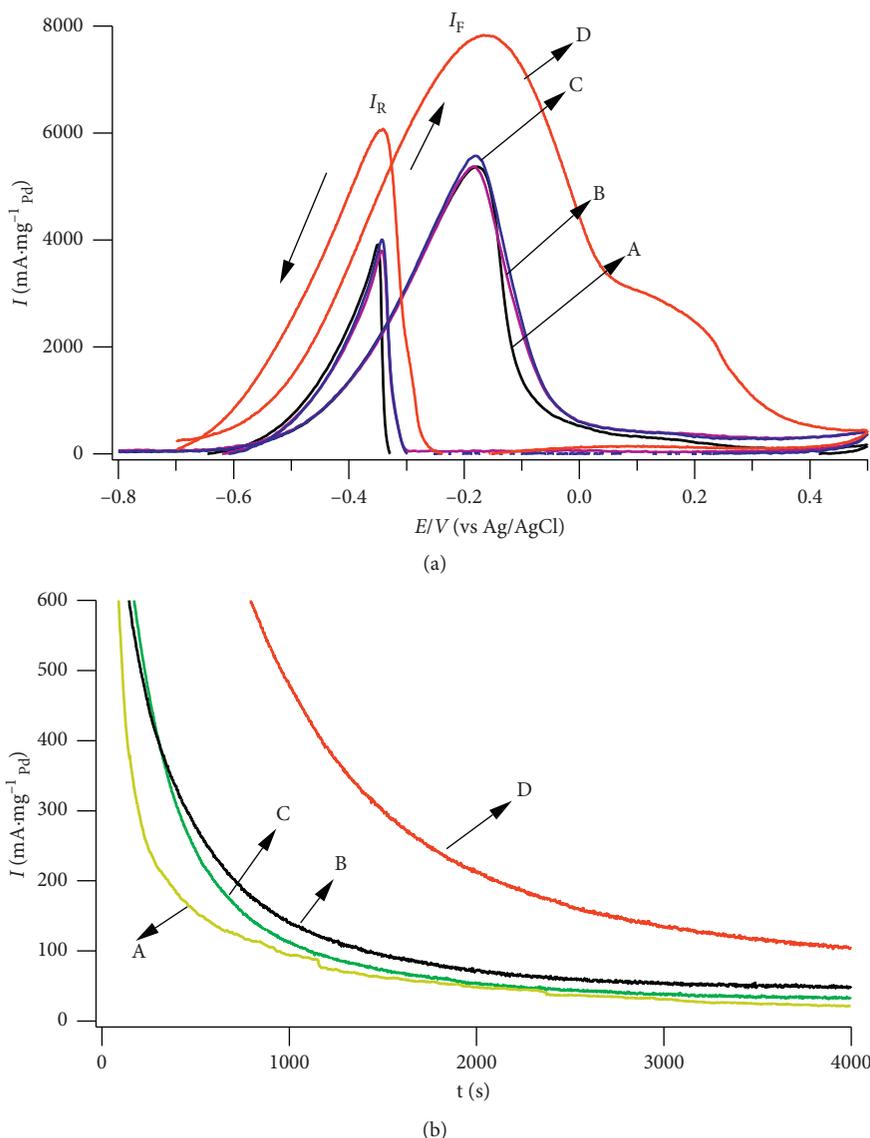


FIGURE 1: CV (a) and CA curves (b) of (A) PGE, (B) PAGE, (C) PSGE, and (D) PASGE catalysts in a (NaOH 0.5 M + C<sub>2</sub>H<sub>5</sub>OH 1 M) solution at a scan rate of 50 mV·s<sup>-1</sup>.

TABLE 1: CV results of Pd/rGO-based catalysts after 15 scanning cycles in a (NaOH 0.5 M + C<sub>2</sub>H<sub>5</sub>OH 1 M) solution at a scan rate of 50 mV·s<sup>-1</sup>.

Catalyst	$I_F$ (mA·mg <sup>-1</sup> Pd)	$I_R$ (mA·mg <sup>-1</sup> Pd)	$I_F/I_R$
PGE	5369	3915	1.37
PAGE	5374	3799	1.41
PSGE	5574	4010	1.39
PNGE	6988	5273	1.33
PASGE	7822	6111	1.28
PASNGE	8800	4367	2.02
PG.N	7457	3967	1.88
PNG.N	8357	4687	1.78
PASG.N	10705	5531	1.94
PASGN.N	16138	7949	2.03

NaBH<sub>4</sub> (PASG.N) showed 1.4 times higher activity than by EG (PASGE) (see Table 1). In addition, after 4000 s of working, the current density of the PASG.N catalyst was 6.5

times higher than that of PASGE. Furthermore, both electrochemical activity and the ratio of the forward scanning peak current density to the reverse scanning peak current density, ( $I_F/I_R$ ) of the PASG.N catalyst (1.93), were also higher than those of the PASGE catalyst (1.28). Consequently, NaBH<sub>4</sub> could be a better agent for Pd-based catalyst reduction than EG.

Na presence may cause increasing adsorption of oxygen and fuel on surface of the catalyst [29], which brings out increase of catalytic activity. To evaluate the role of Na, the electrochemical activity of catalysts with and without addition of Na during synthesis for both EG and NaBH<sub>4</sub> reducing agents was investigated (see Figure 3(a) and Table 1). It is obvious that whatever reducing agents were used during synthesis (EG or NaBH<sub>4</sub>), all Na-doped catalysts showed significantly higher electrocatalytic activity compared with the non-Na-doped catalysts. Therefore, the role of promoter of Na was completely independent of the effect of the

TABLE 2: ICP-OES results of Pd/rGO-based catalysts reduced by EG and NaBH<sub>4</sub>.

Catalysts	Elemental mass fraction by ICP-OES measurement		Theoretical elemental mass fraction	
	Pd (%)	Other metal (%)	Pd (%)	Other metals (%)
PG.E	8.53	—	28.57	—
PNG.E	7.51	2.52 (Na)	26.40	7.61 (Na)
PAG.E	8.03	2.33 (Al)	26.40	7.61 (Al)
PSG.E	7.86	2.54 (Si)	26.40	7.61 (Si)
PASG.E	8.34	0.34 (Al); 2.15 (Si)	27.20	1.36 (Al); 3.42 (Si)
PASGN.E	7.57	2.40 (Na); 0.27 (Al); 2.30 (Si)	25.23	7.25 (Na); 1.26 (Al); 3.15 (Si)
PG.N	9.71	0.15 (Na)	28.57	—
PNG.N	9.21	2.72 (Na)	26.40	7.61 (Na)
PASG.N	8.78	0.34 (Al); 2.41 (Si); 0.12 (Na)	27.20	1.36 (Al); 3.42 (Si)
PASGN.N	8.54	2.62 (Na); 0.29 (Al); 1.83 (Si)	25.23	7.25 (Na); 1.26 (Al); 3.15 (Si)

reducing agent on the electrooxidation of ethanol. Moreover, the results obtained are also consistent with previous conclusions: catalysts modified by the Al-Si system owned a superior activity in comparison with Pd/rGO catalysts and catalysts reduced by NaBH<sub>4</sub>, whose activities are much higher than those reduced by EG.

Besides, the poisoning resistance capacity of these catalysts in the electrochemical ethanol oxidation in alkaline mediums estimated by chronoamperometry (CA) (see Figure 3(b)) provided the same results. After 4000 s of working, the PASGN.N catalytic current density reached 680 mA·mg<sup>-1</sup><sub>Pd</sub> ( $I_F^{4000} \sim 32.27\%$  compared with the value of CA- $I_F^0$  at the beginning), 2.36 times higher than non-Na-doped PASG.N catalyst ( $I_F^{4000} \sim 17.85\% \cdot I_F^0$ ), and 6.1 times higher than Na-doped PASNG.E reduced by EG ( $I_F^{4000} \sim 15.64\% \cdot I_F^0$ ). Consequently, Na presence may assist the Pd-base catalysts in enhancing the resistance against poisoning of intermediate compounds in ethanol electrooxidation in alkaline media.

Figure 4 presents Raman spectra of GO and PASG.N catalyst. The peak intensities of the G band ( $I_G$ ) at  $\sim 1600$  cm<sup>-1</sup> corresponding to the sp<sup>2</sup>-hybrid carbon state in the hexagonal lattice of graphite and the D band ( $I_D$ ) at 1350 cm<sup>-1</sup> being characteristic for the vibration of sp<sup>3</sup>-hybrid C in the disorder structure of graphene sheets are clearly presented in [22]. The Raman spectra of catalysts were also similar to those of GO, but the intensity of  $I_D/I_G$  ratio of catalyst increased in the following order: GO (0.92) < PASG.N (1.02) < PASGN.N (1.10) < PASG.E (1.98). In addition,  $I_D > I_G$  due to the presence of defects as well as the presence of Pd cluster, of metal or metal oxides on the graphene support [20, 30, 31]. This confirmed that the catalyst synthesis using chemical reduction process removes effectively the functional groups containing oxygen on the GO surface to form rGO.

FT-IR spectra of catalysts are shown in Figure 5. In the infrared spectra of graphene oxide, there are some

characteristic vibration bands containing oxygen groups such as O-H near 3500 cm<sup>-1</sup> and around 1400 cm<sup>-1</sup>, C=O at 1760 cm<sup>-1</sup>, and C-O around 1100 cm<sup>-1</sup>, respectively. However, in that of PASGN.N catalyst, intensity of these peaks was reduced clearly. Moreover, the presence of C=C bond near 1600 cm<sup>-1</sup> was found out in the catalyst. Consequently, the reduction from GO to rGO was successful.

TEM images of the catalysts are introduced in Figure 6. The average particles size  $d_n$  was calculated from particle size distribution using the following equation [32]:

$$d_n = \frac{\sum n_k d_k}{\sum n_k}, \quad (1)$$

where  $n_k$  is the frequency of occurrence of particles with size  $d_k$  from the TEM images.

The result showed that a less uniform and sparse dispersion of metallic nanoparticles are described for the catalysts. In addition, the PASG catalysts reduced by both EG and NaBH<sub>4</sub> have a quite homogenous dispersion of active phase (dark spherical particles on rGO surface), but their sizes are different. For example, the PASG.N and PASGN.N catalysts (reduced by NaBH<sub>4</sub>) have their activity particle size from 7 nm to 14 nm, while that of PASG.E catalyst (reduced by ethylene glycol) was three times larger, about 20 nm to 36 nm. It means that reducing agent NaBH<sub>4</sub> is improving the size of the catalytic active phase particle. Furthermore, TEM images of the PASGN.N (Na-doped) (see Figure 6(c)) and PASG.N (non-Na-doped) (see Figure 6(b)) catalyst introduced that Na-doped significantly enhanced the dispersion of metallic nanoparticles on graphene support surface. The metal nanoparticles of PASGN.N catalysts expanded with higher density than those of PASG.N catalyst, which explained the increase in the number of active sites on the surface of graphene support, considerably enhancing the catalytic activity of electrooxidation of ethanol. Moreover, the metal

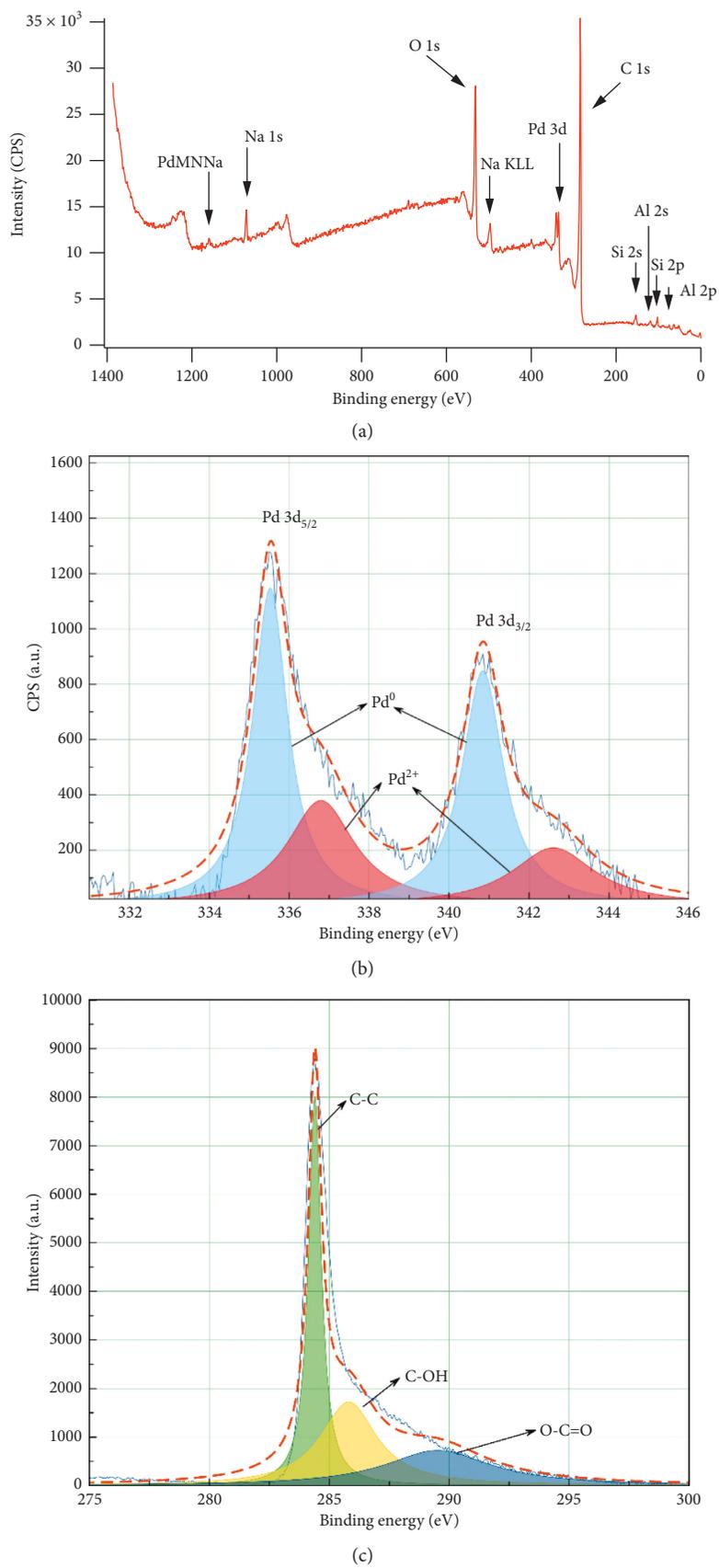


FIGURE 2: XPS spectrum (a), Pd 3d spectrum (b), and C 1s spectrum of the PASG.N catalyst (c).

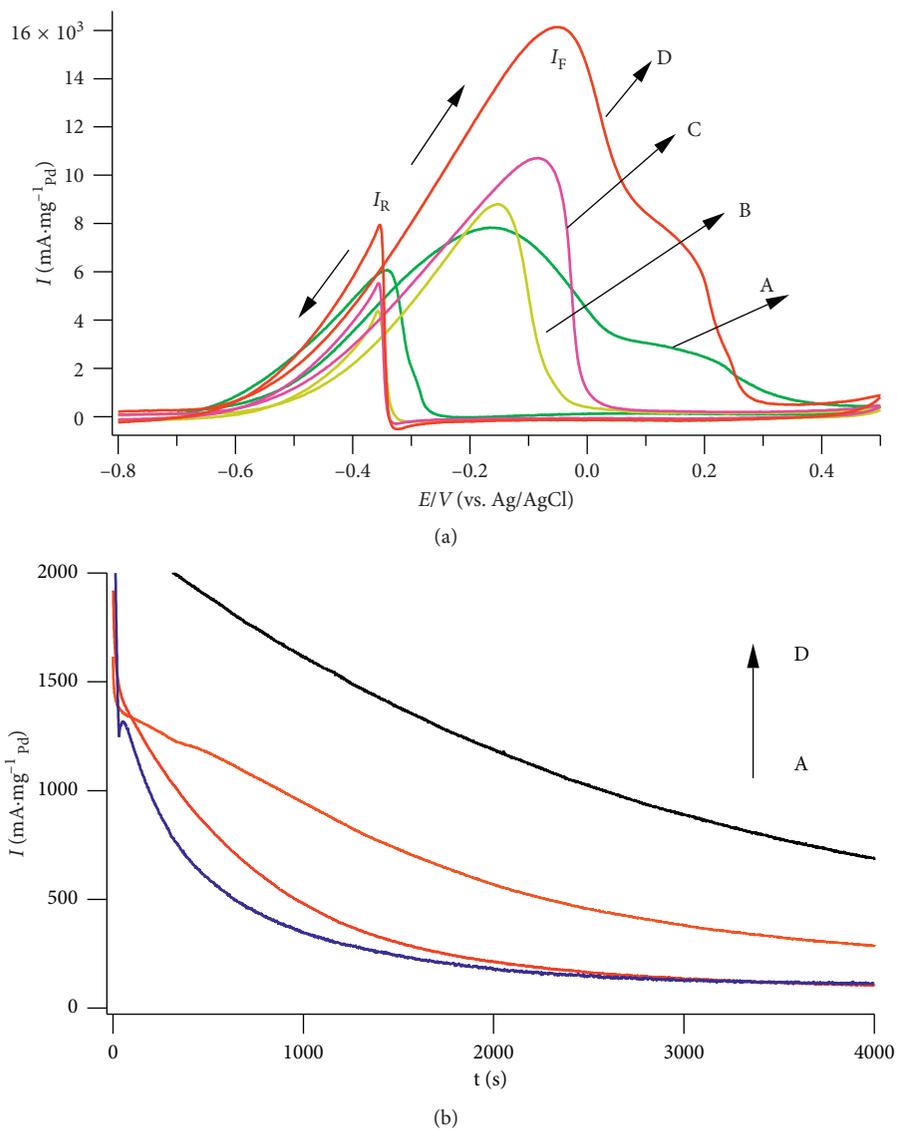


FIGURE 3: CV (a) and CA (b) curves of (A) PASG.E, (B) PASG.N.E, (C) PASG.N, and (D) PASG.N.N catalysts in a (NaOH 0.5 M + C<sub>2</sub>H<sub>5</sub>OH 1 M) solution at a scan rate of 50 mV·s<sup>-1</sup>.

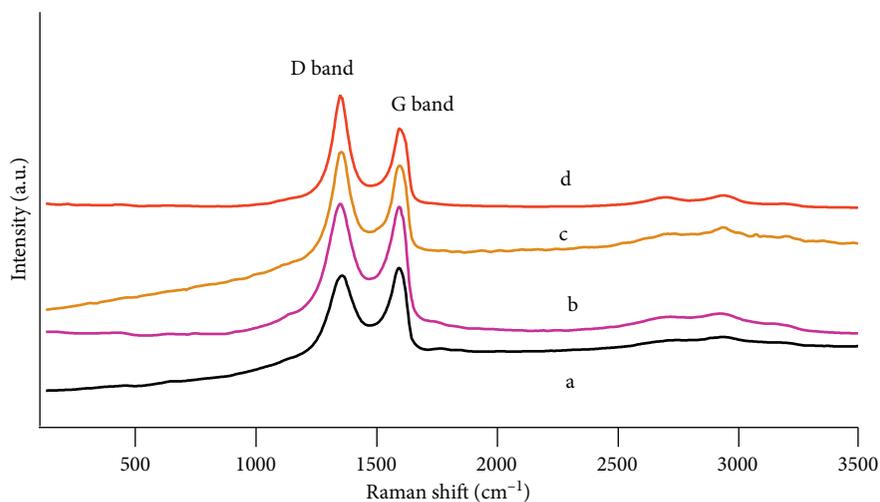


FIGURE 4: Raman spectra of (a) GO, (b) PASG.N, (c) PASG.N.N, and (d) PASG.E.

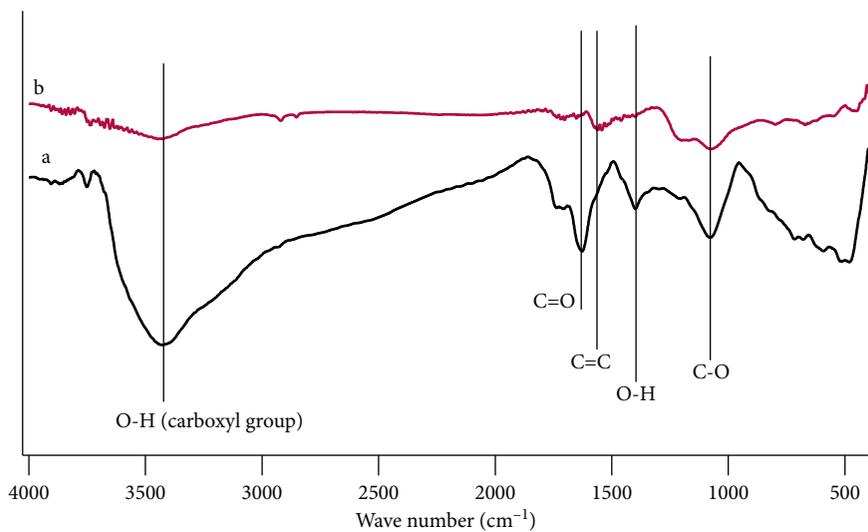


FIGURE 5: FTIR spectra of (a) GO and (b) PASGN.N.

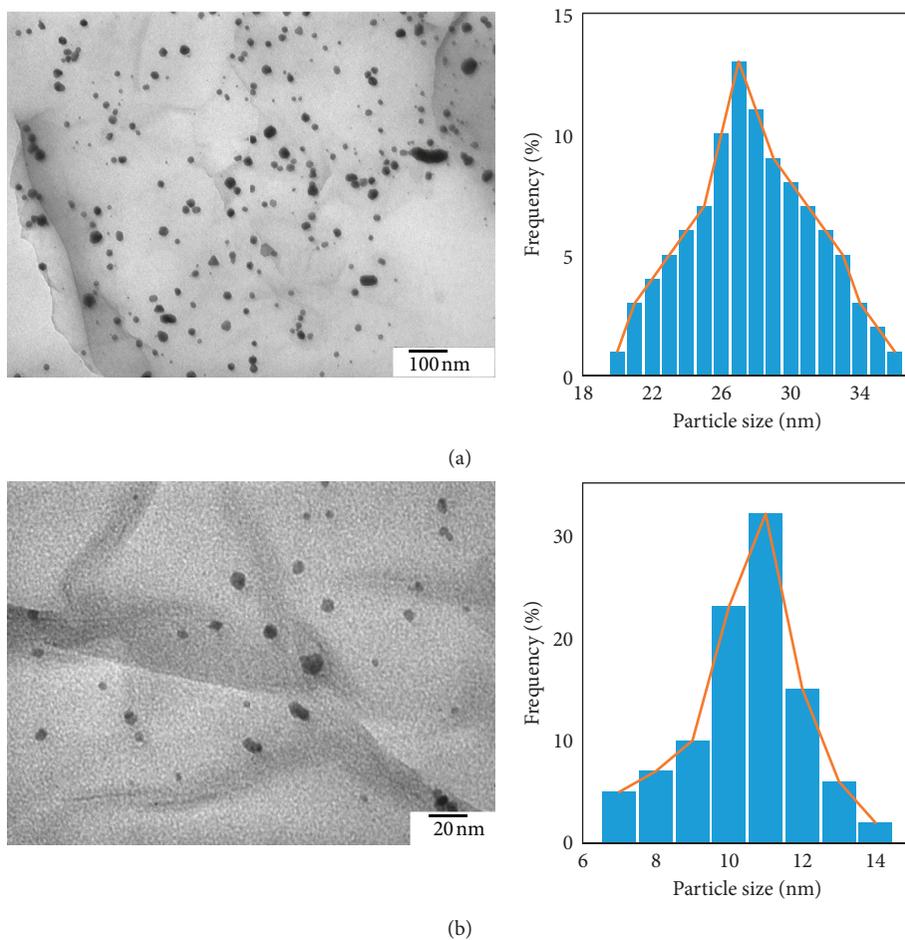


FIGURE 6: Continued.

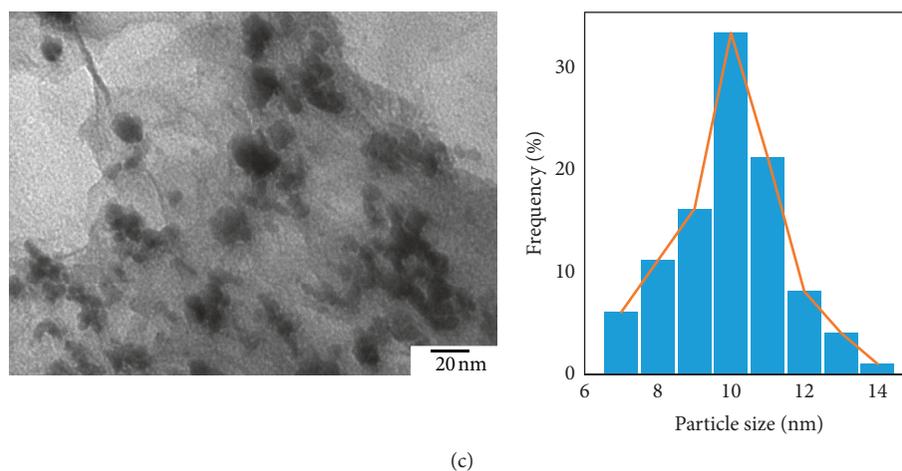


FIGURE 6: TEM images and particle size distributions of PASG.E (a), PASG.N (b), and PASGN.N (c) catalysts with different magnifications.

nanoparticles in the PASGN.N catalyst tend to aggregate from 2 to 3 particles to form larger ones at the edges of graphene sheets.

The EASA (electrochemical active surface area) of the Pd-based electrodes is determined by estimating the charge used in the reduction of palladium (II) oxide into palladium metal and using relation:  $EASA = Q/S$ , where  $Q$  is the Coulombic charge (in mC) and  $S$  is the proportionality constant which is taken  $0.405 \text{ mC}\cdot\text{cm}^{-2}$  in the case of reduction of a monolayer of PdO [4]. Average particles size  $d_n$  and EASA are present in Table 3.

In fact, EASA of catalysts were in descending order as follows:  $PASG.E (150.2 \text{ m}^2\cdot\text{g}^{-1}_{Pd}) < PASG.N (193.7 \text{ m}^2\cdot\text{g}^{-1}_{Pd}) < PASGN.N (207.6 \text{ m}^2\cdot\text{g}^{-1}_{Pd})$ . This affection is similar to the TEM image described in Figure 6. The particles size is higher, the activity surface is lower [33].

On the other hand, the Na addition also improved stability of Pb-based catalyst in ethanol electrooxidation. In order to study the catalytic lifetime of PASGN.N and PASG.N catalyst in alkaline medium, 500 cycles of a successive sweep from  $-0.8 \text{ V}$  to  $0.5 \text{ V}$  were carried out. The corresponding electrochemical activity results were noted in Table 4. The CV curve of the scanning cycles of PASGN.N catalyst was exhibited by the forward scanning peak current density in Figure 7. After the first 15 cycles to activate the catalysts, electrochemical activity of PASGN.N catalyst became stable. Therefore, the highest peak current density of the 15<sup>th</sup> cycle ( $I_F 15^{\text{th}}$ ) was chosen as a reference. After 200 cycles, the electrochemical activity of the catalysts decreased quite slowly where  $I_F 200^{\text{th}}$  was equal to 84% of the reference. The slow reactivity holds up to 500 cycles, where the forward current density value  $I_F 500^{\text{th}}$  was equal to 68% of the reference. Similarly, the electrochemical activity of PASG.N also decreased as the number of sweep rounds increased. However, the rate of decreasing catalytic activity of PASG.N is faster than that of PASGN.N (see Table 4), where its 500<sup>th</sup> current density remained 27%.

Besides, the combination between active phase (Pd nanoparticles) and support, graphene can become more

TABLE 3: EASA result of catalyst.

Catalyst	Average particles size (nm)	EASA ( $\text{m}^2\cdot\text{g}^{-1}_{Pd}$ )
PASG.E	28.07	150.2
PASG.N	10.49	193.7
PASGN.N	9.97	207.6

sustainable under the presence of Al-Si-Na addition, which is observed on TEM images of the catalysts after 500 scanning cycles (see Figure 8). For instance, in case of PASGN.N, the metal particles tend to aggregate into clusters of very large size, from 60 nm to 130 nm, which dispersed in separate zones. The density of metallic nanoparticles on the graphene surface is also considerably reduced while that at the edges of graphene sheets tends to increase. However, in case of PASG.N catalyst, almost no metallic particles are presented on the surface of the graphene after 500 scanning cycles. This result is in accordance with the catalytic deactivation after 500 scanning cycles as described previously.

The morphology characteristic of PASGN.N catalyst before and after 500 scanning cycles were observed more clearly on the SEM image (see Figure 9). The result showed that the catalyst looked as a homogeneous “block;” however, it was broken to pieces after the reaction. Moreover, Figure 9(b) also shows the number of particles with columnar shape. It seems that the active phase Pd may be separated from support and may agglomerate after hundreds of cycles. As a result, catalytic activity was reduced.

Figure 10 presented XRD patterns of PASGN.N catalyst before and after 500 cycles of the reaction. The peak at  $2\theta$  value of  $40.1^\circ$  corresponding to the planes Pd (111) [34, 35] was shown in the pattern of catalyst before the reaction (see Figure 10(a)) while two peaks of planes PdO (110) and PdO (103) [35] were introduced in the catalyst after the reaction. Consequently, PdO crystal is forming during the reaction. This may be a cause of reduction of the catalytic activity.

TABLE 4: Forward current density of PASGN.N and PASG.N catalysts after 500 scanning cycles in a (NaOH 0.5 M + C<sub>2</sub>H<sub>5</sub>OH 1 M) solution at a scan rate of 50 mV·s<sup>-1</sup>.

Catalyst	Forward current density $I_F$ (mA·mg <sup>-1</sup> <sub>Pd</sub> )							
	$I_F$ 15 <sup>th</sup>	$I_F$ 100 <sup>th</sup>	$I_F$ 100 <sup>th</sup> / $I_F$ 15 <sup>th</sup>	$I_F$ 200 <sup>th</sup>	$I_F$ 300 <sup>th</sup>	$I_F$ 400 <sup>th</sup>	$I_F$ 500 <sup>th</sup>	$I_F$ 500 <sup>th</sup> / $I_F$ 15 <sup>th</sup>
PASGN.N	16138	14175	0.88	13816	12751	12342	10864	0.68
PASG.N	10705	9100	0.85	8565	6884	4956	2884	0.27

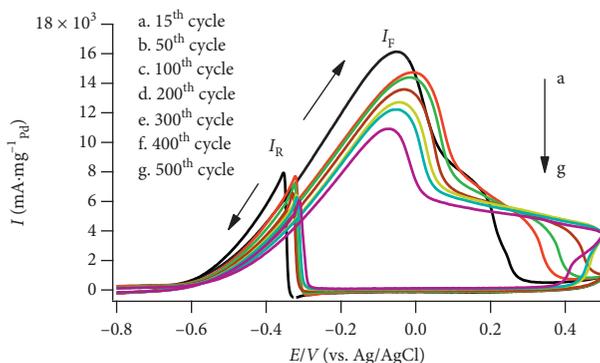


FIGURE 7: CV curves of catalytic PASGN.N after 500 scanning cycles in a (NaOH 0.5 M + C<sub>2</sub>H<sub>5</sub>OH 1 M) solution at a scan rate of 50 mV·s<sup>-1</sup>.

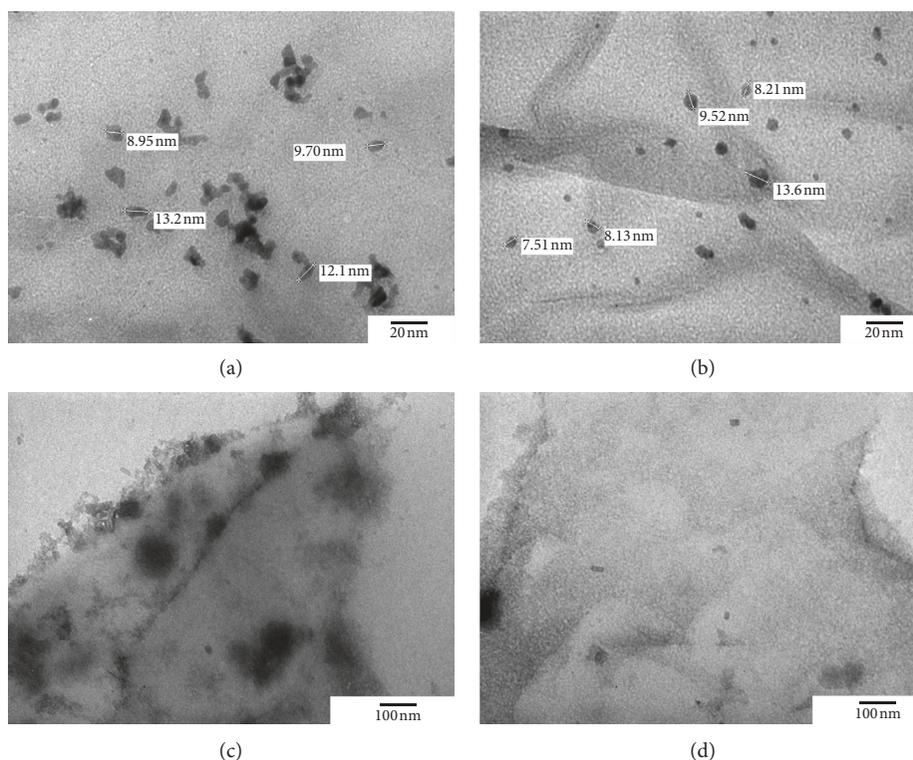


FIGURE 8: TEM images of PASGN.N and PASG.N catalysts before (a, b) and after 500 scanning cycles (c, d) in a (NaOH 0.5 M + C<sub>2</sub>H<sub>5</sub>OH 1 M) solution at a scan rate of 50 mV·s<sup>-1</sup>.

#### 4. Conclusion

In conclusion, electrooxidation of ethanol was carried out on several Pd-based bimetallic or multimetallic catalysts

supported on graphene. For all catalysts investigated, the role of promoting agents was confirmed when catalytic activity was enhanced in the presence of Al, Si, Al-Si, and Al-Si-Na. In addition, in comparison with the reducing

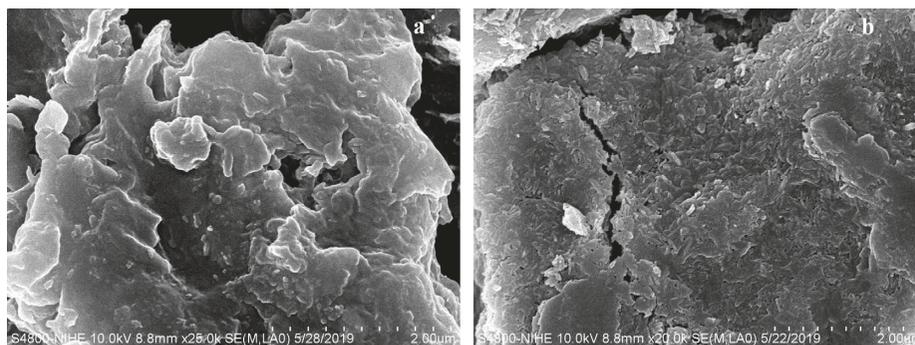


FIGURE 9: SEM images of PASGN.N catalysts before (a) and after (b) 500 scanning cycles in a (NaOH 0.5 M + C<sub>2</sub>H<sub>5</sub>OH 1 M) solution at a scan rate of 50 mV·s<sup>-1</sup>.

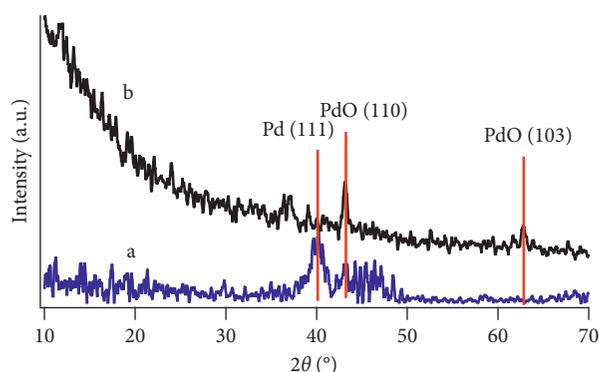


FIGURE 10: XRD patterns of PASGN.N catalysts before (a) and after (b) 500 scanning cycles in a (NaOH 0.5 M + C<sub>2</sub>H<sub>5</sub>OH 1 M) solution at a scan rate of 50 mV·s<sup>-1</sup>.

agent EG during synthesis, NaBH<sub>4</sub> significantly not only improved the dispersion of metal nanoparticles on the support surface but also reduced crystalline size. As a result, catalytic electrochemical activity was increased. Specifically, PASGN.N catalysts presented the superior activity in electrooxidation of ethanol in the alkaline medium when the current density was more than 16000 mA·mg<sup>-1</sup><sub>Pd</sub>, which is the best results reported in this study. This value is higher than activity of Pd-based catalyst with different promoter [20, 36] or activity of Pt-base catalyst [37] with the same promoter. Another result in this particle is that the electrochemical stability of PASGN.N catalyst was relatively good: after 500 scanning cycles, the current density diminished 32% compared with the highest peak current density of the 15<sup>th</sup> cycle. In conclusion, the obtained results have opened a new studying direction about synergistic effects of Al-Si-Na addition which both enhances activity and improves stability of Pd-based catalysts in ethanol electrooxidation in alkaline medium. In the same way, the content of noble metal is also reduced.

## Symbols

$d_k$ :	Particle size
$d_n$ :	Average particle size

EASA:	Electrochemical active surface area
FT-IR:	Fourier transform infrared
ICP-OES:	Inductively coupled plasma-optical emission spectrometry
$I_D$ :	Peak intensity of the D band in Raman spectra/cm <sup>-1</sup>
$I_F$ :	Forward scanning peak current density in cyclic voltammetry curves/mA·mg <sup>-1</sup> <sub>Pd</sub>
$I_F$ 15 <sup>th</sup> :	Highest peak current density of the 15 <sup>th</sup> cycle in cyclic voltammetry curves/mA·mg <sup>-1</sup> <sub>Pd</sub>
$I_F$ 200 <sup>th</sup> :	Peak current density of the 200 <sup>th</sup> cycle in cyclic voltammetry curves/mA·mg <sup>-1</sup> <sub>Pd</sub>
$I_F$ 500 <sup>th</sup> :	Peak current density of the 500 <sup>th</sup> cycle in cyclic voltammetry curves/mA·mg <sup>-1</sup> <sub>Pd</sub>
$I_F^0$ :	Catalytic current density at the beginning in chronoamperometry curves/mA·mg <sup>-1</sup> <sub>Pd</sub>
$I_F^{4000s}$ :	Catalytic current density in chronoamperometry curves/mA·mg <sup>-1</sup> <sub>Pd</sub>
$I_G$ :	Peak intensity of the G band in Raman spectra/cm <sup>-1</sup>
$I_R$ :	Reverse scanning peak current density in cyclic voltammetry curves/mA·mg <sup>-1</sup> <sub>Pd</sub>
$n_k$ :	Frequency of occurrence of particles
Q:	Coulombic charge used in the reduction of palladium (II) oxide into palladium metal/mC
S:	Proportionality constant in the case of reduction of a monolayer of PdO/mC·cm <sup>-2</sup>
SEM:	Scanning electron microscope
TEM:	Transmission electron microscope
XPS:	X-ray photoelectron spectroscopy
XRD:	X-ray diffraction.

## Data Availability

The data used in the study are available from the corresponding authors upon request.

## Additional Points

**Highlights.** Nanocatalysts based on Pd/rGO were synthesized for the electro-oxidation of ethanol in alkaline medium. The random presence of Na was found out when reduced agent NaBH<sub>4</sub> was used instead of EG. Al-Si-Na addition enhances the

activity of Pd-base catalyst and improves its electrochemical stability after 500 scanning cycles. Al-Si-Na addition improves dispersion and combination of the active phase Pd on reduced graphene oxide surface. NaBH<sub>4</sub>-reducing PdAlSiNa/rGO has the highest electrocatalytic activity, 16138 mA·mg<sub>Pd</sub><sup>-1</sup>.

## Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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## Research Article

# Enhanced Photocatalytic Degradation of Rhodamine B Using C/Fe Co-Doped Titanium Dioxide Coated on Activated Carbon

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Carbon and iron co-doped titanium dioxide catalyst coated on activated carbon (Fe-C-TiO<sub>2</sub>/AC) was successfully synthesized using the sol-gel method, followed by hydrothermal treatment. Commercial activated carbon was treated by HNO<sub>3</sub> prior to being coated by the as-synthesized catalyst. The composite was characterized by XPS, XRD, UV-Vis spectrophotometry, IR, TEM, HR-TEM, and BET. The performance of the supported catalysts was evaluated in the degradation of rhodamine B (RhB) in the solution under visible-light irradiation. The results showed that, with the appropriate amount of activated carbon, prepared Fe-C-TiO<sub>2</sub>/AC catalysts exhibited higher catalytic activities and Fe-C-TiO<sub>2</sub>/AC system showed the best performance. The photocatalytic degradation efficiency of Fe-C-TiO<sub>2</sub>/AC was enhanced due to the synergistic effect between AC (adsorption effect) and Fe-C-TiO<sub>2</sub> (photocatalysis effect). This facilitated the photocatalytic degradation of RhB by Fe-C-TiO<sub>2</sub>.

## 1. Introduction

TiO<sub>2</sub> photocatalyst has been widely used in the wastewater treatment and other environmental remediation because of its high efficiency, nontoxicity, propitious recycle ability, and low cost. Besides, the final products of the photocatalysis in the advanced oxidation process are CO<sub>2</sub>, H<sub>2</sub>O, inorganic ions, and minerals that usually have insignificant impacts on environments [1, 2]. However, the application of TiO<sub>2</sub> is limited because the TiO<sub>2</sub> with band gap ~3.2 eV is only activated under UV radiation and it is difficult to recycle. Therefore, modification of catalyst is crucial to enhance its photocatalytic activity. To present, catalytic efficiency of TiO<sub>2</sub> was significantly improved by being doped with metals such as V, Cr, W, and Fe or with metal oxides like ZnO, CuO, and so on for expanding the absorption edge to the visible region [3–6]. Among these metals, TiO<sub>2</sub> doped with Fe is in progress because Fe can replace the positions of Ti<sup>4+</sup> in the crystalline, reducing the band gap energy, which is conducive to the activation in the visible light [3, 4, 7].

Moreover, Fe ions act as traps to incarcerate electrons and hinder the recombination of electron/hole pairs, resulting in the increase in catalysts' performance. In addition, the addition of some nonmetal elements such as N, C, S, P, and halogens into TiO<sub>2</sub> structure can also narrow the band gap of TiO<sub>2</sub>, reinforcing the photocatalytic activity of the catalyst [2, 8]. Some research reported that transition metals/(N, C, S) co-doped into TiO<sub>2</sub> would greatly facilitate the photocatalytic performance of the corresponding catalysts under visible irradiation conditions, which was attributed to the synergistic effects between the doped C and N atoms and lower band gap energy [1, 3]. TiO<sub>2</sub>-based photocatalysts are usually employed either as slurry or on support. In slurry condition, a big challenge lies in the separation and recovery of the small-sized particles after treatment of pollutants, which limits the application of the photocatalyst in real conditions. The utilization of support immobilization such as glass fibers, glass beads, or steel has also been employed. However, they have issue due to adhesion force between the photocatalyst surface and the support [9]. Recently, there are increasing interests in

a synergetic approach. Different materials are usually designed to provide a high surface area to support the catalyst [8, 10]. These materials share some common characteristics: binding to the catalyst, nondestroying catalyst, high surface area, and high affinity to the adsorption of pollutant molecules [10]. Activated carbon is one of the cost-effective synergist with not only clutching the photo-agents and free radicals ( $\text{HO}^\bullet$ ) but also adsorbing pollutant molecules on the photochemical centers of the catalyst apart from its mechanical stability [10]. There are surprisingly quite a few papers using this method, and there is no published work on C/Fe co-doped titanium dioxide coated on activated carbon that is reported in this manuscript. Hence, in the present work,  $\text{TiO}_2$  co-doped iron and carbon coated on activated carbon that was treated by  $\text{HNO}_3$  was prepared by sol-gel followed by solvothermal method. The characterization of the catalyst was conducted by X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), infrared spectroscopy (IR), transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HR-TEM), ultraviolet-visible (UV-Vis) spectroscopy, and Brunauer–Emmett–Teller (BET) surface area measurement. The catalytic activity of the catalyst was examined by the degradation of RhB dye.

## 2. Experimental

### 2.1. Catalyst Preparation

**2.1.1. Chemicals.** TIOT (tetraisopropyl orthotitanate 98%), nitric acid ( $\text{HNO}_3$  68%), ethyl alcohol ( $\text{C}_2\text{H}_5\text{OH}$  99.7%), iron (III) nitrate ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  pure), and rhodamine B ( $\text{C}_{28}\text{H}_{31}\text{ClN}_2\text{O}_3$ ) were purchased from Sigma-Aldrich. Activated carbon Tra Bac (AC—particle sizes from 0.075 mm to 4.75 mm, surface area BET 928  $\text{m}^2/\text{g}$ ) was obtained with the aid of a TriStar 3000 V6.07 A.

### 2.1.2. Preparation of Fe-C-TiO<sub>2</sub> Coated on Activated Carbon Pretreated by HNO<sub>3</sub> (Fe-C-TiO<sub>2</sub>/AC)

- (i) Treatment of carbon with  $\text{HNO}_3$ : The coal is ground to a fine powder 0.16 mm before being washed with water and boiled for 2 hours to eliminate gases such as  $\text{O}_2$ ,  $\text{CO}_2$ , and  $\text{SO}_2$ . Next, extracted carbon was immersed into  $\text{HNO}_3$  12M and stirred for 3 hours at room temperature and then soaked for 24 hours. Finally, activated carbon (AC) was washed several times with distilled water and then dried for 3 hours at  $100^\circ\text{C}$ .
- (ii) Preparation of Fe-C-TiO<sub>2</sub>/AC: 6 mL of TIOT was added into 34 mL of ethyl alcohol to make solution A. Solution B was prepared from 17 mL of ethanol, 0.4 mL of nitric acid (68%), 1.6 mL distilled water, 48.2 mg of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , and 0.2 g of AC. The solution A was dropped into solution B under slow stir for 14 hours at room temperature and left for gelation for 2 days before being autoclaved in a Teflon vessel for 10 hours at  $180^\circ\text{C}$ . The resulted powder was washed and dried at  $100^\circ\text{C}$  for 24 hours to obtain the Fe-C-TiO<sub>2</sub>/AC catalyst.

**2.2. Characterization of As-Synthesized Photocatalyst.** The crystal structure of catalyst was determined by XRD (D8-Advance 5005). Transmission electron microscope (TEM, JEOL JEM-1010 electron Microscope) and high-resolution transmission electron microscopy (HR-TEM, Hitachi H-9000 NAR, Japan Advanced Institute of Science and Technology) were used to investigate the particle size and morphology of the samples. XPS spectra of the prepared samples were measured by an X-ray photoelectron spectroscopy (XPS) (Kratos Axis Ultra—Frederick Seitz Materials Research laboratory-University of Illinois, Urbana-Champaign, USA). The absorbance was conducted by UV-Vis spectroscopy (Tasco-V670 photospectrometer). Functional groups were identified by IR spectroscopy (IR prestige 21). Nitrogen isothermal adsorption (Brunauer–Emmett–Teller (BET)) was determined by TriStar 3000 V6.07 A. Rhodamine B (RhB) concentrations were determined by a UV-Vis spectroscopy at the wavelength of 553 nm (the absorption maximum wavelength of RhB).

**2.3. Photocatalytic Performance of As-Synthesized Photocatalysts.** The catalytic activity of prepared materials was examined by the degradation of RhB solution (20 mg/L) under visible-light irradiation. The compact light (36W) was used instead of solar light with a range of wavelengths from 400 to 700 nm. An appropriate amount of catalyst (1–3 g/L) was added into 100 mL of RhB solution in a 250 mL beaker. The mixture was mixed at a constant rate in the dark for 30 minutes to ensure the desorption/adsorption equilibrium before being irradiated. After certain periods of time, the mixtures were sampled to determine the RhB concentrations by the UV-Vis spectroscopy.

## 3. Results and Discussion

**3.1. Characterization of Synthesized Photocatalysts.** Overall XPS spectra of principal elements Ti 2p, O 1s, C 1s, N 1s, and Fe 2p in synthesized photocatalysts are presented in Figure 1(a). The high-resolution scan over Ti 2p, O 1s, C 1s, N 1s, and Fe 2p spectral regions is shown in Figures 1(b)–1(f), respectively. The Ti 2p spectrum consists of peaks located at 459.1 eV and 464.8 eV, indicating the existence of Ti (IV) in  $\text{TiO}_2$  component [1]. This suggests that the doping of iron and carbon then attached to the AC carrier does not alter the chemical state of  $\text{TiO}_2$ . This result is consistent with the XRD results (Figure 2). O 1s spectrum consists of the main peak at 529.9 eV and shoulder peak at 531.9 eV. These peaks correspond to Ti-O bond and O-H groups in  $\text{TiO}_2$  [8]. This hydrogen hydroxyl group is useful for adsorption of organic substances or it can capture photogenic holes to form  $\text{HO}^\bullet$  free radicals that increase photocatalytic activity of photocatalysts.

The presence of peaks at 711.1 eV and 723.1 eV is attributed to  $\text{Fe}^{\text{III}} 2p_{3/2}$  and  $\text{Fe}^{\text{III}} 2p_{1/2}$ ; it is possible to predict the presence of iron in  $\text{Fe}^{3+}$  oxidation state. In addition, there is also the binding energy value at 709.2 eV corresponding to  $\text{Fe}^{\text{II}} 2p_{3/2}$ , which characterizes the existence of  $\text{Fe}^{2+}$  ions, possibly in FeO [5]. Coexistence of  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$

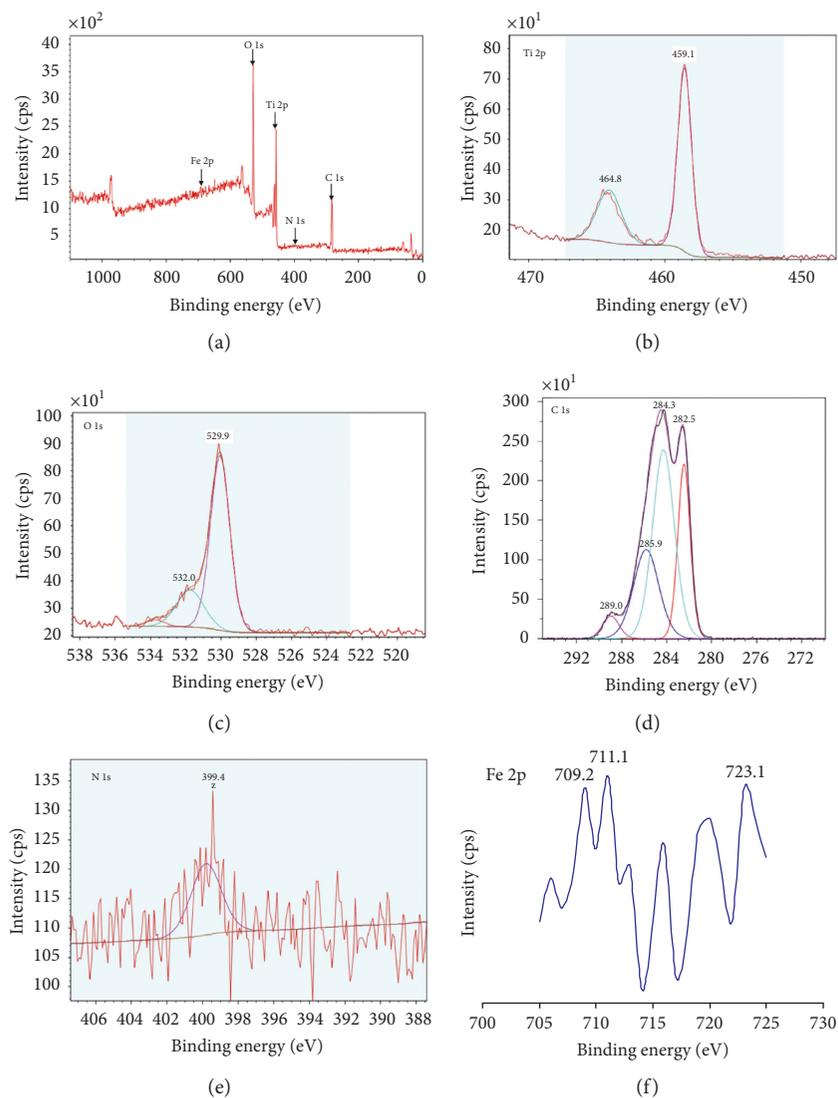


FIGURE 1: XPS spectra of Fe-C-TiO<sub>2</sub>/AC (a), Ti 2p (b), O 1s (c), C 1s (d), N 1s (e), and Fe 2p (f).

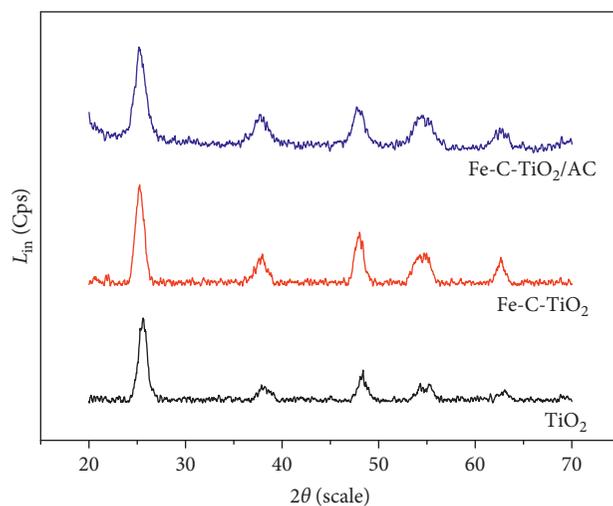
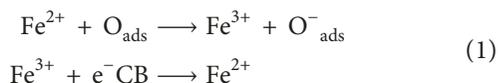


FIGURE 2: XRD patterns of Fe-C-TiO<sub>2</sub>/AC, Fe-C-TiO<sub>2</sub>, and TiO<sub>2</sub>.

can enhance the photocatalytic efficiency based on the following reactions:



in which  $\text{Fe}^{3+}$  acts as a conductive photonic electron trap to prevent recombination of electrons and holes, while  $\text{Fe}^{2+}$  provides electrons to adsorb oxygen on the catalytic surface and helps the charge transfer on the surface faster [1, 5].

Typical peaks of C are shown in Figure 1(d). The main peak with energy value at 284.3 eV is assigned to carbon graphite. The presence of 285.9 eV and 288.4 eV peaks is associated with C-O and C=O bonds of catalytic surface carbonates [11]. The existence of this carbonate radical increases the sensitivity for catalysis, because of the involvement of carbon-containing functional groups in activated carbon [1]. A peak at 282.5 eV corresponds to the Ti-C bond in the nanocrystalline catalyst attached to AC, and this link proves that part of the carbon is involved in replacing the oxygen in the network  $\text{TiO}_2$  anatase crystals. The XPS analysis confirmed that iron and carbon had successfully entered the  $\text{TiO}_2$  network and also showed the successful binding of catalyst to activated carbon activated by  $\text{HNO}_3$ .

The XRD patterns (Figure 2) show that Fe-C- $\text{TiO}_2$  after being coated on activated carbon exhibits the typical peaks referring to the anatase form [6]. The phase composition of nanoscale particles is preserved compared with the original materials (Figure 3).

The TEM images of the Fe-C- $\text{TiO}_2/\text{AC}$  sample (Figure 3(a)) show that the catalyst system contains very fine particles, with typical size of 5 nm, evenly distributed on the surface of activated carbon. The result of HR-TEM (Figure 3(b)) confirms the Fe-C- $\text{TiO}_2$  catalyst binding on AC is based on black spots covered by catalytic spheres [10].

Proposed mechanism of  $\text{TiO}_2$  coating process on AC is shown in Figure 4. After AC was pretreated with  $\text{HNO}_3$ , carbon supplied more hydroxyl and acid groups on the surface, which bond to  $\text{OH}^-$  and  $\text{H}^+$  ions of catalyst to enhance the adhesiveness.

Table 1 shows that the surface areas of pristine AC and AC carrying catalysts measured by BET are different. The reason is that during the treatment of AC,  $\text{HNO}_3$  is a strong oxidant, leading to changes in porous structure, which might reduce the number of small capillaries and increase the number of large ones, therefore reducing the surface area.

IR spectra of pristine  $\text{TiO}_2$ , Fe-C- $\text{TiO}_2$ , and Fe-C- $\text{TiO}_2/\text{AC}$  are presented in Figure 5. Peak at  $1436\text{ cm}^{-1}$  refers to the -COO-Ti vibration. The peaks at  $551\text{ cm}^{-1}$  and  $502\text{--}505\text{ cm}^{-1}$  are assigned to the bonds of Ti-O and Ti-O-C, respectively.

The UV-Vis spectra of the samples are displayed in Figure 6. The results show that by coating Fe-C- $\text{TiO}_2$  on AC, the absorption band of Fe-C- $\text{TiO}_2/\text{AC}$  was significantly expanded to the visible region in comparison with the absorption band of pristine  $\text{TiO}_2$  and Fe-C- $\text{TiO}_2$ . Indeed, as expected, the main absorption edge of  $\text{TiO}_2$  was estimated to be about 398 nm (2.96 eV) due to its intrinsic band gap absorption. The onset of the absorption spectrum of Fe-C-

$\text{TiO}_2$  was shifted to the visible region because of the Fe and C dopants while Fe-C- $\text{TiO}_2/\text{AC}$  presented main absorption spectrum at the region above 480 nm. This result suggests that the Fe-C- $\text{TiO}_2/\text{AC}$  catalyst is more active under visible light.

From the UV-Vis spectra of pristine  $\text{TiO}_2$ , Fe-C- $\text{TiO}_2$ , and Fe-C- $\text{TiO}_2/\text{AC}$  (Figure 7), the band gap energies estimated from the intercept of the tangents to the plots by using Kubelka-Munk method were 2.96, 2.17, and 1.63 eV for pristine  $\text{TiO}_2$ , Fe-C- $\text{TiO}_2$ , and Fe-C- $\text{TiO}_2/\text{AC}$ , respectively.

**3.2. Catalytic Activity of Fe-C- $\text{TiO}_2/\text{AC}$  in the Degradation of RhB under Visible Light.** The comparison of photocatalytic performance of Fe-C- $\text{TiO}_2/\text{AC}$ , Fe-C- $\text{TiO}_2$ , and  $\text{TiO}_2$  with that of pure AC in the degradation of RhB under visible-light irradiation with the same catalyst load (1.6 g/L) is presented in Figure 8. AC adsorbs RhB and reaches the equilibrium after 60 min of reaction, which can be proved by unchanged RhB concentration over time. The results also indicate that Fe-C- $\text{TiO}_2/\text{AC}$  is the best photocatalyst in degradation of RhB in solutions with more than 99% of RhB removal after 90 min while pristine  $\text{TiO}_2$  exhibits the lowest performance (only some 40% of RhB is removed after the same reaction time). Pure AC and Fe-C- $\text{TiO}_2$  present photocatalytic efficiency in between pristine  $\text{TiO}_2$  and Fe-C- $\text{TiO}_2/\text{AC}$ . This illustrates the synergy between adsorption capacity of AC and the improvement of Fe-C- $\text{TiO}_2$  compared with pristine  $\text{TiO}_2$ .

Figure 9 shows that the optimal catalyst load was 1.6 mg/L in the degradation of RhB in solutions while more dilute or concentrated catalyst concentrations will result in lower levels of RhB degradation. In fact, more than 99% of RhB was decomposed after 90 min of visible-light irradiation with a catalyst load of 1.6 mg/L while these figures for the catalyst loads at 1, 1.2, 1.4, 1.8, and 2.5 were, respectively, 40%, 50%, 53%, 78%, and 62%. This can be explained by the fact that the higher quantity of catalyst load may cause the light absorption hindrance, decreasing the efficiency of RhB degradation, whereas the lower catalyst load would lead to lower active sites ready for the degradation of the pollutant.

The photocatalytic degradation of RhB by the Fe-C- $\text{TiO}_2/\text{AC}$  system can be explained by the following mechanism proposal (Figure 10): (1) when  $h\nu \geq (E_C - E_V)$ , then electrons would be excited in the valence band of  $\text{TiO}_2$  by the process:  $\text{TiO}_2 + h\nu (\text{UV}) \longrightarrow \text{TiO}_2 (e_{\text{CB}^-} + h_{\text{VB}^+})$ ; (2) when  $(E_C - E_V) \leq h\nu < (E_C - E_V)$ , electrons can be excited from the Fe-C- $\text{TiO}_2/\text{AC}$  energy level by the following process:  $\text{Fe-C-TiO}_2/\text{C} + h\nu (\text{visible}) \longrightarrow \text{Fe-C-TiO}_2/\text{AC} (e_{\text{CB}^-} + h_{\text{VB}^+})$ ; and (3) when  $(E_V^* - E_V) \leq h\nu < (E_C - E_V)$ , electrons would be excited and moved from the valence band of  $\text{TiO}_2$  to the Fe-C- $\text{TiO}_2/\text{AC}$  energy level by the process:  $\text{TiO}_2 + \text{Fe-C-TiO}_2/\text{C} + h\nu (\text{visible}) \longrightarrow \text{Fe-C-TiO}_2/\text{AC} (e_{\text{CB}^-}) + \text{TiO}_2 (h_{\text{VB}^+})$ . The departed electrons and holes subsequently migrate to the surface of the catalysts and react with adsorbed  $\text{H}_2\text{O}$  and  $\text{O}_2$  molecules, forming  $\text{HO}^\cdot$  and  $\text{O}_2^\cdot$ , respectively.  $\text{HO}^\cdot$  and  $\text{O}_2^\cdot$  radicals are mainly responsible for the degradation of RhB in solution [12].

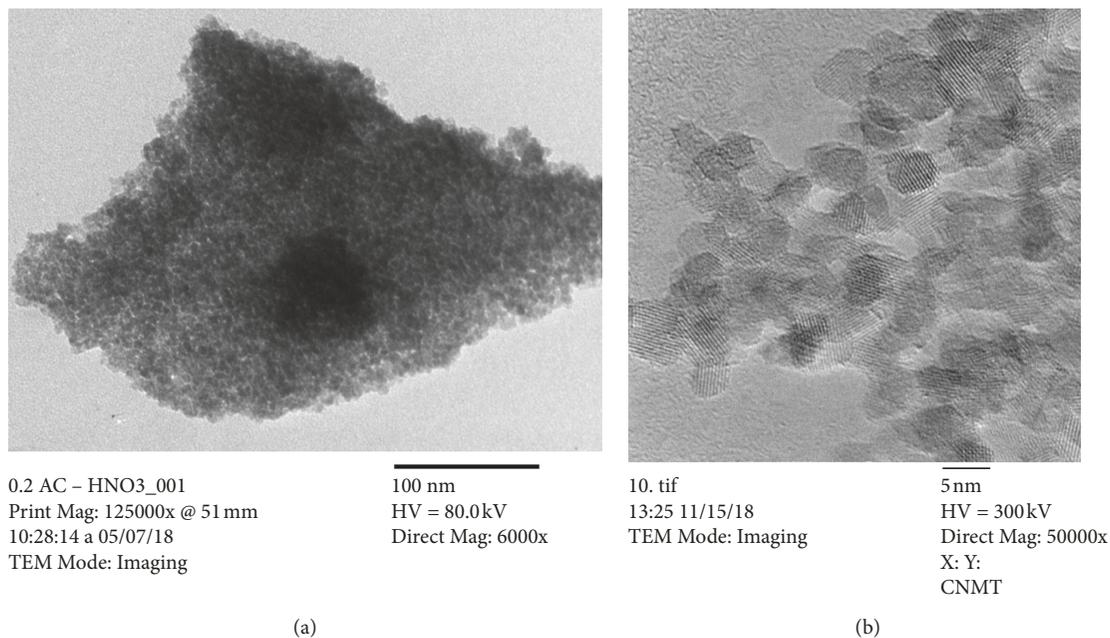


FIGURE 3: TEM images of Fe-C-TiO<sub>2</sub>/AC (a) and HR-TEM of Fe-C-TiO<sub>2</sub>/AC (b).

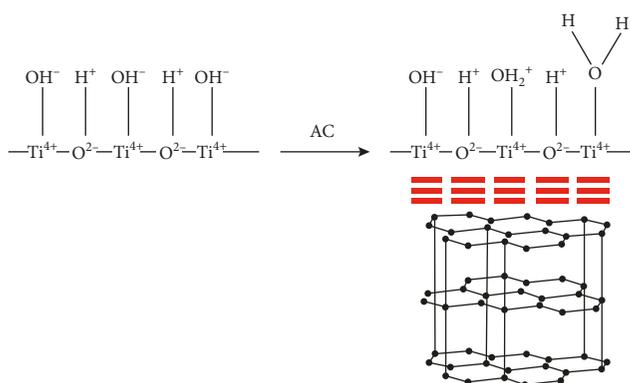


FIGURE 4: Proposed mechanism of TiO<sub>2</sub> coating process on AC.

TABLE 1: Physical properties of AC, Fe-C-TiO<sub>2</sub>, and Fe-C-TiO<sub>2</sub>/AC.

Materials	Mean size (nm) from the XRD results	BET surface area (m <sup>2</sup> ·g <sup>-1</sup> )	V <sub>p</sub> (cm <sup>3</sup> ·g <sup>-1</sup> )
Fe-C-TiO <sub>2</sub> /AC	5.13	264.8	0.30
Fe-C-TiO <sub>2</sub>	4.23	237.2	0.23
AC	—	928.2	—

The catalytic stability in RhB decomposition under visible-light irradiation was studied. After each decomposition cycle (90 min), the catalyst was centrifuged and washed with distilled water and then used for further treatment of RhB in solution. The results show that the catalyst exhibited good photocatalytic activity after 5 cycles, as shown in Figure 11. The ability to decompose RhB over 5 cycles remained high (>87%). This research has proved that Fe-C-TiO<sub>2</sub>/AC is a highly durable, economically suitable, and practical catalyst.

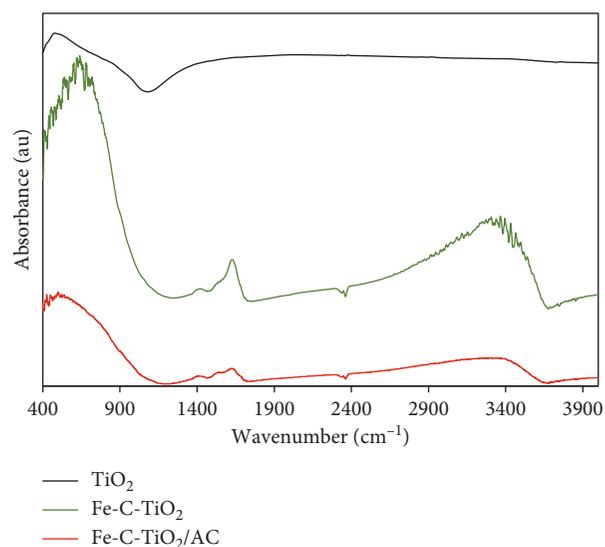


FIGURE 5: IR spectra of Fe-C-TiO<sub>2</sub>/AC, Fe-C-TiO<sub>2</sub>, and TiO<sub>2</sub>.

## 4. Conclusions

The Fe-C-TiO<sub>2</sub> catalyst was successfully carried on the AC treated by HNO<sub>3</sub>. The nature of the catalyst remained to be unchanged regarding phase composition, particle sizes, and structure. Furthermore, the large surface area of AC adsorbs more organic molecules, leading to enhance the RhB degradation in solutions. The catalyst after being deposited on AC carriers activated with HNO<sub>3</sub> has better photocatalytic activity than activated carbon without catalysts. The Fe-C-TiO<sub>2</sub>/AC catalyst also presented better photocatalytic performance in RhB degradation compared with pristine TiO<sub>2</sub> and with Fe-C-TiO<sub>2</sub>. The optimal catalyst load for RhB

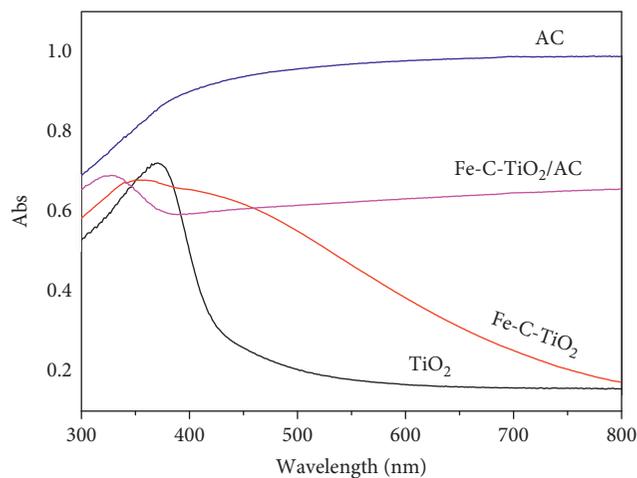


FIGURE 6: UV-Vis spectra of pure AC, Fe-C-TiO<sub>2</sub>/AC, Fe-C-TiO<sub>2</sub>, and TiO<sub>2</sub>.

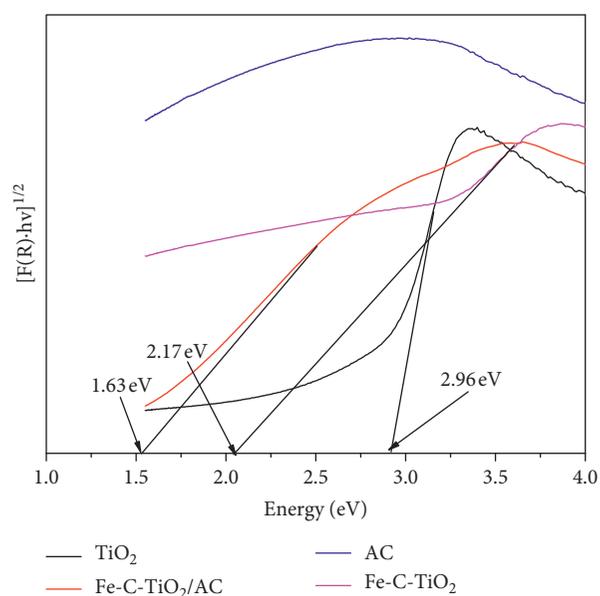


FIGURE 7: Plot of  $[F(R) \cdot hv]^{1/2}$  vs energy (eV) for pure AC, Fe-C-TiO<sub>2</sub>/AC, Fe-C-TiO<sub>2</sub>, and TiO<sub>2</sub>.

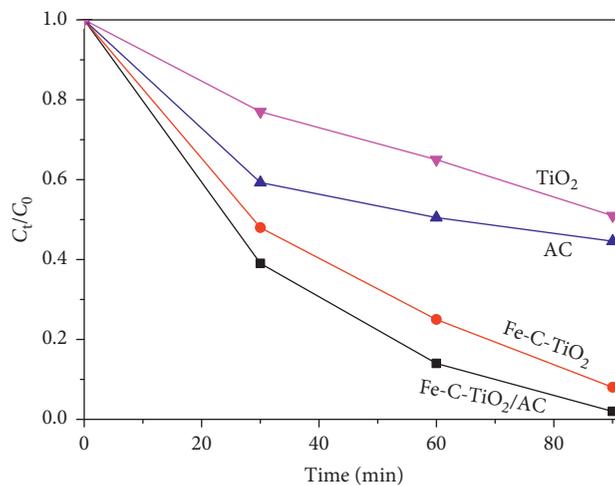


FIGURE 8: Comparison of photocatalytic activity of Fe-C-TiO<sub>2</sub>/AC, Fe-C-TiO<sub>2</sub>, and TiO<sub>2</sub> with that of pure AC.

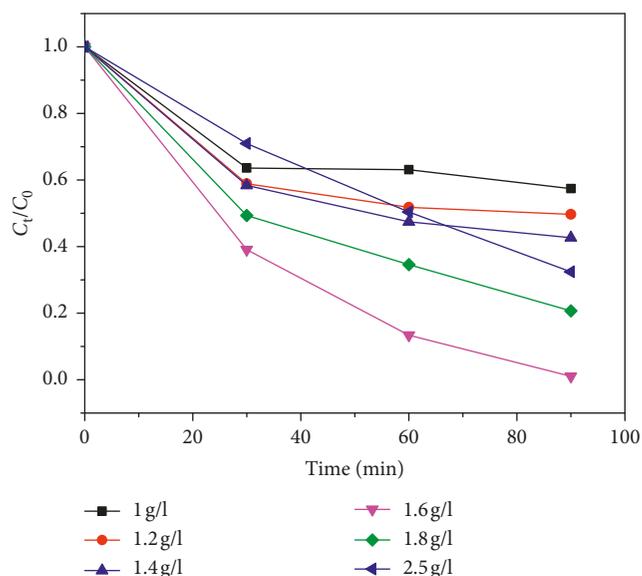


FIGURE 9: Optimization of catalyst load in the degradation of RhB by Fe-C-TiO<sub>2</sub>/AC.

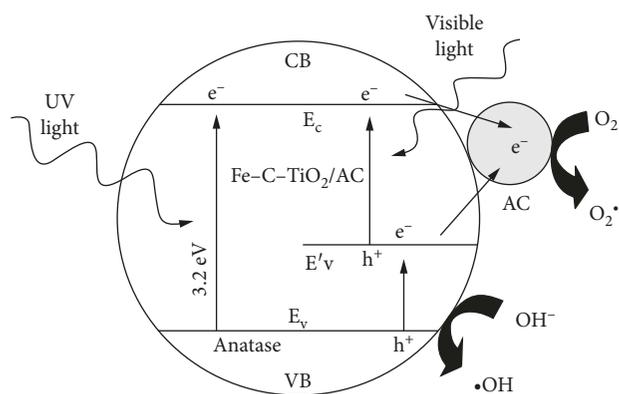


FIGURE 10: Schematic mechanism of photocatalytic degradation of RhB by Fe-C-TiO<sub>2</sub>/AC (adopted from [12]).

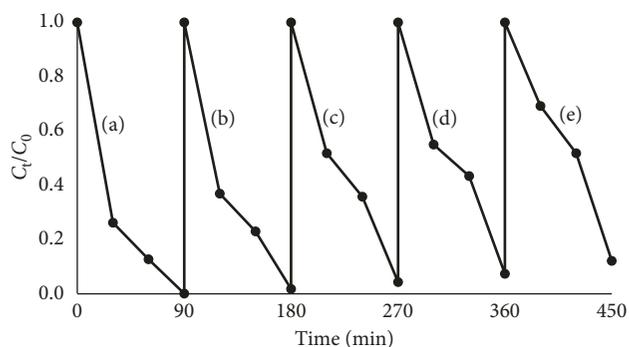


FIGURE 11: Photocatalytic recycling of Fe-C-TiO<sub>2</sub>/AC in RhB decomposition: first cycle (a); second cycle (b); third cycle (c); fourth cycle (d); fifth cycle (e).

decomposition (initial concentration of 20 mg/L) was found to be of 1.6 g/L. The catalysts with larger size favor the catalyst separation from solution and recycling. The Fe-C-

TiO<sub>2</sub> carried on AC sample is a potential catalyst in degradation of toxic organic compounds under visible-light irradiation.

## Data Availability

The data used to support the findings of this study are included within the article.

## Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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## Research Article

# Modeling and Optimization of the BSCF-Based Single-Chamber Solid Oxide Fuel Cell by Artificial Neural Network and Genetic Algorithm

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Fuel cells could be a highly effective and eco-friendly technology to transform chemical energy stored in fuel to useful electricity and thus are presently appraised as a standout among the most encouraging advancements for future energy demand. Solid oxide fuel cells (SOFCs) have several advantages over other types of fuel cells, such as the flexibility of fuel used, high energy conversion, and relatively inexpensive catalysts due to high-temperature operation. The single chambers, wherein the anode and cathode are exposed to the same mixture of fuel, are promising for the portable power application due to the simplified, compact, sealing-free cell structure. The empirical regression models, such as artificial neural networks (ANNs), can be used as a black-box tool to simulate systems without solving the complicated physical equations merely by utilizing available experimental data. In this study, the performance of the newly proposed BSCF/GDC-based cathode SOFC was modeled using ANNs. The cell voltage was estimated with cathode preparation temperature, cell operating temperature, and cell current as input parameters by the one-layer feed-forward neural network. In order to acquire the appropriate model, several network structures were tested, and the network was trained by backpropagation algorithms. The data used during the training, validation, and test are the actual experimental results from our previous study. The optimum conditions to achieve maximum power of the cell were then determined by the genetic algorithm and the developed ANN.

## 1. Introduction

Fuel cells could be a highly effective and eco-friendly technology to transform chemical energy stored in fuel to useful electricity and thus are presently appraised as a standout among the most encouraging advancements for future energy demand [1]. Among different classes of fuel cells, the solid oxide fuel cell (SOFC) has displayed an extraordinary integration of benefits, including high energy efficiency, broad fuel versatility, significant contamination allowance, and low waste discharge [2, 3]. Currently, yttria-stabilized zirconia (YSZ), a zirconia-based electrolyte, is the

most widely utilized electrolyte as it has sufficient oxide-ion conductivity and, furthermore, demonstrates suitable phase durability in both oxidizing and reducing environments [4]. However, in order to lessen the ohmic polarization loss, the zirconia-based electrolyte needs a very high operation temperature  $\sim 1000^{\circ}\text{C}$ , which provides adequate oxygen conductivity. Therefore, high temperature places rigorous constraints on its accompanying materials. Reducing the operation temperature to  $500\text{--}800^{\circ}\text{C}$ , classified as the intermediate temperature range, is supposed to elongate the lifespan of SOFC, minimize its degradation rate, and diversify the range of material selections [5].

On the contrary, reducing operation temperature requires a new pair of electrolyte-cathode, which is more ion conductive than the conventional pair of Y-stabilized  $\text{ZrO}_2$  and  $(\text{La}_{1-x}\text{Sr}_x)\text{MnO}_3$ . Therefore, the nickel cermet has been the unanimous selection for the anode composition. LAMOX is an oxide conductor family based initially on the parent  $\text{La}_2\text{Mo}_2\text{O}_9$  crystal. The lanthanide-doped LAMOX has the fundamental characteristics of an electrolyte at intermediate temperatures such as high ion conductivity [6, 7] and good phase stability [8]. However, the LAMOX composition is only occasionally investigated as the SOFC electrolyte.

On the cathode side,  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$  (BSCF) is usually suggested as a candidate in the intermediate temperature range, in perspective of its exceptional catalytic activity toward oxygen reduction combined with high ion conductivity [9], low electrochemical surface-exchange resistance [10], and reasonable fabrication cost [10]. However, the perovskite of BSCF does have its own drawback. The composition has the phase instability problem, similar to many other perovskites with cobalt on the B site [11]. It should be noted that the cathodic loss contributes the significant part of SOFC's polarization loss. The large cathode polarization loss normally occurs from the fact that the mixed conductor of the cathode perovskite frequently shows the ionic conductivity significantly lower than its electronic conductivity [12, 13]. Hence, a composite cathode of ionic conductor and mixed conductor is adopted to minimize the cathodic loss.

The BSCF, gadolinium-doped ceria (GDC), and  $\text{La}_{1.8}\text{Dy}_{0.2}\text{Mo}_2\text{O}_9$  (LDM) powders, therefore, were synthesized and characterized for fuel cell evaluation. The effect of different preparation conditions on the fuel cell behavior was found in this study. On the contrary, modeling and simulation of SOFCs are useful approaches to investigate effects of various design parameters and operating conditions on SOFC performances and also to help in SOFC improvements. The obtained results can be used in optimization, control, improvement, and design of the fuel cell system [14–16]. Currently, there are plenty of models that have been published to contribute more knowledge of the fuel cell phenomena. The approaches for fuel cell modeling can be classified into two categories: theoretical and empirical [15, 17, 18]. In the theoretical mathematical approach, the spatial dimensions of the models vary from simplified zero (0-D) [19, 20] and one (1-D) [18, 21–23] to more complex two (2-D) [24–27] and three (3-D) [28–30], with different characteristics and targets to different research purposes. The mathematical models, which are generally founded based on momentum, mass, and energy conservation laws, necessitate the information about many parameters and properties of the fuel cell system, the complicated equations, and the time-consuming numerical techniques. Therefore, using theoretical models makes the problem too complicated and impractical for some engineering applications.

Another approach, namely, empirical or data-driven modeling, might be more practical for the fuel cell user from the viewpoint the SOFC behavior can be inferred without deeply understanding the internal components [15, 17].

The empirical approaches can be applied to simulate the object's behavior without an algorithmic solution, merely by utilizing available experimental data. These approaches include least-squares support vector machine (LS-SVM) [31] and the Hammerstein model [32, 33]. Among them, artificial neural network (ANN) presents some advantages such as high nonlinearity, matches experimental data with a low degree of error, and does not require any specific analytical equations and system descriptions. ANN is a black-box model, whereas numerical models allow for the examination of parameter distributions inside the cell. Numerical models may also be more accurate than ANN models if, for example, the operating conditions change significantly during dynamic operation. However, utilization of ANNs for modeling SOFCs appears a very promising way due to its rapid computation. Genetic algorithms (GAs) are a class of metaheuristic searching optimization techniques inspired by the mechanics of natural evolution and genetics [34]. Compared to conventional optimization methods, GAs are remarkably simple, robust, and able to handle the nondifferentiable, discontinuous, or multimodal problems. GAs have been successfully applied in a wide range of applications in various engineering, manufacturing, and management areas [35].

In this study, the performance of the BSCF/GDC-based cathode SOFC was modeled using ANNs. The cell voltage was estimated with cathode preparation temperature, cell operating temperature, and cell current as input parameters by the one-layer feed-forward neural network. In order to acquire the appropriate model, several network structures were tested, and the network was trained by back-propagation algorithms. The data used during the training, validation, and test have been obtained from the actual experimental results from our previous study [36]. The optimum condition to achieve maximum power was then determined by genetic algorithms and the developed ANN.

## 2. Experiments and Methodology

**2.1. Experiments.** The description of experimental configuration could be found in our study [36, 37]. The brief explanation of the cell is summarized as follows. The porous structure of the anode-supported cell was fabricated through the following steps. Commercial NiO (>99.5%), 1000°C calcined GDC, and 1000°C calcined LDM powders were mixed in a weight ratio of 4.8:3.2:0.8. Then, the mixture was mixed with 15 wt.% of graphite flash, uniaxial pressed, and then sintered for 2 h at 1175°C to form an anode with a size of ~0.4 mm in thickness and ~13.2 mm in diameter.

$\text{La}_{1.8}\text{Dy}_{0.2}\text{Mo}_2\text{O}_9$  (LDM) electrolyte was applied to the polished porous anode pellet by the spin-coating method with a desired thickness of ~60  $\mu\text{m}$ . As mentioned above, BFSC cannot be applied directly onto LDM due to chemical reaction. Therefore, it needs an additional barrier layer to prevent undesirable reaction.

A barrier layer of 0.5 wt.%  $\text{Fe}_2\text{O}_3$ -doped  $\text{Gd}_{0.1}\text{Ce}_{0.9}\text{O}_{1.95}$  (i-GDC) was applied on the LDM layer for one time to form NiO + GDC/LDM/i-GDC button. The button was then co-sintered at 1225°C for 5 hours with a heating and cooling rate of 2°C  $\text{min}^{-1}$ .

To complete the final cell of NiO + GDC/LDM/i-GDC/BSCF + GDC, the surface of the i-GDC layer was screen-printed on by the blend of composite cathode and then sintered in air at 1000°C (cell a), 1015°C (cell b), 1025°C (cell c), or 1050°C (cell d) for 2 h. In this study, three single-cell sets were fabricated, all of which use a cathode gradient. The composite layer of 50 wt.% BSCF and 50 wt.% GDC was applied onto the i-GDC; meanwhile, the composite layer of 90 wt.% BSCF and 10 wt.% GDC layer was exposed to the air atmosphere.

The configuration of the fuel cell system of NiO + GDC/LDM/i-GDC/GDC-BSCF is shown in Figure 1(a). Two Au wires were connected to the single cell for current collecting, using the Keithley 238 source-measure unit. There is a coil arranged before the cell, which extends the heating time for the inflow. Both the coil and the cell were placed inside a quartz tube, together with a thermocouple which monitors the cell temperature. To activate the anode on-site, an extra Ni + GDC disk was attached above the anode. A sketch of the button cell was represented in Figure 1(b). The dimensions of the system are summarized in Figure 1(c).

The cell was operated in a mixture of methane/air with the flow rate of 650 sccm and the molar ratio of 1.5 : 1. The data were collected on the current density and the cell voltage of the fuel cell button for each combination of the sintering temperature of the cathode (1000, 1015, 1025, and 1050°C) and the cell operating temperatures (625, 650, 675, and 700°C).

**2.2. Artificial Neural Network Models.** Artificial neural network (ANN) is an information processing method inspired by the biological nervous systems. An ANN consists of a number of highly interconnected nodes, called neurons, which are able to receive and transmit the data [38, 39]. Feed-forward multilayer architectures, the simplest form of ANNs, are composed of an input layer, one or more hidden layers, and an output layer. The number of neurons in the input and output layers is equal to the number of inputs and outputs in the system to be modeled. Each neuron is linked to all neurons in the following layer by methods of weighted connections. The input of a neuron is the weighted aggregate of the data from its linked neurons. The response or output of a neuron is the transformation of its input using an appropriate activation function. The neurons will equally transmit their responses to all the neurons in the next layer. Input neurons do not activate their inputs; they just receive and send them to all the neurons in the first hidden layer. The number of neurons in the hidden layers is an important parameter which impacts the precision of the estimation. If too few neurons are used, the ANN might not have enough flexibility to satisfactorily approximate the data. However, if larger than the necessary number of neurons is included, the network then becomes overfitting, and it can memorize the data exactly but fail to generalize to a new situation [40]. In general, there is no rule for the number of neurons in the hidden layer, and it is usually determined by experiments. Figure 2 shows a feed-forward artificial neural

network (3-5-1) structure with the input of operating temperature, sintering temperature, and current.

The activation function is used to calculate the output response of a neuron and can take any form, linear or nonlinear. The popular activation function, which is also employed in this study, is the logistic sigmoid [41]. The general form of the function is given as  $f(x) = 1/(1 + e^{-x})$ .

In order to enhance the performance of the network, the supplied input-output data should be normalized. In this study, the input data ( $x_i$ ) are scaled to the normalized value ( $x_{\text{norm}}$ ) as follows:

$$x_{\text{norm}} = 0.8 \frac{(x - x_{\text{min}})}{x_{\text{max}} - x_{\text{min}}} + 0.1, \quad (1)$$

where  $x_{\text{max}}$  and  $x_{\text{min}}$  are the maximum and minimum of the experimental data, respectively.

The values of mean squared error (MSE) and coefficient of determination ( $R^2$ ) are frequently employed to evaluate the performance of the ANN. They were, respectively, calculated as follows [42]:

$$\text{MSE} = \frac{1}{n} \sum_{i=1}^n (t_i - a_i)^2, \quad (2)$$

$$R^2 = \frac{(\sum_{i=1}^n (t_i - \bar{t})(a_i - \bar{a}))^2}{\sum_{i=1}^n (t_i - \bar{t})^2 \sum_{i=1}^n (a_i - \bar{a})^2},$$

where  $n$  is the total data points,  $t_i$  is the predicted value from the networks,  $a_i$  is the experimental response, and  $\bar{t}$  and  $\bar{a}$  are the average of predicted value and actual value, respectively.

There are several important factors affecting fuel cell performance, including cathode and anode structure, electrolyte material and thickness, cell temperature, and inlet and outlet gas compositions. In this study, two significant factors, namely, cathode sintering temperature and cell operating temperature, were examined. The range for sintering temperature is from 1000°C to 1050°C, and the range for the operating temperature is from 625°C to 700°C. As depicted in our earlier report, the sintering temperature affects the structure of the obtained cathode. The range for the investigated parameters is explained as follows. At the cathode sintering temperature below 1000°C, the low degree crystallization of BSCF minimizes the redox reaction, thus reducing the fuel cell performance. On the contrary, the phase compatibility between BSCF and GDC is ensured only up to 1050°C. Similarly, at the lower operating temperature of 600°C, there are not enough kinetic rate of ionic conducting, leading to poor performance of the fuel cell. However, at operating temperature over 700°C, the BSCF crystal becomes unstable under the methane/air atmosphere, which limits the performance of the fuel cell.

Therefore, the network architecture is designed with three inputs, one hidden layer, and one output. The inputs are current density, sintering temperature of the cathode, and cell operating temperature. The network was trained using the backpropagation algorithm [43]. The maximum number of epochs and the minimum performance gradient are assigned to 400 and  $10^{-5}$ , respectively. Training

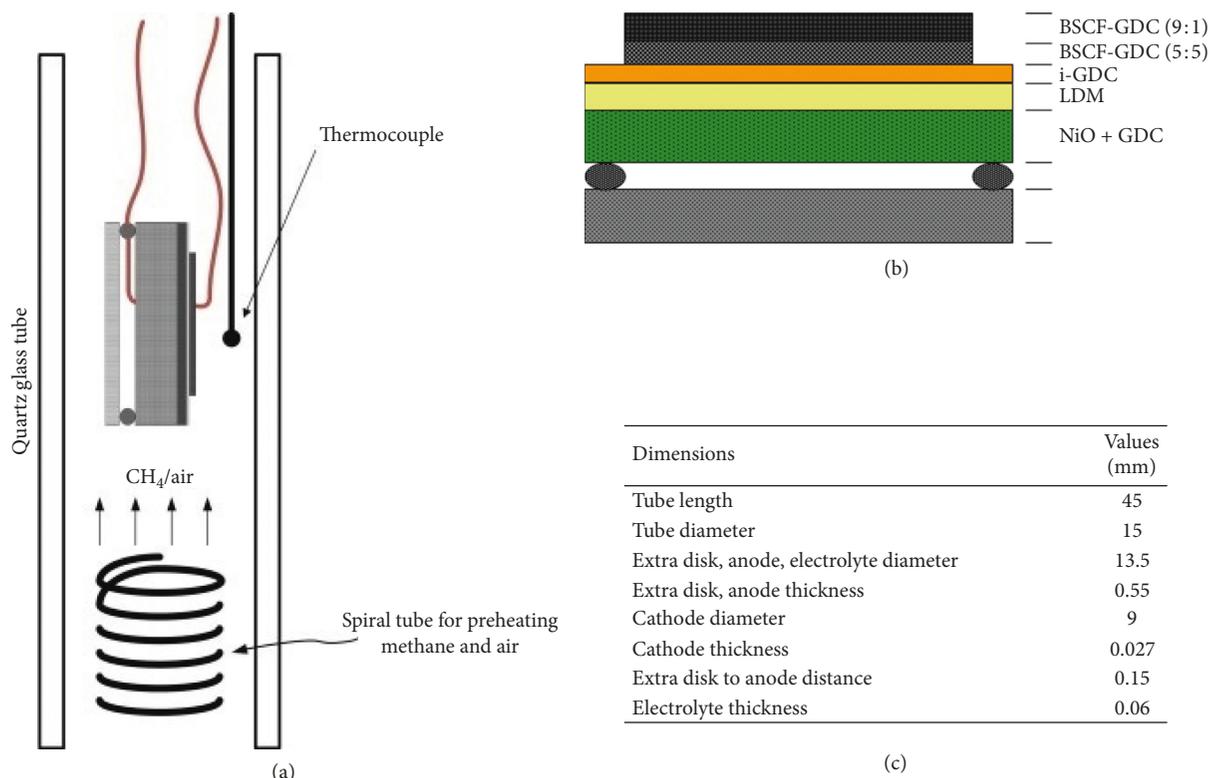


FIGURE 1: (a) Configurations of single-chamber solid oxide fuel cells (SOFCs) and the detail of anode-supported cell [37]. (b) A sketch of the button cell. (c) Geometry dimensions of the experimental setup.

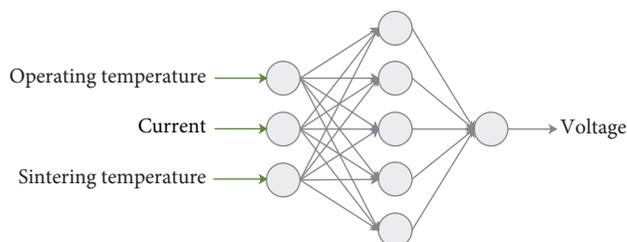


FIGURE 2: Artificial neural network (3-5-1) structure.

stops when the maximum number of epochs is reached or when either the MSE or performance gradient is less than the predetermined goal. Through various trial experiments, the appropriate network structure for the current simulation is decided. The data sets were randomly divided into three subsets, namely, training, validation, and test, each of which contains 70%, 20%, and 10% number of samples, respectively. The validation and test sets are essential for the evaluation of the validation and modeling power of the networks.

The parameters of the model from the neural network were stored and used to optimize the power density using genetic algorithms in the next section.

**2.3. Optimization by Genetic Algorithms.** Genetic algorithms (GAs) are heuristic search algorithms inspired by

the evolutionary ideas of natural selection and genetics. Genetic algorithms start with randomly generated chromosomes from the feasible region to produce a population. The fitness of each chromosome was defined by the objective function after converting the chromosomes to natural values. The algorithms iteratively modify a population of individual solutions analogous to processes happening in the nature—selection, reproduction, and mutation. The best fitness of the population comes toward an optimal solution by the principle of “survival of the fittest” [44]. The basic steps of genetic algorithms can be summarized as follows:

- (1) Randomly generating a primary population of  $N$  individuals
- (2) Producing the next generation by crossing over and mutation among individuals
- (3) Selecting the new population of  $N$  individuals from the parents and generation of (2)
- (4) Creating the next population by iterating steps (2) and (3) until the maximum number of generations is reached

The algorithm flow of the GA approach is shown in Figure 3.

The objective function in this study is the power density of the fuel cell, which is defined as

$$P = I \times V, \quad (3)$$

where  $P$  is the power density ( $\text{mW}\cdot\text{cm}^{-2}$ ),  $I$  is the current density ( $\text{mA}\cdot\text{cm}^{-2}$ ) and is the input to the ANN model, and  $V$  is the cell voltage (V) which is estimated from the ANN model.

The design variables in the optimization problem are the inputs of the artificial neural network model. Their corresponding intervals were discussed in the previous section and are summarized as follows:

- (i) Sintering temperature of the cathode, [1000–1050] ( $^{\circ}\text{C}$ )
- (ii) Operating temperature of the cell, [625–700] ( $^{\circ}\text{C}$ )
- (iii) Electric current of the cell, [0–1500] ( $\text{mA}\cdot\text{cm}^{-2}$ )

The binary GA was used as the optimization method. A MATLAB™ program which was adapted from the literature [45] is used for the GA computations. The parameters of the GA such as population size and mutation probability values were set to be 100 and 0.10, respectively. The survival of the chromosomes was determined as the roulette wheel selection with elitism; it means that the best solution is always survive to the next population. The number of generations was assigned to be 500.

### 3. Results and Discussion

**3.1. Microstructure of the Button Cell.** In order to better understand the structure of the fabricated single cell, the single cell after  $I$ - $V$  measurement was observed using the SEM method. The microstructure of the single cell in a cross-sectional image is shown in Figure 4. The SEM image shows an electrolyte thickness of  $\sim 60\ \mu\text{m}$ , total cathode thickness (including 2 layers) of  $\sim 27\ \mu\text{m}$ , and barrier layer i-GDC thickness of  $6\text{--}8\ \mu\text{m}$ . Moreover, the cross section shows well adherence between the cathode, i-GDC, electrolyte, and anode layers. Note that a crack of electrolyte at the left-hand side was formed by breaking out for the SEM measurement. Finally, the good adherence between layers and appropriate microstructures reveal that it is a good technique to fabricate the single cell for experimental and simulation study.

**3.2. Artificial Neural Network Model Validation.** An artificial neural network was used for modeling the cell voltage of the fuel cell. Experimental data obtained under different operating conditions were used to train and validate the neural network model. In ANN modeling, the number of hidden neurons is critical because excessive neurons will cause overfitting; however, too small number of neurons may not adequately capture the complexity of the system [46]. After performing some trials, the sufficient number of neurons in the hidden layer was 7. Consequently, a 3-7-1 feed-forward ANN architecture was employed in this study.

The results of the ANN modeling were described using current versus cell voltage graphs (or  $I$ - $V$  plots) and were compared with data from experiments. The correlation coefficients ( $R^2$ ) for three subsets (training, validation, and testing) were 99.92%, 99.88%, and 99.87%, respectively. The

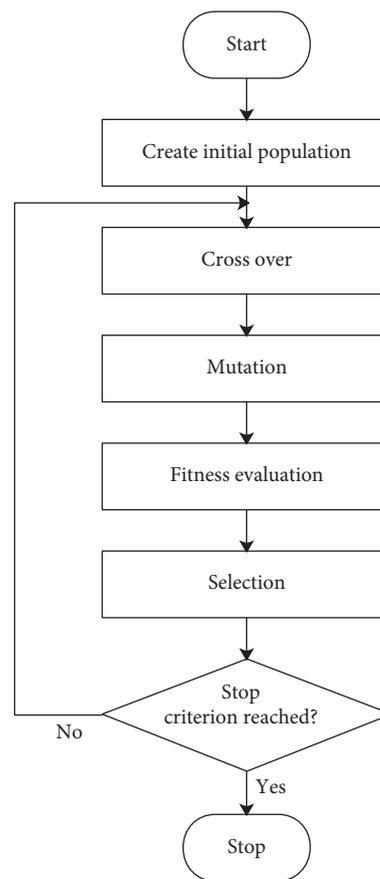


FIGURE 3: Block diagram of the genetic algorithm process.

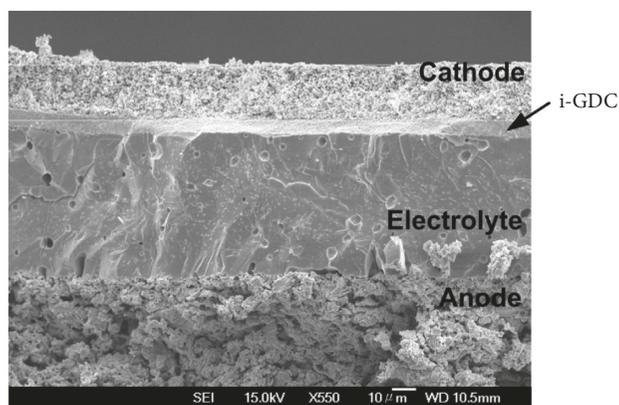


FIGURE 4: The cross-sectional image shows the interface structure of the cell.

MSE values for three subsets (training, validation, and testing) were  $4.19 \times 10^{-5}$ ,  $7.14 \times 10^{-5}$ , and  $7.04 \times 10^{-5}$ , respectively. The correlation coefficient and MSE of all data were 99.91% and  $5.06 \times 10^{-5}$ , respectively.

Figure 5 shows the cell performances from the ANN modeling and the experimental data at the cathode sintering temperature of  $1000^{\circ}\text{C}$  as the operating temperature changes from  $625^{\circ}\text{C}$  to  $700^{\circ}\text{C}$ . The correlation and MSE for this subset are 99.95% and  $2.86 \times 10^{-5}$ , respectively.

Figure 6 presents the cell voltage versus current density curves of the ANN predictions and the experimental data at

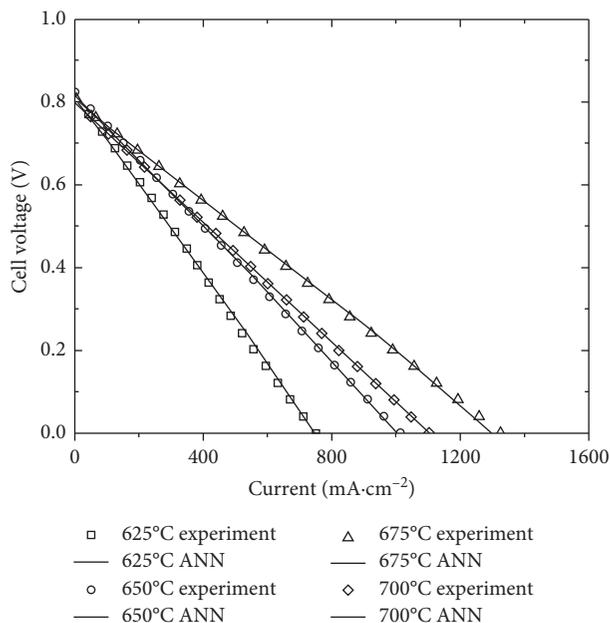


FIGURE 5: Comparison of  $I$ - $V$  curves for the cathode sintered at  $1000^{\circ}\text{C}$  and operated at different temperatures by the ANN model and experimental data.

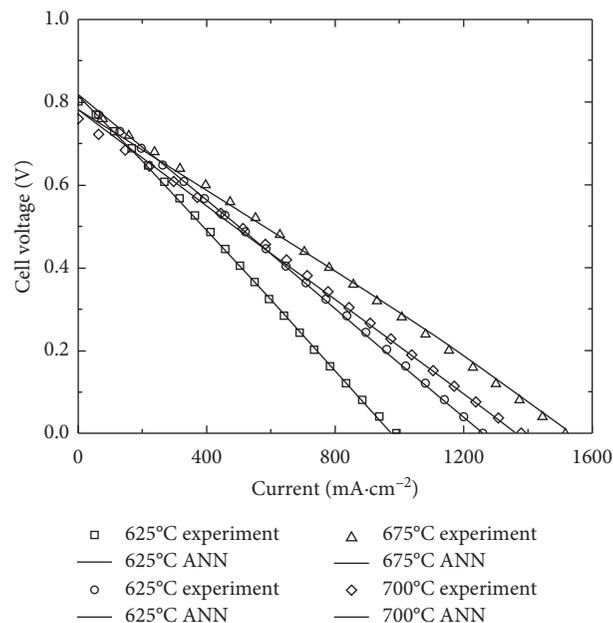


FIGURE 7: Comparison of  $I$ - $V$  curves for the cathode sintered at  $1025^{\circ}\text{C}$  and operated at different temperatures by the ANN model and experimental data.

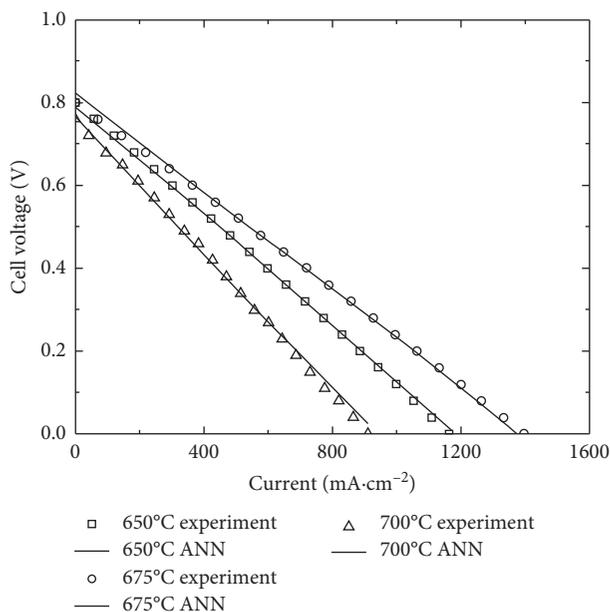


FIGURE 6: Comparison of  $I$ - $V$  curves for the cathode sintered at  $1015^{\circ}\text{C}$  and operated at different temperatures by the ANN model and experimental data.

$1015^{\circ}\text{C}$  of cathode sintering temperature as the operating temperature is varied from  $650^{\circ}\text{C}$  to  $700^{\circ}\text{C}$ . The correlation coefficient and MSE of the model for this subset are 99.83% and  $9.74 \times 10^{-5}$ , respectively.

In Figure 7, it can be seen that the cell voltage versus current density curves with various operating temperatures modeled by the ANN agrees well with the experimental data at the sintering temperature of  $1025^{\circ}\text{C}$ . The operating

temperature ranges from  $625^{\circ}\text{C}$  to  $700^{\circ}\text{C}$ . The results show that the ANN model is in good agreement with the experimental data with a correlation coefficient of 99.89% and a MSE of  $6.58 \times 10^{-5}$ .

Figure 8 shows  $I$ - $V$  curves of the cells with the sintering temperature of  $1050^{\circ}\text{C}$  from the ANN and experimental data as the operating temperature changes from  $650^{\circ}\text{C}$  to  $700^{\circ}\text{C}$ . The correlation coefficient is 99.98%, and the MSE is  $1.28 \times 10^{-5}$  for this subset. The results show a good agreement between the model estimated and the experimental data.

From the results, it can be obtained that the ANN model succeeded in predicting the SOFC performance at an acceptable level of precision. It also confirms the capability of the ANN in investigating the effect of various parameters on its behavior.

**3.3. Sensitivity Analysis.** In order to identify the critical parameters and their degree of importance on the response outputs, a sensitivity analysis should be investigated. The analysis shows that the network output varies corresponding to the change of inputs and identifies the more sensitive parameters, which should be controlled precisely. The results of this analysis would also contribute deeper understanding about the model parameters for the design process.

In this study, the sensitivity analysis based on the weight matrix was chosen because of its simplicity. From the weight magnitude, several expressions have been proposed which have common properties: calculation of the product of the weights  $w_{ij}$  that connects the input neuron  $i$  and the hidden neuron  $j$  and  $v_{jk}$  that connects the hidden neuron  $j$  and the output neuron  $k$  for each of the

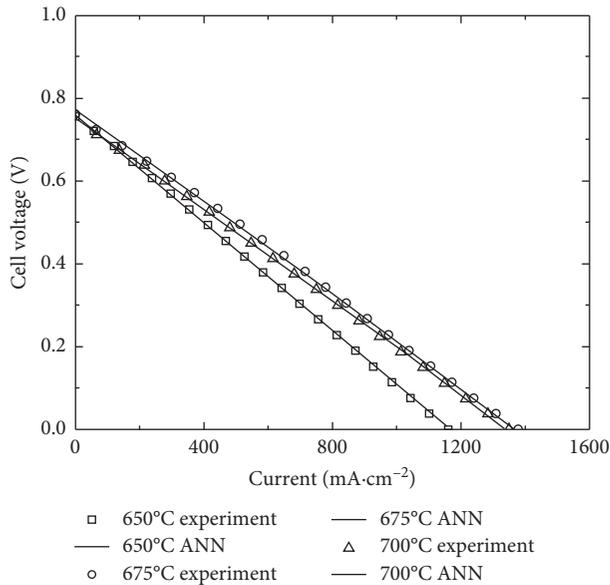


FIGURE 8: Comparison of  $I$ - $V$  curves for the cathode sintered at  $1050^{\circ}\text{C}$  and operated at different temperatures by the ANN model and experimental data.

hidden neurons of the network, which gives the sum of the calculated products. The following equation, reported by Garson [47], is widely used:

$$Q_{ik} = \frac{\sum_{j=1}^L \left( \left( w_{ij} / \sum_{r=1}^N w_{rj} \right) v_{jk} \right)}{\sum_{i=1}^N \left( \sum_{j=1}^L \left( \left( w_{ij} / \sum_{r=1}^N w_{rj} \right) v_{jk} \right) \right)}, \quad (4)$$

in which  $\sum_{r=1}^N w_{rj}$  is the sum of the connection weights between the  $N$  input neurons and the hidden neuron  $j$ .  $Q_{ik}$  denotes the effect of the input  $i$  on the output  $k$ , in relation to the other input variables.

The relative significance of each input variable on the output is presented in Figure 9. From the results, it can be obtained that the most important factor affecting the cell voltage is the sintering temperature of the BSCF cathode.

The importance of sintering temperature of the BSCF cathode was also reported in our previous study [36] or it can be seen in Figure 10. From the figure, even though the sintering temperature differs slightly, the cell power performance is significantly affected. Therefore, the sintering temperature should be precisely controlled and carefully decided in order to obtain the cell's best performance.

**3.4. Optimization Results.** From the artificial neural network modeling results, genetic algorithm was utilized to search the optimum condition for the power density. The decision parameters were the sintering temperature of the cathode, operating temperature of the furnace, and current density. The boundary constraints for the design parameters were indicated earlier in Section 2.3. The fitness function is the power density.

Figure 11 depicts the fitness values (maximum and mean) of the population versus generation. As indicated

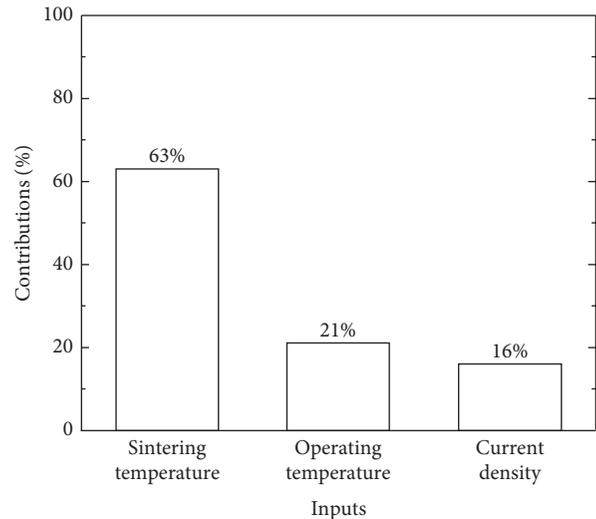


FIGURE 9: Relative contribution of input variables on cell voltage.

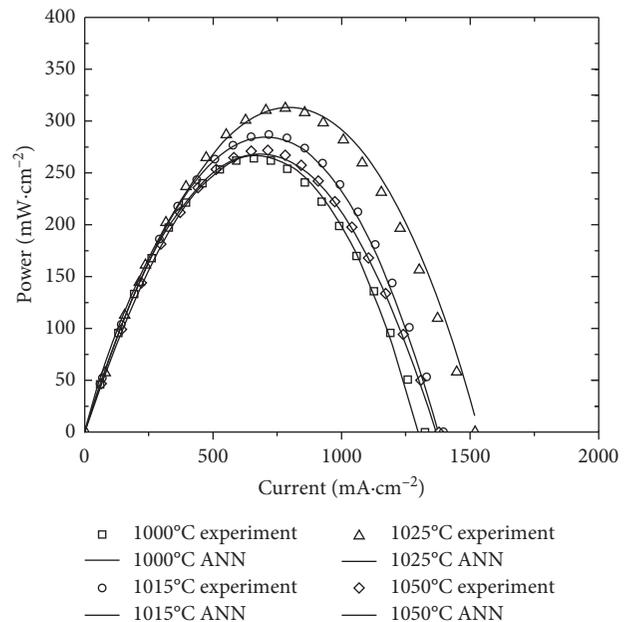


FIGURE 10: The power performance of the cell at different sintering temperatures.

in the figure, after about 20 generations, the value of fitness function attained a maximum value and then remained unchanged. After 100 generations, the maximum fuel cell power density of  $451.64 \text{ mW}/\text{cm}^2$  could be achieved at the sintering temperature of  $1005^{\circ}\text{C}$ , operating temperature of  $668^{\circ}\text{C}$ , and current density of  $777 \text{ mA}/\text{cm}^2$ .

## 4. Conclusions

In this study, an artificial neural network was successfully applied to model the behavior of a BSCF-based single-chamber solid oxide fuel cell. The ANN model can adequately predict the SOFC performance without knowledge of numerous physical, chemical, and electrochemical factors

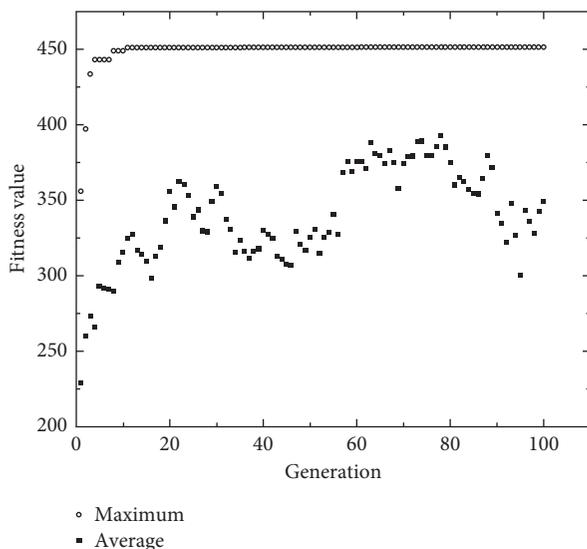


FIGURE 11: The fitness values versus generation.

and is validated with actual experimental data. The proposed network has a simple structure with one hidden layer and a small number of neurons. The prediction from the ANN model matched the experimental data with a low degree of error. From the trained ANN, the power density was estimated as fitness function, and the genetic optimization algorithm was employed to predict the optimal cell parameters such as sintering temperature of the cathode, operating temperature of the furnace, and current density of the cell. The maximum power density is  $451.64 \text{ mW/cm}^2$ , which could be achieved at the sintering temperature of  $1005^\circ\text{C}$ , operating temperature of  $668^\circ\text{C}$ , and current density of  $777 \text{ mA/cm}^2$ . The results suggested that the BSCF should be fabricated at  $1005^\circ\text{C}$ , and the button cell should be operated at  $668^\circ\text{C}$ .

### Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

### Disclosure

Part of this study (with different cathode materials-LSCF) was presented at the Third International Conference on Computational Science and Engineering in Ho Chi Minh City, Vietnam, November 2016.

### Conflicts of Interest

The authors declare that they have no conflicts of interest.

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## Research Article

# Influence of Organoclay on the Flame Retardancy and Thermal Insulation Property of Expandable Graphite/Polyurethane Foam

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The rigid polyurethane foams (RPUFs) filled with organoclay cloisite 20A and expandable graphite (EG) were prepared by the one-step expanding foam method. Flame behavior, mechanical properties, and thermal conductivity of the composites were investigated. The vertical burning test (UL-94V) and limiting oxygen index (LOI) showed that the flame retardancy was increased proportionally with the content of EG in PU composite. However, the presence of EG filler impaired the thermal insulation and the compressive strength of the composite. In this report, we proved that organoclay could improve the compressive strength, thermal insulation, and flame retardancy of EG/polyurethane composites. This work can contribute to the development of environment-friendly flame-retardant products for green growth.

## 1. Introduction

Rigid polyurethane foams (RPUFs) are commonly used in the construction industry as an insulating and soundproof barrier because of their low thermal conductivity, low density, high compression strength, and excellent adhesion [1, 2]. Additionally, RPUF can be frequently found as an insulation layer in pipes, tanks, refrigerators, boats, and aircraft [3, 4]. However, RPUFs are flammable materials and release polluted gases if burned, limiting its application [5].

The most effective and simplest method to improve the flame-retardant properties of RPUF is the addition of flame-retardant additives into the polymer matrix. The common additives include halogen, phosphorus, and nitrogen compounds [6–12]. Unfortunately, these flame-retardant

compounds generate toxic gases in the burning process which are harmful to people and the environment [13, 14].

Expandable graphite (EG) is an intumescent fire retardant material and has been widely utilized in the polyurethane matrix. When EG is exposed to a heat source, it will be expanded to a carbonaceous layer on the surface of the PU composite. This char layer prevents oxygen diffusion and mass and heat transfer between the flame and PU matrix, thus discontinuing the self-sustained combustion of the composite [15–20]. Modesti et al. [13, 16] investigated the fire behavior of low-density EG/PUF and proved that good flame-retardant composites could be acquired by increasing EG loading. However, the presence of EG reduced the compressive strength of EG/PUF composites [13, 15, 19–21]. Moreover, it was also found that the thermal

conductivity of the EG/PUF composites increased in comparison with pure PUF [13, 15, 20–24]. The higher thermal conductivity could hamper the application of PUFs as a thermal insulation material. So, it is necessary to develop novel EG/RPUF composites that meet the requirement of high flame retardancy while retaining mechanical strength and thermal insulation. Nonetheless, there have been few reports devoted to solving the problem.

Organoclay is known as a common reinforcement for polymers because of its unique properties such as nanoscale lamellar structures, high aspect ratio, and high tensile strength [25, 26]. Besides, it was also found that the flame-retardant properties of PU foam were enhanced upon the incorporation of nanoclay [27, 28]. In this work, we demonstrated that incorporation of organoclay into EG/PU composite is an effective, simple, and scalable method to improve the mechanical, thermal insulation, and flame-retardant properties of the polyurethane foams.

## 2. Materials and Methods

**2.1. Materials.** The polyol used for RPUF preparation was a polypropylene glycol with the viscosity at  $20^{\circ}\text{C} = 1500 \pm 300$  cps (MCNS Inc.) containing *n*-pentane (technical grade) as a blowing agent. The isocyanate used was 4,4'-diphenylmethane diisocyanate (MDI) with NCO % = 31% and average functionality = 2.8 (Tosoh Corporation, Japan). Additional components used for RPUF composites were expandable graphite flakes (EG): +50 mesh ( $>300\ \mu\text{m}$ ,  $\geq 75\%$  minimum), pH =  $5 \div 10$  (Sigma-Aldrich), and cloisite 20A: d-spacing (001) =  $31.5\ \text{\AA}$  (Southern Clay Products Inc., Texas, USA).

**2.2. Preparation of the Rigid Foam.** Rigid polyurethane foam was prepared by the one-step expanding foam method using cast molding. EG and cloisite 20A were dispersed into the polyol before adding isocyanate. Polyol, blowing agent, and additives were mixed and stirred together until a uniform mixture was obtained. Afterward, a certain amount of isocyanate MDI (MDI/polyol = 1.4 w/w) was added into the mixture with vigorous stirring for 10 s. The mixture was then quickly poured into a mold to produce PU foam. For the completion of the polymerization between MDI and polyol, the molds containing PU were kept in an oven at  $70^{\circ}\text{C}$  for 24 h. Finally, the PU foams were separated from the mold and the hard surface of the foams was removed. The components of the flame-retardant foam are given in Table 1.

**2.3. Characterizations.** The horizontal and vertical burning tests were carried out with the GT-MC35F-2 horizontal and vertical flame chamber, according to the standard horizontal burning test (ASTMD 635-98) and the standard vertical burning test (ASTMD 3801-96). The size of the specimen was  $130 \times 13 \times 3\ \text{mm}^3$  (length  $\times$  width  $\times$  thickness). Limiting oxygen index (LOI) was determined by a Yasuda 214 instrument on the sample whose size was  $130 \times 10 \times 10\ \text{mm}^3$  according to ASTMD 2863-97. Thermal gravimetric analysis

(TGA) was performed on a LABSYS Evo STA under air with the heating rate of  $10^{\circ}\text{C}\cdot\text{min}^{-1}$  from  $30^{\circ}\text{C}$  to  $800^{\circ}\text{C}$ . The thermal conductivity of the foams was measured with a THB-500-Transient hot bridge (Linseis) instrument according to standard DIN EN 993-15. The size of the samples was  $60 \times 40 \times 5\ \text{mm}^3$ . The sensor was sandwiched between two sheets of the sample. The compression test of the composites was taken on an Instron 3383 system, and the size of samples was  $50 \times 50 \times 50\ \text{mm}^3$  according to the standard ISO 4898. The rate of compression was  $5\ \text{mm}\cdot\text{min}^{-1}$ . The surface morphology of RPUF composites before and after burning was observed by using a Hitachi S-4800 scanning electron microscope instrument with an accelerating voltage of 5 kV at the room temperature. Transmission electron micrographs (TEM) were taken by a JEM 1400 (JEOL, Japan) of 70 nm thick layers of the composites. The TEM specimen was prepared by an epoxy embedding method at ambient temperature. The crystal structures of PU composites were determined by AD8 Advance diffractometer with scan detectors and Cu K $\alpha$  radiation ( $\lambda = 1.5406\ \text{\AA}$ ), a tube voltage of 40 kV, and a current of 40 mA.

## 3. Results and Discussion

**3.1. Flame-Retardant Properties of the Foams.** Flame-resistant properties of RPUF composites with different contents of EG and Cloisite 20A were investigated by the horizontal-vertical burning test (UL-94) and the LOI test. The results of the burning test are presented in Figure 1 and Table 2. The surface of burned composites was covered by worm-like structures of the expanded graphite char layer which could protect the PU matrix. The horizontal test (Figure 1(a) and Table 2) exhibited that the pure RPUF burned very fast and completely. By contrast, the flame of EG-filled composites was stopped in front of the first mark and the flame retardancy of the EG-containing composite reached UL94HB rating. In the case of the vertical burning test, the neat RPUF and the RPUF filled with 5 wt% EG burnt up to the holding clamp, so the samples failed according to the classification of UL94V test. When the loading of EG was 10 wt% or higher, the burning of samples stopped immediately after taking out from the flame source, implying that the sample passed V0-rating (Figure 1(b)).

The flame retardancy of PU composites was further investigated by LOI experiments (Figure 2). According to the ASTMD 2863-97 standard, a material is classified as flame retardant if the LOI value is above 23%. As indicated in Figure 2, the inclusion of EG significantly enhanced the flame retardancy of the foam, changing pure RPUF from a highly flammable material (LOI value: 20.2%) to a flame-resistant composite. The LOI value was increased proportionally with the content of EG. In particular, RPUF with 20 wt% EG showed the LOI value up to 30.5% (Table 2).

To clearly understand the flame-retardant behavior, the structure of EG/RPUF composites before and after burning test was observed by SEM images (Figure 3). Initially, EG stiff flakes with the size of 300–500  $\mu\text{m}$  was distributed at some locations in the PU matrix as shown in Figures 3(a) and 3(b).

TABLE 1: Compositions of RPUF samples.

No.	Samples	Polyol (wt %)	MDI (wt %)	Flame-retardant additives	
				EG (wt %)	Cloisite 20A (wt %)
1	Pure RPUF	41.67	58.33	—	—
2	EG5-RPUF	39.58	55.42	5	—
3	EG10-RPUF	37.50	52.50	10	—
4	EG15-RPUF	35.42	49.58	15	—
5	EG15-20A2.5-RPUF	34.38	48.12	15	2.5
6	EG15-20A5-RPUF	33.33	46.67	15	5
7	EG17.5-RPUF	34.38	48.12	17.5	—
8	EG17.5-20A2.5-RPUF	33.33	46.67	17.5	2.5
9	EG20-RPUF	33.33	46.67	20	—



FIGURE 1: Images of the samples after the horizontal (a) and vertical burning tests (b): (1) pure RPUF; (2) EG5-RPUF; (3) EG10-RPUF; (4) EG15-RPUF; (5) EG15-20A2.5-RPUF; (6) EG15-20A5-RPUF; (7) EG17.5-RPUF; (8) EG17.5-20A2.5-RPUF; (9) EG20-RPUF.

TABLE 2: Flame-retardant and physical properties of RPUF composites.

No.	Sample	HB-rating	V-rating	LOI (vol%)	Stress at 10% strain (Mpa)	Thermal conductivity ( $W \cdot m^{-1} \cdot K^{-1}$ )
1	Pure RPUF	300 mm/min. -fail	Fail	20.2	0.2464	0.028
2	EG5-RPUF	HB	Fail	23.7	0.2421	0.036
3	EG10-RPUF	HB	V-0	25.9	0.2367	0.047
4	EG15-RPUF	HB	V-0	28.1	0.2313	0.053
5	EG15-20A2.5-RPUF	HB	V-0	28.5	0.2485	0.048
6	EG15-20A5-RPUF	HB	V-0	28.7	0.2536	0.041
7	EG17.5-RPUF	HB	V-0	29.2	0.2284	0.055
8	EG17.5-20A2.5-RPUF	HB	V-0	29.4	0.2426	0.05
9	EG20-RPUF	HB	V-0	30.5	0.2217	0.058

After burning, the surface of the composite was covered entirely by spongy expanded graphite (Figures 3(c) and 3(d)). This phenomenon was also reported in the previous literature which found that EG was expanded more than 100 times its original size under higher temperatures by fast volatilization of the intercalation [29, 30]. The expanded graphite thus acted as a physical barricade which inhibited the oxygen diffusion and mass and heat transfer between the flame and PU matrix.

However, the presence of EG in PU foams increased the thermal conductivity and diminished the mechanical behavior of the composites. In order to solve this problem, we

incorporated organoclay into EG/PU composites. The LOI test indicated that, with the same EG content, the clay-additive could lead to an increase of LOI value of EG/PU foam. In particular, in comparison with EG15-RPUF (LOI value of 28.1%), EG15-20A2.5-RPUF, and EG15-20A5-RPUF, samples displayed higher LOI values of 28.5% and 28.7%, respectively. The similar behavior was observed when adding 2.5 wt% clay to EG17.5-RPUF. There may be two factors attributed to the enhancement in the LOI value of the EG/clay/RPUF composite. Firstly, clay increased the viscosity of polyol so the dispersion of the EG filler in the

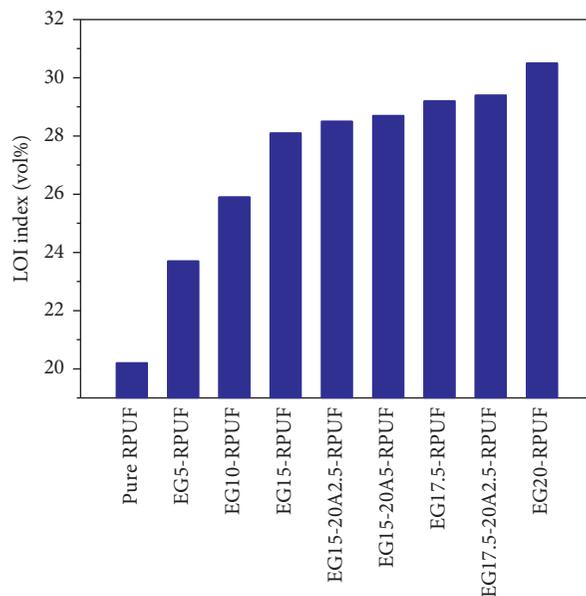


FIGURE 2: LOI values of the PU foams using different flame-retardant additives.

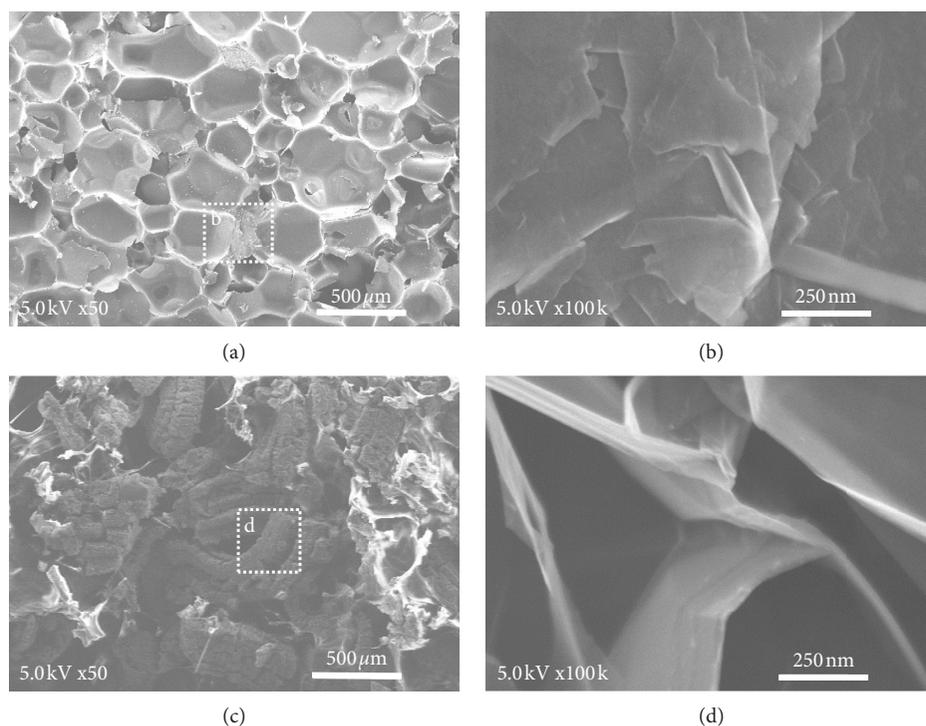


FIGURE 3: SEM micrographs of EG/RPUF composite before (a) and after (c) burning and their high magnification images (b) and (d), respectively.

polymer matrix was improved. Besides, as the burning occurs, organoclay forms a char layer on the surface of the materials, which prevents the heat transfer and the permeability of oxygen into the material as well as the evaporation of inflammable degradation products [31]. Thus, clay and EG exhibited a synergetic effect in the improvement of flame retardancy of PU composites.

**3.2. Thermal Stability of the Composites.** To better understand the role of EG and clay to the flame-retardant behavior of PU composite, the thermal stability of these composites was studied by TGA (Figure 4). The degradation of all samples consisted of two steps. The first maximum weight loss temperature,  $T_{1max}$ , of pure PU was about 330°C due to the depolycondensation of PU [32]. In the case of

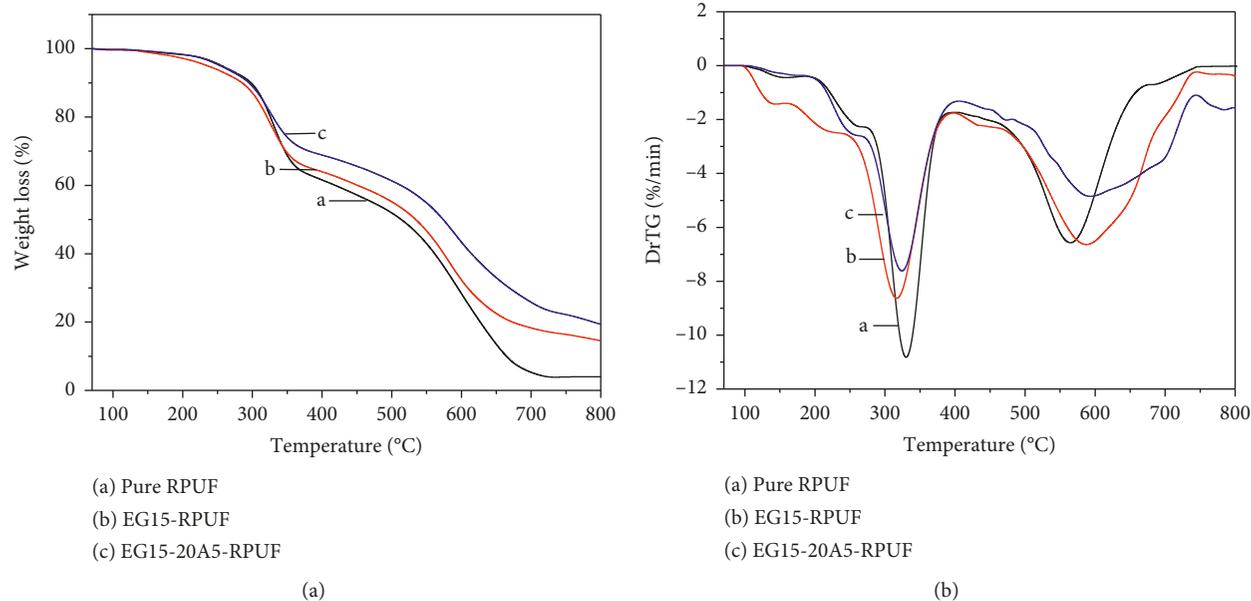


FIGURE 4: (a) TGA and (b) DTG curves of pure PU foam and the PU composites.

EG15-RPUF composite,  $T_{1max}$  decreased to 318°C that was assigned for the volatilization of the intercalated substances of EG, which started at about 300°C. For EG15-20A5-RPUF composite, the first maximum weight loss took place at 315°C, due to the decomposition of the ammonium modifier in the clay. The second maximum weight loss temperature  $T_{2max}$  of pure PU, EG15-RPUF, and EG15-20A5-RPUF was about 568, 574, and 585°C, respectively. The thermal stability of EG15-RPUF sample was slightly improved compared to the pure counterpart resulting from char formation of EG at a high temperature which slowed down the decomposition of the polymer. In the case of EG15-20A5-RPUF composite, organoclay constituted nanostructured barriers that delayed the diffusion of volatiles. As a result, the EG/clay/RPUF composite had better thermal stability than the EG/RPUF composite.

**3.3. Mechanical Properties.** To evaluate the mechanical properties of the pure RPUF and the RPUF composites, the compressive strength of the foams was measured, and the result is shown in Figure 5 and Table 2. These data showed that the presence of 15 wt% EG significantly reduced the compressive strength of RPUF from 0.2464 MPa to 0.2313 MPa at 10% strain. This may have been owing to the fact that microsized EG flakes caused the low compatibility between EG and the polyurethane polymer matrix. Furthermore, the big size of EG particles induced an inhomogeneous cell structure of the foam which affects the mechanical stability of the cellular structure. The result was consistent with previous reports [22–24].

By contrast, the compressive strength of the EG-PU foam increased upon adding clay. In particular, by adding 2.5 wt% clay to EG15-RPUF, the compressive strength of the EG15-20A2.5 composite increased notably from 0.2313 MPa

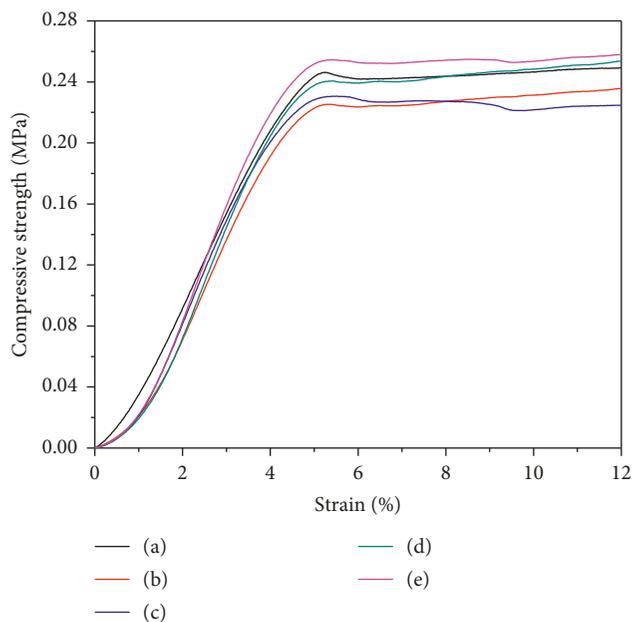


FIGURE 5: The compressive strength of the PU foams: (a) pure RPUF; (b) EG15-RPUF; (c) EG20-RPUF; (d) EG15-20A2.5-RPUF; (e) EG15-20A5-RPUF.

to 0.2485 MPa, which is comparable to neat PU foam. A further addition to 5 wt% clay, the compressive strength of EG15-20A5RPUF displayed a slight increase to 0.2536 MPa. As shown in Figure 6(a), the  $2\theta$  peak of pure clay is 2.8°. According to Bragg's Law, the calculated  $d$ -spacing ( $d_{001}$ ) of clay is 31.5 Å, which is consistent with the datasheet of Cloisite 20A provided by the supplier Southern Clay Products Inc. However, there were no distinct features in the small angle XRD pattern of the clay/EG/PU composite. The result revealed silicate layers in nanometer size were mostly

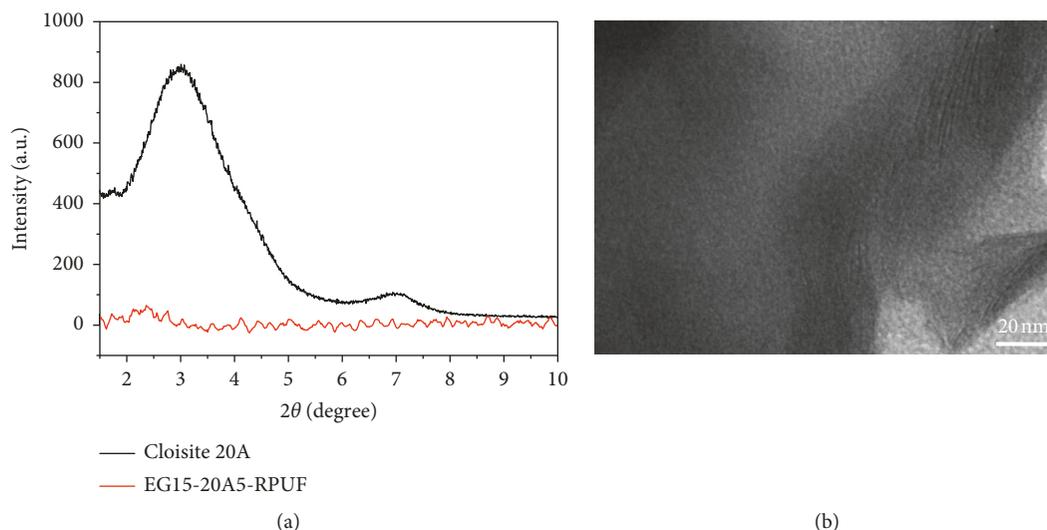


FIGURE 6: XRD patterns of clay and the RPUF composite (a) and TEM micrograph of EG15-20A5-RPUF composite (b).

exfoliated with a certain amount of intercalation in the PU matrix, which was further confirmed by TEM image (Figure 6(b)). The dispersion of exfoliated organoclay increased the interfacial interaction between clay and PU matrix that may enhance the compressive strength of the composite. In addition, the clay made polyol more viscous, which decreased the accumulation of EG, hence improving the dispersion of EG in the polymer. Thus, the presence of clay could enhance the compressive strength of the EG/PU composites.

**3.4. Thermal Conductivity.** The thermal conductivity of RPUF composites is represented in Figure 7 and Table 2. It was clear that adding EG filler to PU foam caused a significant increase in the thermal conductivity of PU composites. Adding 15 wt% EG increased the thermal conductivity of the EG15-RPUF composite by ~90%. If the content of EG was 20%, the thermal conductivity increased to  $0.058 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ , which was twice as much as pure RPUF. EG is a high thermal-conductive material, increasing the rate of heat transfer. As a result, EG impeded the insulation property of a PU foam.

The addition of clay reduced the thermal conductivity of the EG/RPUF composites. EG15-20A2.5-RPUF has a thermal conductivity of  $0.048 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ , lower than that of EG15-RPUF ( $0.053 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ ). The thermal conductivity of EG15-20A5-RPUF was further decreased by 23% compared to EG15-RPUF. It may have been due to the fact that silicate nanolayers created defects and formed effective barriers against the phonon transfer in the EG/PU matrix, therefore disrupting the thermal conducting network. The addition of organoclay seems to be a suitable method to improve the thermal insulation of the EG/RPUF composite.

#### 4. Conclusions

In this work, flame retardancy, mechanical property, and thermal conductivity of the EG/RPUF and EG/organoclay/

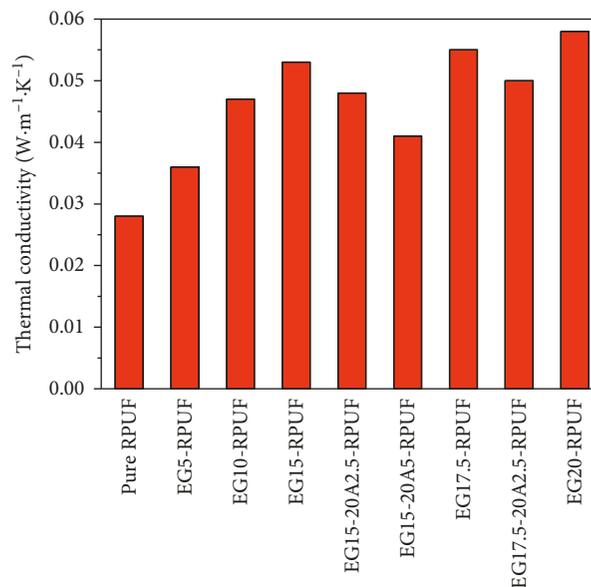


FIGURE 7: Thermal conductivity of pure RPUF and RPUF composites.

RPUF composites were investigated. Although the introduction of EG into the PU polymer matrix significantly enhanced the flame retardancy of the foam, the thermal insulation and compressive strength were reduced. Organoclay was incorporated into EG/PU composites to minimize this drawback. The LOI test indicated that, with the same EG content, the addition of organoclay could increase the LOI value of EG/PU foam. Furthermore, the compressive strength and thermal insulation of the composite were also improved in the presence of organoclay. The organoclay content of 2-3 wt% was suitable to incorporate into EG/PU composite. The combination of EG and organoclay is a potential method for the fabrication of flame-retardant PU foams. This report could make a contribution to developing eco-friendly flame-retardant PU products in the future.

## Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

## Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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## Research Article

# Kinetics, Isotherm, Thermodynamics, and Recyclability of Exfoliated Graphene-Decorated $\text{MnFe}_2\text{O}_4$ Nanocomposite Towards Congo Red Dye

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Herein, we described the use of exfoliated graphene- (EG-) decorated magnetic  $\text{MnFe}_2\text{O}_4$  nanocomposite ( $\text{EG@MnFe}_2\text{O}_4$ ) for the removal and adsorption of Congo red (CR) dye from wastewater. Firstly, the precursors (EG,  $\text{MnFe}_2\text{O}_4$ ) and  $\text{EG@MnFe}_2\text{O}_4$  were fabricated, characterized using several physical analytical techniques such as X-ray powder diffraction (XRD), scanning electron microscope (SEM), transmission electron microscopy (TEM), and  $\text{N}_2$  adsorption/desorption isotherm measurement. For the adsorption experiments, the effect of contact time (0–240 min), concentration (10–60 mg/L), solution pH (2–10), adsorbent dosage (0.03–0.07 g), and temperature (283–313 K) was rigorously studied. To elucidate the adsorption mechanism and behaviour of CR over  $\text{EG@MnFe}_2\text{O}_4$  and  $\text{MnFe}_2\text{O}_4$  adsorbents, the kinetic models (pseudo-first-order, pseudo-second-order, Elovich, and Bangham) and isotherm models (Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich) have been adopted. The kinetic results indicated that models adhered to the pseudo-second-order equation, exhibiting the chemisorption mechanism in heterogeneous phase. Meanwhile, the isotherm results revealed the adsorption of CR over  $\text{EG@MnFe}_2\text{O}_4$  obeyed the monolayer behaviour (Langmuir model) rather than multilayer behaviour (Freundlich equation) over  $\text{MnFe}_2\text{O}_4$ . The thermodynamic study also suggested that such adsorption was an endothermic and spontaneous process. With high maximum adsorption capacity (71.79 mg/g) and good recyclability (at least 4 times),  $\text{EG@MnFe}_2\text{O}_4$  can be a potential alternative for the adsorptive removal of CR dye from water.

## 1. Introduction

Research interest in nanomaterials (metalorganic frameworks, nanoparticles, porous nanomaterials, etc.) has become an integral part in the development of future technologies [1–4]. Among these, multiferroic nanomaterials (e.g.,  $\text{MFe}_2\text{O}_4$ , M

stands for transition metals) have afforded an abundance of widely practical applications, hence, giving rise in research interests, especially in environmental remediation [5, 6]. With their outstanding properties in inherent structure, such as excellent magnetism for easy separation, high chemical stability, and tunable production in both laboratory scale and

industrial scale, many studies focused on ferrites and their modified compounds on the removal and degradation of contaminants [7–9]. Among these emergent pollutants [10–12], however, synthetic dyes (e.g., Congo red, CR) have been considered as potential carcinogenic chemicals because they can contain several toxic functional groups and nondegradable skeletons including amine, imine, and benzene rings (Scheme 1), and hence, this topic has been paid much attention over the past decades [9, 13–16].

In terms of eliminating dye compounds, some works reported the outstanding removal efficiency using ferrite nanoparticles [17–19]. For example, Wojciech et al. investigated the adsorption of acid dye Acid Red 88 using magnetic  $\text{ZnFe}_2\text{O}_4$  spinel ferrite nanoparticles. With relatively high surface area ( $139\text{ m}^2/\text{g}$ ), this ferrous material has given a desirable maximum adsorption capacity, at  $111.1\text{ mg/g}$  [20]. Interestingly, Mahmoodi et al. also reported the use of sodium dodecyl sulfate (SDS) as a strongly modified agent for nickel ferrite nanoparticle (NFN) to remove a wide range of dyes including basic blue 41 (BB41), basic green 4 (BG4), and basic red 18 (BR18) with a considerable improvement in maximum adsorption capacity compared with nonmodified counterparts (control samples) [21]. These reports inspired many breakthroughs to chemically modify the ferrite structures to enhance the absorbability towards dye molecules.

Generally, the ferrites can be easily modified by coatings containing diverse functional groups, which facilitate the capture of dyes. Exfoliated graphene (EG), a typically modified material synthesizing from natural graphene, can be a brilliant candidate [22]. Although EG presents as a primary adsorbent, one of the biggest drawbacks of EG material is the difficulty to separate it from the mixture after the adsorption process due to its low density towards water [23]. Moreover, EG itself can be hardly regenerated by common methods, thus, restraining its practical applications [24]. Therefore, combination between EG and ferrites may be an optimum solution aiming at taking advantage of both attractive properties.

Herein, EG-decorated  $\text{MnFe}_2\text{O}_4$  (namely,  $\text{EG@MnFe}_2\text{O}_4$ ) as a promising adsorbent for the adsorption of CR as an emerging and typical dye was addressed. This material was firstly characterized using several analytical techniques such as X-ray powder diffraction (XRD), scanning electron microscope (SEM), Fourier-transform infrared spectroscopy (FT-IR), transmission electron microscopy (TEM), and  $\text{N}_2$  adsorption/desorption isotherm measurement and used for kinetic and isotherms studies. Moreover, a series of parameters including contact time, dosage, solution pH, and temperature were employed to compare the adsorption between  $\text{MnFe}_2\text{O}_4$  with and without EG decoration. To confirm the recyclability,  $\text{EG@MnFe}_2\text{O}_4$  could be recycled for many times. To our best knowledge, its characterization and application for CR remediation was not previously addressed; hence, more investigations need to be conducted.

## 2. Materials and Methods

**2.1. Chemicals and Instruments.** Natural graphite flake (GF) was obtained from Yen Bai province, Vietnam. The material

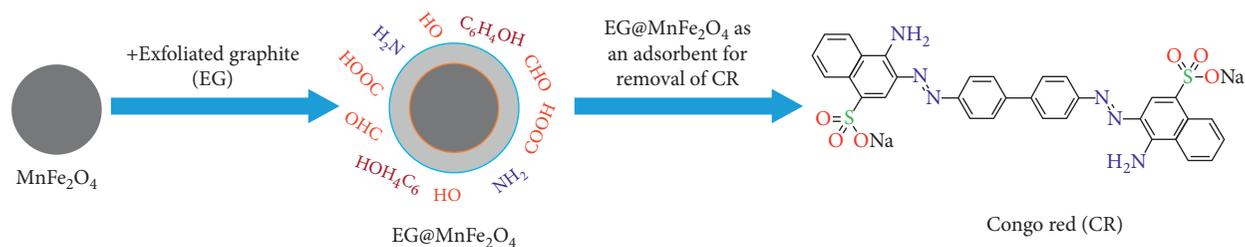
was selected to have the particle size of 60 mesh. Chemicals including Congo red,  $\text{H}_2\text{SO}_4$  (98%), and  $\text{H}_2\text{O}_2$  (30%) were purchased from Merck. The XRD profile was obtained using the D8 Advance Bruker powder diffractometer with  $\text{Cu-K}\alpha$  beams used as excitation sources. The SEM images with the magnification of 7000x were captured with the S4800 instrument (Japan) with an accelerating voltage source (15 kV). The infrared FT-IR spectra obtained by the Nicolet 6700 spectrophotometer were used to explore the characteristics of chemical bonds and functional groups. CR concentration was determined with UV-vis spectrophotometer at wavelength of 500 nm.

**2.2. Synthesis of EG.** The EG porous material was produced from the natural flaky graphite source by the microwave-irradiated method [22]. Initially, flaky graphite was carefully immersed in a mixture of  $\text{H}_2\text{SO}_4$  (98%) and  $\text{H}_2\text{O}_2$  (30%) (100:7 by volume) at room temperature during 2 hours. Next, the chemically treated solid was repeatedly washed with  $\text{H}_2\text{O}$  and neutralized by diluted NaOH solution. The exfoliation of bulky powder was performed by the microwave-irradiated oven (750 W, 10 sec). The as-received EG sample can be collected and stored for the characterization and experiments.

**2.3. Synthesis of  $\text{MnFe}_2\text{O}_4$ .** Manganese-based magnetic nanoparticle  $\text{MnFe}_2\text{O}_4$  was produced using the conventional polymerized-complex method according to our recent work [25]. Citric acid (93 g) was mixed with 140 mL of ethylene glycol and distilled water (2:5 by volume) and heated up  $80^\circ\text{C}$  under air atmosphere. Then, an amount of 0.303 g- $\text{MnCl}_2\cdot 6\text{H}_2\text{O}$  solid was poured into the above mixture and heated up at  $130^\circ\text{C}$ . After 2 hours, the polymeric resin precursor was transferred into heat-resistant furnace and heated up at  $1000^\circ\text{C}$  for 2 h and allowed to cool down at room temperature. The black as-received sample can be collected and stored for the characterization and experiments.

**2.4. Synthesis of  $\text{EG@MnFe}_2\text{O}_4$ .** The synthesis procedure was followed as reported previously [26]. A mixture of 0.7 g  $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$  and 0.25 g- $\text{Mn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$  was dissolved in 50 mL  $\text{H}_2\text{O}$ , and heated up at  $90^\circ\text{C}$  under stirring continuously. After that, 50 mL citric acid solution (0.02 M) was added dropwise slowly and stirred for 60 min. 0.8 g-EG was carefully poured into such solution, and then  $\text{NH}_3$  solution was added to reach the weakly basic solution (pH 8-9). After 30 min, a slow addition of  $\text{NH}_3$  solution for the second time into the beaker (pH 10) was employed. The mixture was dried at  $80^\circ\text{C}$  and calcined at  $700^\circ\text{C}$  during 120 min to obtain as-received sample.

**2.5. Experimental Batch.** To determine the absorbability of EG towards CR, batch experiments could be conducted by an addition of adsorbent (0.5 g/L) into 100 mL of dye solutions (20–60 mg/L). The samples were employed to agitate on the shaker table. Preliminary runs indicated that the adsorption process reached an equilibrium state during



SCHEME 1: Schematic process for the formation of EG@MnFe<sub>2</sub>O<sub>4</sub> for the removal of Congo red.

210 min. After the adsorption completion, the adsorbent was extracted from the aqueous solution using a filter syringe, while remaining concentration of dye was measured by the UV-vis spectrophotometer at 500 nm. The removal efficiency ( $H\%$ ) and adsorption capacity ( $Q$ ) was calculated on the basis of the concentrations by the following equations:

$$H(\%) = \frac{C_0 - C_e}{C_0} \cdot 100,$$

$$Q_t = \frac{C_0 - C_t}{m} \cdot V, \quad (1)$$

$$Q_e = \frac{C_0 C_e}{m} \cdot V,$$

where  $C_0$  and  $C_e$  are, respectively, the initial and equilibrium dye concentrations,  $V$  is the volume of solution, and  $m$  represents the weight of adsorbent.

### 3. Results and Discussion

#### 3.1. Structural Characterization

**3.1.1. PXRD Spectra of EG, MnFe<sub>2</sub>O<sub>4</sub>, and EG@MnFe<sub>2</sub>O<sub>4</sub> Materials.** To compare the crystallinity of EG@MnFe<sub>2</sub>O<sub>4</sub> with their precursors including EG and MnFe<sub>2</sub>O<sub>4</sub>, the PXRD was used as a means of analysis. According to the observation from Figure 1, the profile of EG material witnessed a sharp peak at 26.6°, which was highly commensurate with previous publications, proving that EG has been successfully synthesized [27]. At a glance, the figure for MnFe<sub>2</sub>O<sub>4</sub> had an apparent difference with that for EG mentioned. Indeed, there was an abundance of main peaks emerging at 24.4°, 34.0°, 36.7°, 50.0°, 54.5°, 62.5°, and 64.8°. Many works reported the same PXRD profiles of MnFe<sub>2</sub>O<sub>4</sub> by various synthesis pathways (microwave-assisted ball-milling, wet-milling, solvothermal, etc.) [28–33]. The third diffraction spectrum belongs to EG@MnFe<sub>2</sub>O<sub>4</sub>, which had the mutual patterns of EG and MnFe<sub>2</sub>O<sub>4</sub>. Accordingly, a sharp peak at 26.6° again repeated at the constant position in the spectrum of EG@MnFe<sub>2</sub>O<sub>4</sub> confirmed that the EG was successfully decorated in MnFe<sub>2</sub>O<sub>4</sub>. More interestingly, several peak traces of MnFe<sub>2</sub>O<sub>4</sub> can be observed in the spectrum of EG@MnFe<sub>2</sub>O<sub>4</sub>. However, their signal intention seems very low, mainly because the EG may coat the peripheral shell of the MnFe<sub>2</sub>O<sub>4</sub> nanoparticles. These results were totally in line with recent studies on the same structure [34–36].

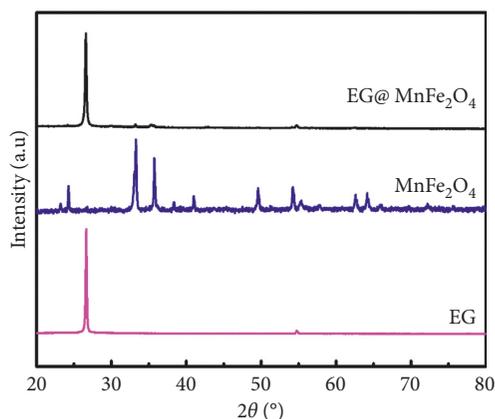


FIGURE 1: XRD spectra of EG, MnFe<sub>2</sub>O<sub>4</sub>, and EG@MnFe<sub>2</sub>O<sub>4</sub>.

**3.1.2. SEM Images of EG@MnFe<sub>2</sub>O<sub>4</sub> Materials.** To gain more understanding about the morphological properties of EG@MnFe<sub>2</sub>O<sub>4</sub> material, the SEM technique can be used. Based on the SEM images in Figure 2, which showed at two various magnification levels (50 and 100 μm), it is evident that the EG@MnFe<sub>2</sub>O<sub>4</sub> structure exposed a heterogeneous, highly defective, amorphous morphology. This phenomenon may be due to the effect of a full decoration by EG nanosheets, which MnFe<sub>2</sub>O<sub>4</sub> is dispersed on the flexible graphene sheet, resulting in the typical kind of rough surface of EG@MnFe<sub>2</sub>O<sub>4</sub>. Kalimuthu also reported the same morphology of MnFe<sub>2</sub>O<sub>4</sub>/graphene produced by eco-friendly hydrothermal and in situ polymerization method, offering a deep degree of wrinkled and unsmooth surface [37].

**3.1.3. TEM Images of EG and EG@MnFe<sub>2</sub>O<sub>4</sub> Materials.** TEM technique is necessary to gain insight into inherent structure of exfoliated graphite and exfoliated graphite decorated MnFe<sub>2</sub>O<sub>4</sub> materials. Figure 3 illustrates the SEM images of above materials at various scales 1 μm and 200 nm. Figures 3(a) and 3(b) show the highly opaque towards electron beams, and hence, implying that the EG obtained a thick structure [38]. In contrast, the structure of EG@MnFe<sub>2</sub>O<sub>4</sub> in Figures 3(c) and 3(d) indicates a considerable difference from the EG structure. As illustrated, the existence of black spots in the opaque EG region can be due to the presence of MnFe<sub>2</sub>O<sub>4</sub> particles, demonstrating the fact that MnFe<sub>2</sub>O<sub>4</sub> particles were decorated by the EG sheets [39].

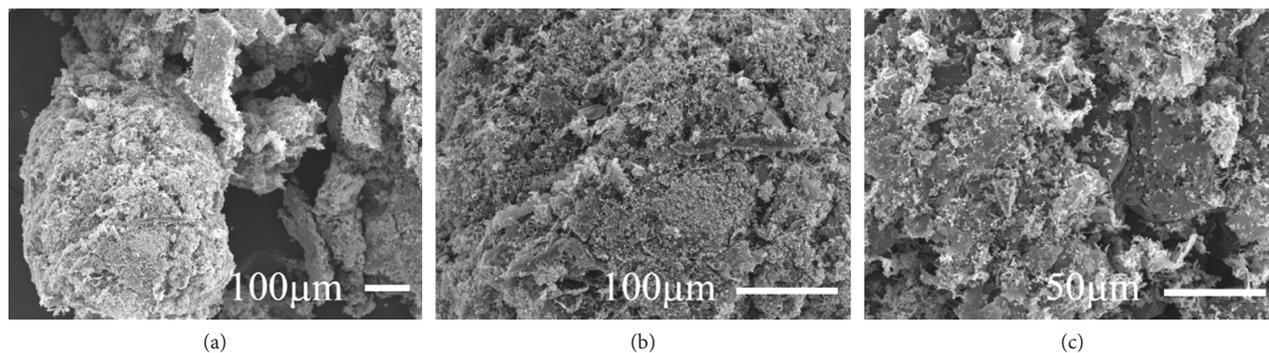


FIGURE 2: SEM images of EG@MnFe<sub>2</sub>O<sub>4</sub>.

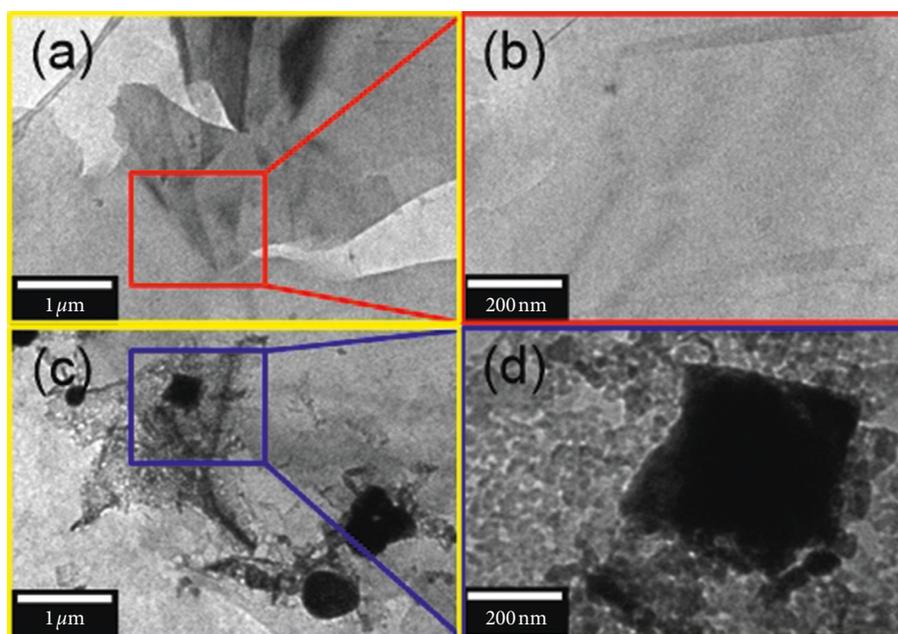


FIGURE 3: TEM images of EG (a, b) and EG@MnFe<sub>2</sub>O<sub>4</sub> (c, d) materials.

**3.1.4. N<sub>2</sub> Adsorption/Desorption Isotherm Measurement of EG and EG@MnFe<sub>2</sub>O<sub>4</sub>.** To characterize more properties of the inherent structure, the nitrogen adsorption/desorption isotherm of EG and EG@MnFe<sub>2</sub>O<sub>4</sub> can be measured at 77 K and is illustrated in Figure 4(a). Generally, these isotherms mostly exhibit no hysteresis loops, representing a type II isotherm, means that both they were likely to offer a low degree of porosity. Indeed, the surface area values calculated by BET theory and pore volume of EG and EG@MnFe<sub>2</sub>O<sub>4</sub> were relatively low, but those of EG were slightly higher than those of EG@MnFe<sub>2</sub>O<sub>4</sub> composite, at 33.0 m<sup>2</sup>/g, 0.1299 cm<sup>3</sup>/g compared with 40.95 m<sup>2</sup>/g, and 0.1559 cm<sup>3</sup>/g, respectively. These results can be due to the effect of aggregation under magnetism of MnFe<sub>2</sub>O<sub>4</sub>, resulting in the depletion in porosity in EG@MnFe<sub>2</sub>O<sub>4</sub> [40, 41]. Meanwhile, pore size distribution plots of both materials in Figure 4(b) also show the existence of both micropore (<2 nm) and mesopore (2–50 nm) in their structures.

**3.1.5. EDS Mapping Spectrum of EG@MnFe<sub>2</sub>O<sub>4</sub>.** EDS mapping technique plays an important role in identifying how the components of EG@MnFe<sub>2</sub>O<sub>4</sub> are included. Herein, Figure 5 shows the composition of elements existed in EG@MnFe<sub>2</sub>O<sub>4</sub>, which mainly consisted of carbon, iron, oxygen, and manganese. Especially, the mean content of iron in EG@MnFe<sub>2</sub>O<sub>4</sub> can be measured, at 6.4%. In addition, the saturation magnetization value of EG@MnFe<sub>2</sub>O<sub>4</sub> was found to be 1.5 emu/g, suggesting that EG@MnFe<sub>2</sub>O<sub>4</sub> is possibly eligible to separate from an aqueous solution using a simple magnet [42, 43]. Consequently, the EG@MnFe<sub>2</sub>O<sub>4</sub> structure obtained a combination of EG and MnFe<sub>2</sub>O<sub>4</sub> components [34–36].

### 3.2. Adsorption Studies

**3.2.1. Effect of pH.** Theoretically, the pH is one of the most influential parameters in any adsorption process, because

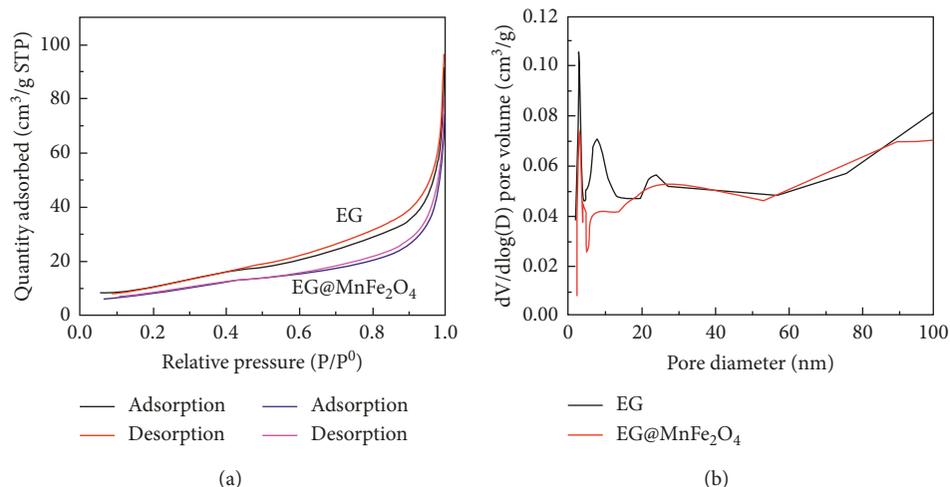


FIGURE 4: N<sub>2</sub> adsorption-desorption isotherm measurement (a) and pore size distribution (b) plots of EG and EG@MnFe<sub>2</sub>O<sub>4</sub> materials.

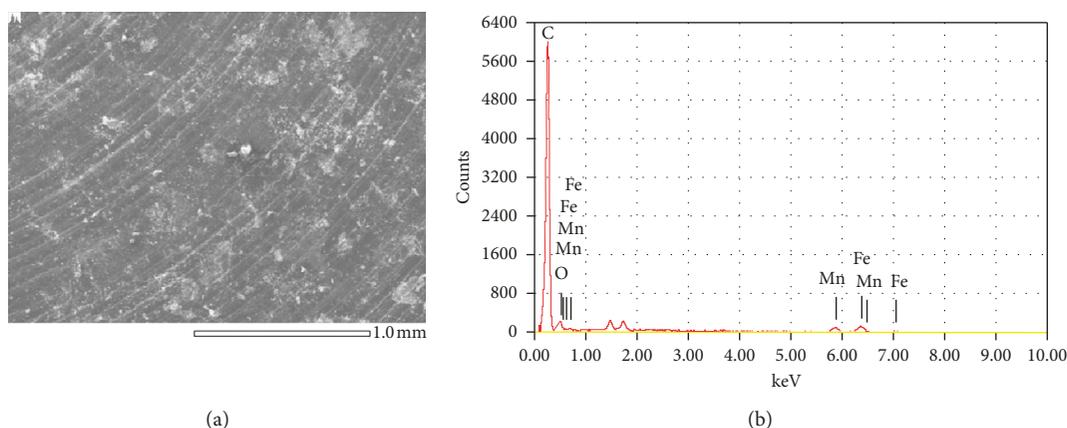


FIGURE 5: EDS mapping spectrum of EG@MnFe<sub>2</sub>O<sub>4</sub>.

the acidic, neutral, or basic solutions affect the charge natures (e.g., anionic, cationic, and zwitterionic) of adsorbate molecules and surface of adsorbent [44–48]. To compare the difference between MnFe<sub>2</sub>O<sub>4</sub> and EG@MnFe<sub>2</sub>O<sub>4</sub> materials in terms of CR adsorption efficiency, a range of pH from 2 to 12, which can be tuned by alkaline and acidic solutions, was investigated (Figure 6).

At a glance, it is evident that the adsorption uptake by EG@MnFe<sub>2</sub>O<sub>4</sub> was remarkably higher than that by MnFe<sub>2</sub>O<sub>4</sub> at any pH values. In detail, the highest adsorption capacity towards CR onto EG@MnFe<sub>2</sub>O<sub>4</sub> could attain at nearly 66 mg/g under the pH condition of 6.0, while the optimal pH figure for MnFe<sub>2</sub>O<sub>4</sub> was determined at 4.0, giving a capacity of only 35.5 mg/g. Enhancing the CR amount absorbed on EG@MnFe<sub>2</sub>O<sub>4</sub> may be contributed by the component of EG coating, which contains functional groups essential for the adsorption. In our previous reports, we demonstrated the role of surface functional groups in improving the adsorption capacity of adsorbate [49, 50]. On the other hand, the CR adsorption of EG@MnFe<sub>2</sub>O<sub>4</sub> by pH parameter seems to slightly drop, about 50 mg/g at the relatively weak acidic or basic media. By contrast, the adsorption of CR by

MnFe<sub>2</sub>O<sub>4</sub> at neutral or strongly basic solution was highly likely to be uncondusive. These results suggested that the decoration of EG may be a considerable advantage because EG@MnFe<sub>2</sub>O<sub>4</sub> material can obtain higher uptake at a harsher adsorption condition (e.g., at very strong basic/acidic solutions) in comparison to its precursor MnFe<sub>2</sub>O<sub>4</sub>. Based on the above results and analysis, we decided to conduct the next experiments under the pH condition at 4 and 6 for EG@MnFe<sub>2</sub>O<sub>4</sub> and MnFe<sub>2</sub>O<sub>4</sub> as adsorbents, respectively.

**3.2.2. Effect of Dosage.** Optimizing the dosage of materials is of significance to boost the cost-effectiveness in any treatment process [51]. Herein, we investigated a series of dosage by adding the amount (0.03–0.07 g) of EG@MnFe<sub>2</sub>O<sub>4</sub> (a) and MnFe<sub>2</sub>O<sub>4</sub> into 100 mL CR solution at the initial concentration of 60 mg/L under room temperature. After that, the concentration residuals were determined by the spectroscopy method. The effect of dosage on CR adsorption capacity was plotted and is shown in Figure 7. It is evident that the adsorption uptake by EG@MnFe<sub>2</sub>O<sub>4</sub> was

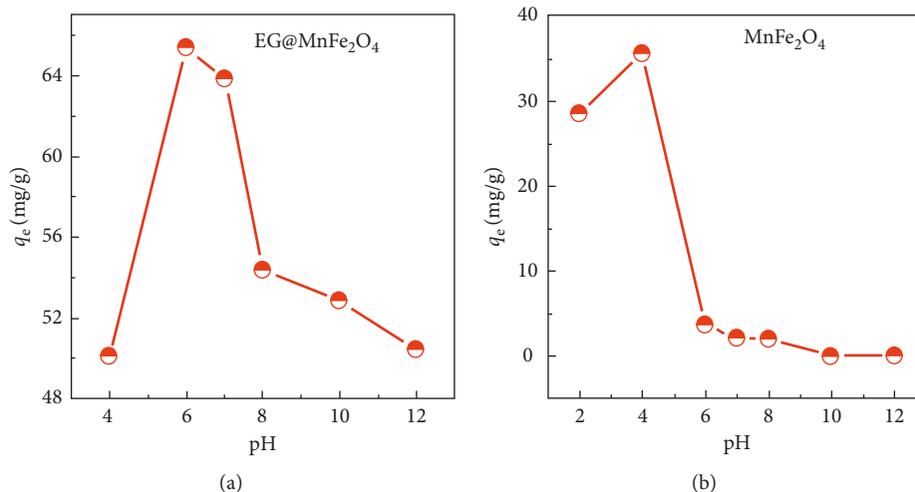


FIGURE 6: Effect of pH on the adsorption efficiency of CR over the EG@MnFe<sub>2</sub>O<sub>4</sub> (a) and MnFe<sub>2</sub>O<sub>4</sub> (b) materials. Experimental conditions included adsorbent dose of 0.5 g/L, solution volume of 100 mL, and dye concentration of 60 mg/L at various pH (2–12). Experiments were run at room temperature (25°C) during 210 min.

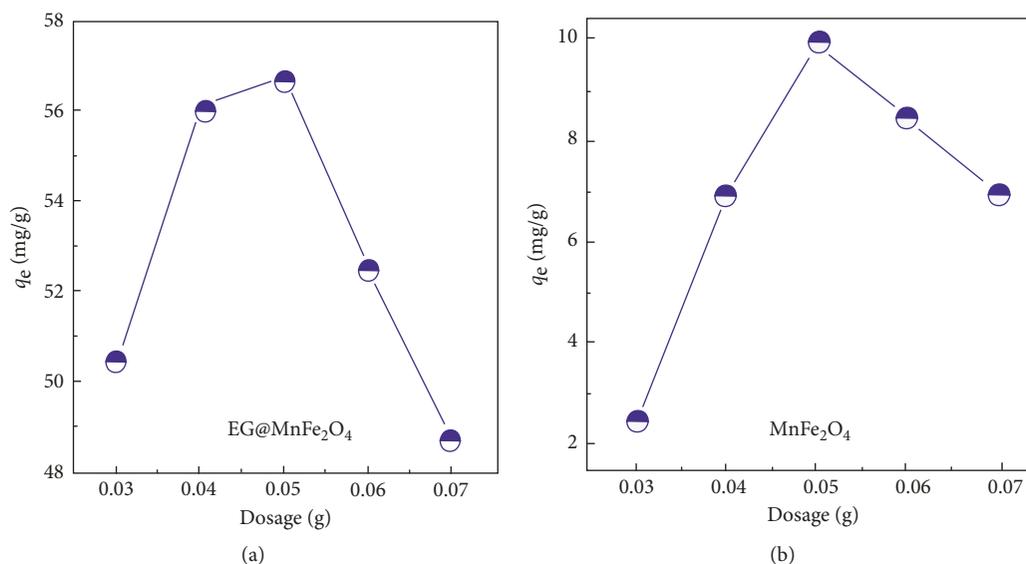


FIGURE 7: Effect of dosage the adsorption efficiency of CR over the EG@MnFe<sub>2</sub>O<sub>4</sub> (a) and MnFe<sub>2</sub>O<sub>4</sub> (b) materials. Experimental conditions included solution volume of 100 mL and dye concentration of 60 mg/L at pH 4 for MnFe<sub>2</sub>O<sub>4</sub> and pH 6 for EG@MnFe<sub>2</sub>O<sub>4</sub>. Experiments were run at room temperature (25°C) during 210 min.

remarkably higher than that by MnFe<sub>2</sub>O<sub>4</sub> at any dosage values. Moreover, larger amount of adsorbents (0.03–0.05 g for both EG@MnFe<sub>2</sub>O<sub>4</sub> and MnFe<sub>2</sub>O<sub>4</sub>) led to an enhancement in CR adsorption capacity, reached the peaks of capacity at 57 and 10 mg/g, respectively. However, the adsorption efficiency rapidly dropped down until pouring higher dosage of 0.05 g. This phenomenon may be mainly due to larger amount of adsorbents resulting in hampering the mass transfer of CR molecules into the pores of materials and changing the physical properties of solution (e.g., viscosity) [52, 53]. Consequently, the optimal dosage, which compromises all factors affecting the adsorption uptake, was found at 0.05 g.

**3.2.3. Effect of Contact Time and Adsorption Kinetics.** According to the optimized conditions obtained from Figures 6 and 7, we carried out the kinetic experiments to investigate the influence of contact time on adsorbability towards CR of EG@MnFe<sub>2</sub>O<sub>4</sub> and MnFe<sub>2</sub>O<sub>4</sub> at various concentrations (20–60 mg/L). Figure 8(a) shows the plots of the adsorption capacity ( $Q_t$ , mg/g) against contact time ( $t$ , min). It is obvious that CR dye over EG@MnFe<sub>2</sub>O<sub>4</sub> was rapidly absorbed during the first 60 minutes and steadily proceeded until the process became equilibrium. At the opposite trend, the plot in Figure 8(b) for MnFe<sub>2</sub>O<sub>4</sub> showed a relatively gradual increase in adsorption capacity, in which adsorption at 50 mg/L gave the better adsorption results than others.

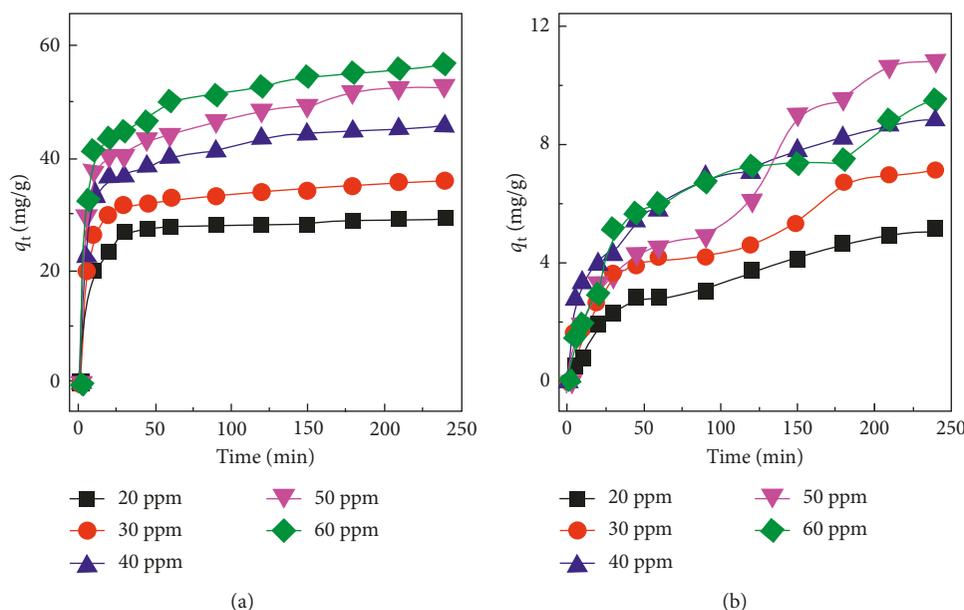


FIGURE 8: Effect of material dosage on CR adsorption capacity onto EG@MnFe<sub>2</sub>O<sub>4</sub> (a) and MnFe<sub>2</sub>O<sub>4</sub> (b). Experimental conditions: solution volume of 100 mL, and dye concentrations of 20–60 mg/L at pH 4 for MnFe<sub>2</sub>O<sub>4</sub> and pH 6 for EG@MnFe<sub>2</sub>O<sub>4</sub>. Experiments were run at room temperature (25°C) during the period of 0–240 min.

To gain more insight into the profound effect of contact time, an array of commonplace kinetic equations (e.g., pseudo-first-order, pseudo-second-order, Elovich, and Bangham) were adopted and are shown in Figures 9 and 10 [52, 53]. After evaluating these models based on the coefficients of determination ( $R^2$ ), adsorption mechanism in CR/EG@MnFe<sub>2</sub>O<sub>4</sub> and CR/MnFe<sub>2</sub>O<sub>4</sub> systems can be elucidated. Experimental data were transformed onto a mathematically linear form, which can be fitted by using the Origin Lab® version 9.0 software. Among the most prevalent kinetic models, the pseudo-first-order and pseudo-second-order models were applied herein. While equation (2) tends to explain the rate of adsorption relating to the number of unabsorbed sites from EG@MnFe<sub>2</sub>O<sub>4</sub> and MnFe<sub>2</sub>O<sub>4</sub>, equation (3) describes the adsorption of CR over these magnetic nanocomposites through a chemisorption mechanism controlled by functional groups available on the surface of adsorbents [54].

$$\log(q_e - q_t) = \log q_e - \frac{k_1 \cdot t}{2.303}, \quad (2)$$

where  $k_1$  (1/min) is defined as the pseudo-first-order adsorption rate constant,  $q_t$  (mg/g) is defined as the adsorption capacity at the period time  $t$  (min), and  $q_e$  (mg/g) is defined as equilibrium adsorption capacity at the equilibrium period (min).

$$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{t}{q_e}, \quad (3)$$

$$H = k_2 \cdot q_e^2, \quad (4)$$

where  $k_2$  (g/mg min) is defined as the pseudo-second-order adsorption constant rate and  $H$  (mg/g min) is defined as initial adsorption rate (equation (4)).

Tables 1 and 2 show the parameters of these models and their respective values at five CR concentrations (20, 30, 40, 50, and 60 mg/L) by over EG@MnFe<sub>2</sub>O<sub>4</sub> and MnFe<sub>2</sub>O<sub>4</sub>, respectively. According to Table 1, which listed kinetic parameters of the CR adsorption models over EG@MnFe<sub>2</sub>O<sub>4</sub>, the coefficients of determination  $R^2$  for pseudo-second-order model (0.9987–0.9997) at all CR concentrations were far higher than those for pseudo-first-order model (0.8396–0.9749), indicating that the predicted data were well fitted with experimental data. This was also supported by Figures 9(a) and 9(b), which experimental data were depicted by the models. It is evident that the data points distributed well on the linear lines of pseudo-second-order model rather than the pseudo-first-order model. At the same trend for the CR adsorption models over MnFe<sub>2</sub>O<sub>4</sub>, Table 2 and Figures 10(a) and 10(b) show excellent fitness with  $R^2$  (0.8234–0.9706) better than the others (0.6957–0.9672). Therefore, the adsorption of CR over both adsorbents obeyed the pseudo-second-order model with the dominance of chemisorption process via electrostatic attraction between adsorbent and adsorbate, while the other tends to be ineligible to explain the adsorption mechanisms. Ali et al. also reported the lower fitness of pseudo-first-order model in describing the adsorption mechanism [55]. Liu et al. proved the role of the surface functional groups in enhancing the adsorbability on modified activated carbon [56]. More interestingly, based on the values of  $Q_2$ , the adsorption of CR over EG@MnFe<sub>2</sub>O<sub>4</sub> (29.61–57.54 mg/g) was observed to be so far higher than that over MnFe<sub>2</sub>O<sub>4</sub> (6.34–18.19 mg/g).

Otherwise, other two equations including (Elovich and Bangham) can be used to assess the adsorption kinetic of CR over EG@MnFe<sub>2</sub>O<sub>4</sub> and MnFe<sub>2</sub>O<sub>4</sub>. In detail, the Elovich equation (equation (5)) assumes that the heterogeneous

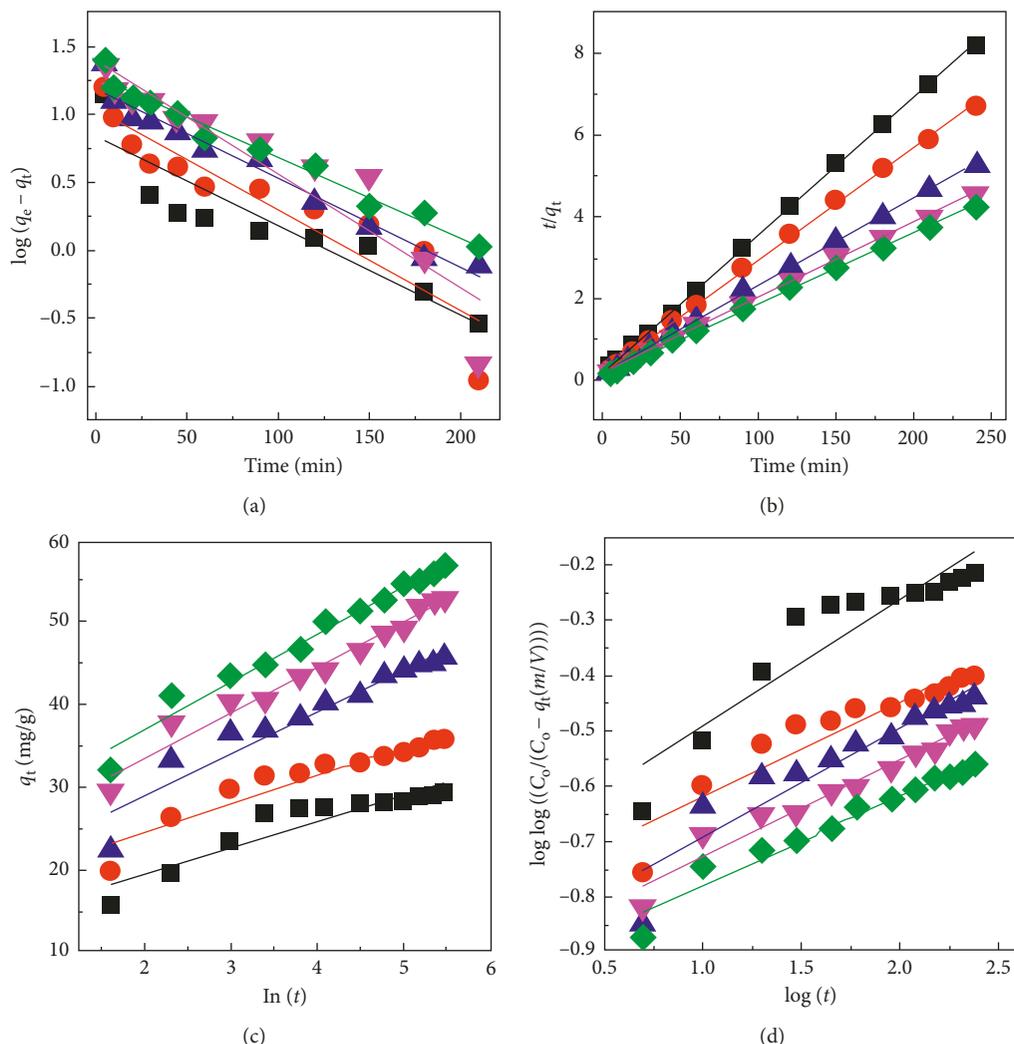


FIGURE 9: Linear plots of kinetic models: (a) pseudo-first-order, (b) pseudo-second-order, (c) Elovich, and (d) Bangham for the adsorption of CR over EG@MnFe<sub>2</sub>O<sub>4</sub>.

diffusion towards gases on heterogeneous surfaces or liquid/gas phase is related to the reaction rate and diffusion factor. Meanwhile, the Bangham equation (equation (6)) is typical for intraparticle diffusion mechanism of CR molecules over EG@MnFe<sub>2</sub>O<sub>4</sub> and MnFe<sub>2</sub>O<sub>4</sub> materials at room temperature. These equations can be described as follows:

$$Q_t = \frac{1}{\beta} \cdot \ln(\alpha \cdot \beta) + \frac{1}{\beta} \cdot \ln(t), \quad (5)$$

where  $\alpha$  (mg/g) and  $\beta$  (g/mg) are defined as adsorption and desorption rates of CR molecules over EG@MnFe<sub>2</sub>O<sub>4</sub> and MnFe<sub>2</sub>O<sub>4</sub>.

$$\log \log \left( \frac{VC_o}{VC_o - Q_t \cdot m} \right) = \log \left( \frac{k_B}{2.303 V} \right) + \alpha_B \cdot \log(t), \quad (6)$$

where  $k_B$  is defined as the Bangham equation constant and  $m$  (g) and  $V$  (mL) are defined as dosage and volume of adsorbent and solution, respectively.

According to the results from Table 1, all kinetic data by Elovich model fitted well with the experimental data due to their better goodness ( $R^2 = 0.8427-0.9705$ ) rather than those by Bangham model ( $R^2 = 0.8453-0.9512$ ), revealing the heterogeneous diffusion of CR over EG@MnFe<sub>2</sub>O<sub>4</sub>. Figures 9(c) and 9(d) were also eligible to support these results since the data points were distributed well on the linear lines of Elovich model. For analysing the adsorption data of CR onto MnFe<sub>2</sub>O<sub>4</sub> via the Elovich and Bangham models, however, Figures 10(c) and 10(d) indicate the former model (0.9272–0.9901) was only better fitted with the adsorption of CR at concentrations 30–50 mg/L than the latter (0.8007–0.9616). For observation with more detail in Table 2, the CR adsorption rates ( $\alpha$ , mg/g min) were extremely higher than CR desorption rates ( $\beta$ , g/mg) onto EG@MnFe<sub>2</sub>O<sub>4</sub>, while the figures for MnFe<sub>2</sub>O<sub>4</sub> present the lower difference. This therefore follows that the adsorption of CR over EG@MnFe<sub>2</sub>O<sub>4</sub> was more inclining to be favourable than over MnFe<sub>2</sub>O<sub>4</sub>.

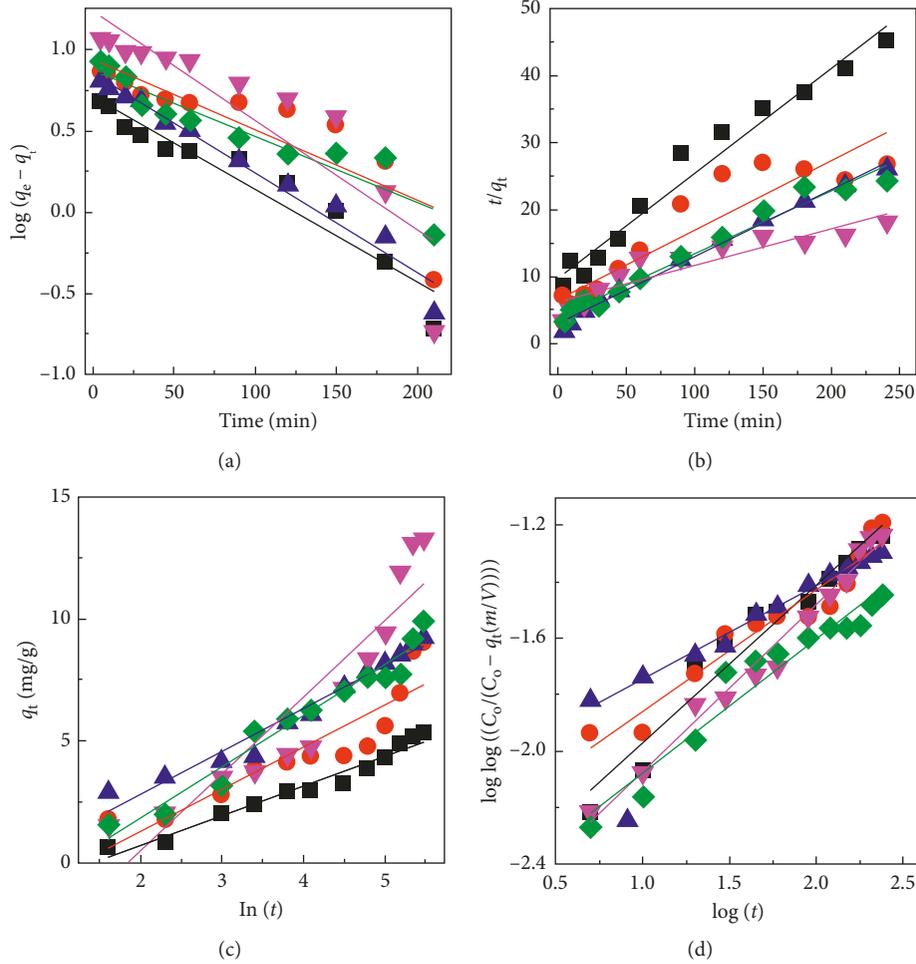


FIGURE 10: Kinetic plots of kinetic models: (a) pseudo-first-order, (b) pseudo-second-order, (c) Elovich, and (d) Bangham for the adsorption of CR over  $\text{MnFe}_2\text{O}_4$ .

TABLE 1: Kinetic parameters of the CR adsorption models over  $\text{EG@MnFe}_2\text{O}_4$ .

Kinetic models	Parameters	Concentration (mg/L)				
		20	30	40	50	60
Pseudo-first-order	$k_1$ ( $\text{min}^{-1}/(\text{mg/L})^{1/n}$ )	0.0152	0.01695	0.01519	0.01920	0.01365
	$Q_1$ (mg/g)	6.92	10.82	15.43	24.71	18.98
	$R^2$	0.8396	0.8380	0.9635	0.8622	0.9749
Pseudo-second-order	$k_2 10^4$ ( $\text{g}/(\text{mg}\cdot\text{min})$ )	1.838	1.181	0.738	0.581	0.404
	$Q_2$ (mg/g)	29.61	36.10	46.51	53.82	57.54
	$H = k_2 Q_2^2$	6.2065	6.4960	6.2657	5.914	7.471
	$R^2$	0.9997	0.9992	0.9991	0.9974	0.9987
Elovich	$\beta$ (g/mg)	0.32	0.29	0.20	0.18	0.17
	$\alpha$ ( $\text{mg}/(\text{g}\cdot\text{min})$ )	214.27	597.31	210.61	346.76	477.96
	$R^2$	0.8489	0.8870	0.9128	0.9683	0.9705
Bangham	$k_B$ ( $\text{mL}/(\text{g}\cdot\text{L})$ )	0.0440	0.0373	0.0297	0.0289	0.0263
	$\alpha_B$	0.2280	0.1717	0.1974	0.1742	0.1631
	$R^2$	0.8453	0.8578	0.8707	0.9571	0.9512

3.2.4. *Effect of Concentration and Adsorption Isotherms.* The isotherm models play a crucial role in better understanding the correlation between equilibrium concentration and adsorption capacity in liquid/solid phase at a constant temperature [57]. Several common isotherm

equations including Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich (D–R) can be used to investigate such relationship [58–61]. To conduct adsorption isotherm investigation, the initial concentration of CR was in the range from 20 to 60 mg/L. The plots of equilibrium

TABLE 2: Kinetic parameters of the CR adsorption models over MnFe<sub>2</sub>O<sub>4</sub>.

Kinetic models	Parameters	Concentration (mg/L)				
		20	30	40	50	60
Pseudo-first-order	$k_1$ (min <sup>-1</sup> /(mg/L) <sup>1/n</sup> )	0.013	0.010	0.014	0.016	0.009
	$Q_1$ (mg/g)	5.12	8.67	7.13	17.31	7.42
	$R^2$	0.9187	0.6957	0.9672	0.7726	0.8762
Pseudo-second-order	$k_2$ (g/(mg·min))	0.238	0.07	0.03	0.019	0.035
	$Q_2$ (mg/g)	6.34	9.63	10.00	18.19	10.57
	$H = k_2 Q_2^2$	9.57	6.52	2.94	6.14	3.92
	$R^2$	0.9663	0.8234	0.9882	0.8312	0.9706
Elovich	$\beta$ (g/mg)	0.82	0.58	0.57	0.32	0.48
	$\alpha$ (mg/(g·min))	2.9	4.9	1.2	0.50	0.67
	$R^2$	0.9592	0.8007	0.9616	0.8472	0.9558
Bangham	$k_B 10^4$ (mL/(g·L))	6.82	1.17	1.96	5.01	6.39
	$\alpha_B$	0.559	0.434	0.327	0.590	0.475
	$R^2$	0.9439	0.9272	0.9901	0.9803	0.9333

adsorption capacity against equilibrium concentration are afforded to describe the mentioned models. In detail, the definition of four isotherms can be described as follows. Firstly, the Langmuir equation (equation (7)) assumes that the adsorption of CR molecules onto EG@MnFe<sub>2</sub>O<sub>4</sub> and MnFe<sub>2</sub>O<sub>4</sub> surface tends to reach the monolayer adsorption behaviour. This process may be caused by dynamically balancing the relative rates of adsorption/desorption without lateral interaction of CR molecules [62].

$$\frac{1}{Q_e} = \left( \frac{1}{Q_m K_L} \right) \frac{1}{C_e} + \frac{1}{Q_m}, \quad (7)$$

$$R_L = \frac{1}{1 + K_L C_e}, \quad (8)$$

where  $Q_e$  (mg/g),  $Q_m$  (mg/g), and  $C_e$  (mg/L) are defined as equilibrium adsorption capacity, maximum adsorption capacity, and equilibrium CR concentration, respectively.  $K_L$  (L/mg) is defined as Langmuir's constant [63].  $R_L$  is a separate parameter and can be defined by equation (8). Based on the magnitude of  $R_L$  parameter, there are four kinds of adsorption processes: " $R_L$  is larger than 1.0" referring to unfavourable process, " $R_L$  is as equal as 1.0" referring to linear process, " $R_L$  is in range from 0 to 1.0" referring to favourable process, and " $R_L$  is as equal as 0" referring to irreversible process [64]. In addition, describing the multilayer adsorption behaviour is based on the Freundlich isotherm (equation (9)). This model proposes that the adsorption process occurs on heterogenous phase surfaces without any uniform distribution of heat of energies.

$$\ln Q_e = \ln K_F + \frac{1}{n} \ln C_e, \quad (9)$$

where  $K_F$  (mg/g) (L/mg) and  $1/n$  are Freundlich's constant and exponent of nonlinearity, respectively, which can be determined from the intercept and slope of the Freundlich equation. Moreover,  $1/n$  value shows the linearity of adsorption or the degree of curvature of the isotherms, and hence, its magnitude in the range from 0.1 to 0.5 indicates

the good favourability of the adsorption of CR over EG@MnFe<sub>2</sub>O<sub>4</sub> and MnFe<sub>2</sub>O<sub>4</sub>. One of the most useful isotherm models is the Temkin equation (equation (10)), which serves to describe the influence of indirect interactions between CR molecules and "adsorption sites" of EG@MnFe<sub>2</sub>O<sub>4</sub> and MnFe<sub>2</sub>O<sub>4</sub> adsorbents [65].

$$Q_e = B_T \ln K_T + B_T \ln C_e, \quad (10)$$

$$B_T = \frac{RT}{b}, \quad (11)$$

where  $B_T$ ,  $K_T$  (L/g), and  $b$  (J/mol) are determined from slope and intercept from equations (10) and (11).  $R$  is the ideal gas constant (8.314 J/mol·K). Finally, the Dubinin-Radushkevich (D-R) isotherm (equations (12)) is used to explain the state of chemical/physical adsorption with D-R activity coefficient  $B$  (mol<sup>2</sup>/kJ<sup>2</sup>) and adsorption capacity  $Q_m$  (mg/g), Polanyi potential  $\epsilon$  (kJ/mol), and energy of adsorption  $E$  (kJ/mol), which can be calculated from equations (13) and (14):

$$\ln q_e = \ln Q_m - B\epsilon^2, \quad (12)$$

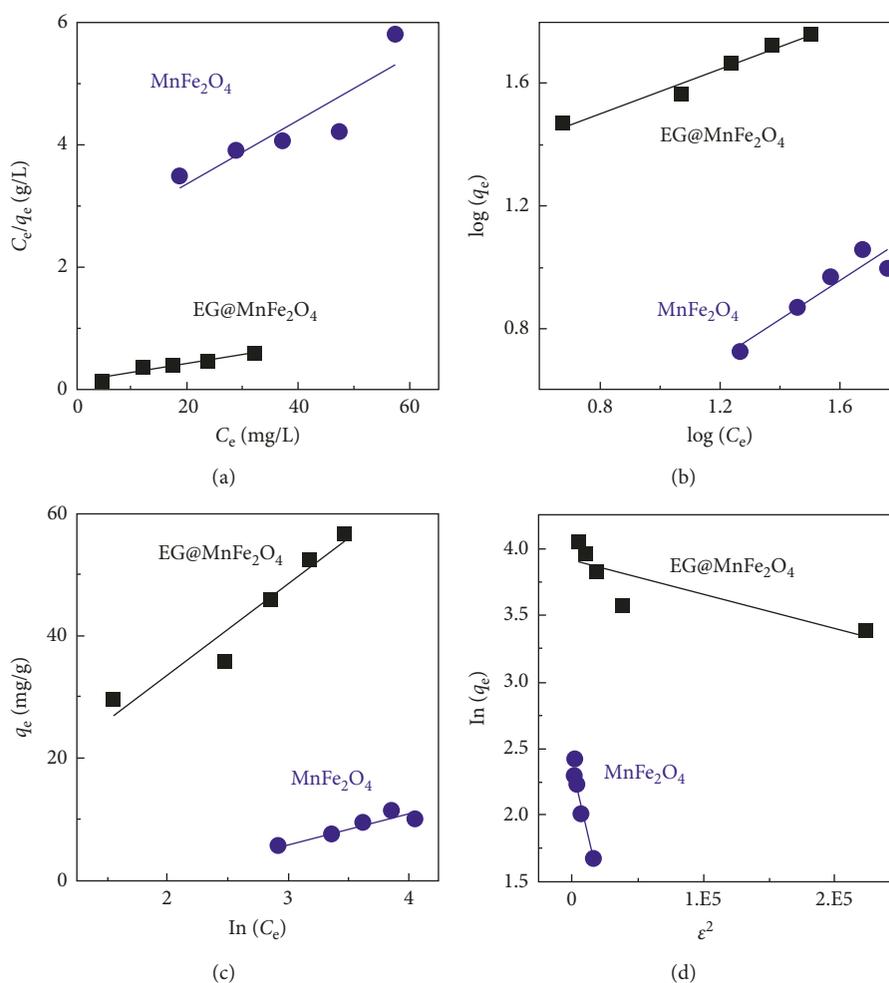
$$\epsilon = RT \ln \left( 1 + \frac{1}{C_e} \right), \quad (13)$$

$$E = \frac{1}{\sqrt{-2B}}, \quad (14)$$

Table 3 lists the parameters, values, and  $R^2$  of isotherm models for the adsorption of CR, and Figure 11 shows linear plots of isotherm models including Langmuir, Freundlich, Temkin, and D-R. It is clear that the adsorption of CR over EG@MnFe<sub>2</sub>O<sub>4</sub> obeyed the Langmuir equation because of the highest  $R^2$  (0.9572) and experimental data well fitted on the linear, assuming that the monolayer adsorption behaviour is likely to be a dominant process [66]. Meanwhile, adsorption of CR over MnFe<sub>2</sub>O<sub>4</sub> adhered to the Freundlich models ( $R^2 = 0.8519$ ), which is more inclining to occur upon multilayer adsorption behaviour. In addition,  $R_L$  (0.4–0.9) and  $1/n$  (0.39–0.63) constant values confirmed that the sorption of

TABLE 3: Isotherm parameters over EG@MnFe<sub>2</sub>O<sub>4</sub> and MnFe<sub>2</sub>O<sub>4</sub>.

Model	Parameters	Value	
		EG@MnFe <sub>2</sub> O <sub>4</sub>	MnFe <sub>2</sub> O <sub>4</sub>
Langmuir	$k_L$ (L/mg)	0.0018	0.0210
	$Q_m$ (mg/g)	71.79	19.57
	$R_L = 1/(1 + K_L C_0)$	0.90	0.44
	$R^2$	0.9572	0.7310
Freundlich	$k_F$ (mg/g)/(mg/L) <sup>1/n</sup>	14.956	0.885
	1/n	0.39	0.63
	$R^2$	0.9274	0.8519
Temkin	$k_T$ (L/mg)	1.00	6.01
	$B_T$	16.58	4.87
	$R^2$	0.8687	0.8205
D-R	B (kJ <sup>2</sup> /mol <sup>2</sup> )	2.64	0.46
	$Q_m$ (mg/g)	50.69	11.302
	E (J/mol)	435.19	103.75
	$R^2$	0.5811	0.8483

FIGURE 11: Linear plots of isotherm models: (a) Langmuir, (b) Freundlich, (c) Temkin, and (d) D-R for the adsorption of CR over EG@MnFe<sub>2</sub>O<sub>4</sub> and MnFe<sub>2</sub>O<sub>4</sub>.

CR over EG@MnFe<sub>2</sub>O<sub>4</sub> and MnFe<sub>2</sub>O<sub>4</sub> was the favourable process. Based on the results from Table 3, the maximum adsorption capacity ( $Q_m$ ) calculated from Langmuir

equation can be found at 71.79 and 19.57 mg/g for EG@MnFe<sub>2</sub>O<sub>4</sub> and MnFe<sub>2</sub>O<sub>4</sub>, respectively. These results are compared with those of previous studies (Table 4), showing

TABLE 4: Compared BET surface area and maximum adsorption capacity of various materials.

No.	Adsorbents	BET surface area (m <sup>2</sup> /g)	Maximum adsorption capacity (mg/g)	Ref.
1	EG@MnFe <sub>2</sub> O <sub>4</sub>	33.0	71.79	This study
2	MnFe <sub>2</sub> O <sub>4</sub>	45.7	19.57	This study
3	Anilinepropylsilica xerogel	150	22.62	[67]
4	NaBentonite	25.7	35.84	[68]
5	Kaolin	20.28	5.44	[68]
6	Zeolite	8.31	3.77	[68]
7	Bentonite	32	40.4	[69]
8	Kaolin	168.8	11.88	[70]
9	Activated red mud	20.7	7.08	[71]
10	Activated coir pitch	—	6.72	[72]

the higher  $Q_m$  values than porous adsorbent mentioned. Therefore, EG@MnFe<sub>2</sub>O<sub>4</sub> can be a promising candidate for the adsorption of CR in wastewater.

**3.3. Thermodynamic Study.** In general, the thermodynamic equation, which is represented in equation (15), can be used to diagnose the adsorption occur spontaneously or not and to elucidate the influence of temperature on the adsorption of CR over EG@MnFe<sub>2</sub>O<sub>4</sub> and MnFe<sub>2</sub>O<sub>4</sub>. Because the determination of  $K_C$  is based on equation (16), the thermodynamic equation can be rewritten by a linear form (van't Hoff isotherm equation) as shown in equation (17).

$$\Delta G = -RT \ln K_C, \quad (15)$$

$$\ln K_C = \frac{C_A}{C_e}, \quad (16)$$

$$\ln K_C = \left( \frac{-\Delta H}{R} \right) \cdot \frac{1}{T} + \frac{\Delta S}{R}, \quad (17)$$

where  $K_C$  and  $T$  (K) are defined as the adsorption equilibrium constant and temperature, respectively;  $C_A$  (mg/g) and  $C_e$  (mg/L) are the equilibrium CR concentrations in solid phase and solution phase, respectively;  $\Delta H$  (kJ/mol),  $\Delta S$  (kJ/mol K), and  $\Delta G$  (kJ/mol) are defined as standard enthalpy and entropy and Gibb's free energy.

Figure 12(a) plots the impact of temperature (283–313 K) on CR adsorption onto EG@MnFe<sub>2</sub>O<sub>4</sub>. Obviously, boosting the temperature led to a slight enhancement in the adsorption capacity. The correlation between temperature and equilibrium constant is described in Figure 11(b), which shows the plot of  $\log(K_C)$  against  $(1/T)$ . As can be seen from Figure 12(b), experimental data were fitted well with the thermodynamic model. Moreover, high  $R^2$  in Table 5 confirms that the van't Hoff equation obtained the excellent fitness; thus, it can be used to identify the standard thermodynamic constants (e.g.,  $\Delta H$ ,  $\Delta S$ , and  $\Delta G$ ). A positive  $\Delta H$  reveals that the adsorption process of CR onto EG@MnFe<sub>2</sub>O<sub>4</sub> tends to be endothermic. These results were highly in line with many previous works studying the adsorption of CR over various porous materials [73–77]. Meanwhile, positive value of  $\Delta S$  shows an increase in disorder levels occurring in heterogeneous phase because of migration between aqueous solution and CR molecules during sorption [78]. Finally, the Gibbs free energy with minus values is

eligible to assert that the adsorption of CR on EG@MnFe<sub>2</sub>O<sub>4</sub> was a spontaneous process.

**3.4. Recyclability Study.** On the other hand, to assess the cost-effectiveness and practical applicability of any solid adsorbent, recyclability study needs to be investigated. Herein, we selected the best materials for recyclability performance. Therefore, EG@MnFe<sub>2</sub>O<sub>4</sub> can be regenerated according to the following procedure. To begin with, CR-loaded EG@MnFe<sub>2</sub>O<sub>4</sub> separated from the first run was washed with 10 mL ethanol for 3 times and then with 10 mL distilled water for another 3 times. The nanomaterial was reactivated at 105°C and then used for the next use. The number of recyclability experiments was repeated to be 5 runs. The first reuse was found to be 58.41%, which was the same percentage as the standard run (60%). However, the second and third runs witnessed the slight decrease in removal efficiency, at approximately 46 and 40%. This result was commensurate with a previous work reporting about the adsorption of Congo red from aqueous solution by zeolitic imidazolate framework-8 [79]. The percentage of CR removal for another runs was rapidly dropped down. As a result, the EG@MnFe<sub>2</sub>O<sub>4</sub> can be totally recycled at least four times, revealing good stability and regeneration performance of EG@MnFe<sub>2</sub>O<sub>4</sub> material in eliminating the CR dye.

**3.5. Proposed Mechanism.** It is known that the dissociation constant (pKa) of Congo red is 4.0 [80]. In addition, we measured the point of zero charge (pHpzc) of MnFe<sub>2</sub>O<sub>4</sub> and EG@MnFe<sub>2</sub>O<sub>4</sub> at 5.0, and 6.8, respectively. In adsorption factors, pH 6 is best condition to make the maximum removal efficiency. This can be explained based on the theory of electrostatic interaction.

In fact, at  $\text{pH} < \text{pKa}$  (CR) = 4.0, the solute tends to contain more protons, and the surface of EG@MnFe<sub>2</sub>O<sub>4</sub> also becomes more positively charged. This phenomenon appears an electrostatic repulsion between the surface of EG@MnFe<sub>2</sub>O<sub>4</sub> and CR cations, thus resulting in a decrease in adsorption. In contrast, when the pH value is higher than pKa of CR but lower than pH<sub>pzc</sub> of EG@MnFe<sub>2</sub>O<sub>4</sub>, or  $4.0 < \text{pH} < \text{pH}_{\text{pzc}} = 6.8$ , CR molecules are deprotonated to transfer a form of anion while EG@MnFe<sub>2</sub>O<sub>4</sub> surface is still positively charged due to  $\text{pH} < \text{pH}_{\text{pzc}}$ . This results in an electrostatic attraction, leading to a considerable increase in

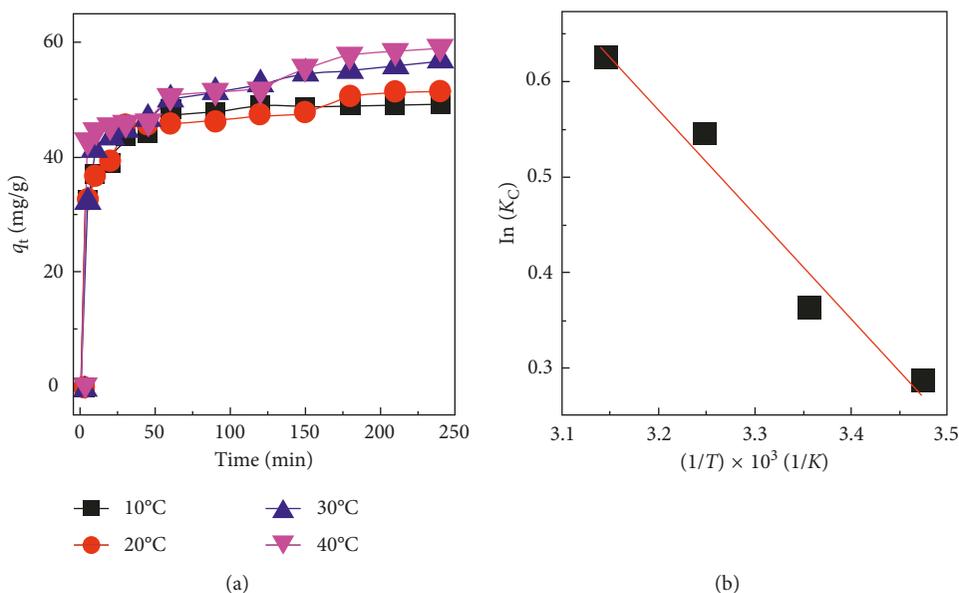


FIGURE 12: Effect of temperature on adsorption of CR over EG@MnFe<sub>2</sub>O<sub>4</sub> (a) and thermodynamic study (b). Experimental conditions included solution volume of 100 mL at pH 4 for MnFe<sub>2</sub>O<sub>4</sub> and pH 6 for EG@MnFe<sub>2</sub>O<sub>4</sub>. Experiments were run at various temperatures (10–40°C).

TABLE 5: Thermodynamic parameters for the adsorption of CR over EG@MnFe<sub>2</sub>O<sub>4</sub>.

van't Hoff equation	$\Delta H^\circ$ (kJ/mol)	$\Delta S^\circ$ (J/mol K)	$\Delta G_{283}$ (kJ/mol)	$\Delta G_{293}$ (kJ/mol)	$\Delta G_{303}$ (kJ/mol)	$\Delta G_{313}$ (kJ/mol)
$\ln K_C = -1.097(1/T) + 4.081$ $R^2 = 0.9688$	9.12	33.93	-0.652	-0.991	-1.331	-1.670

adsorption. In this study, you can see the optimum pH at 6, which is appropriate to the above analysis. However, overcoming the  $\text{pH}_{\text{pzc}}$  value tends to intercept the adsorption because both surfaces of EG@MnFe<sub>2</sub>O<sub>4</sub> and CR molecules are negatively charged, causing a decline in the decontamination of CR dye. Consequently, the adsorption process is more likely to be favourable at pH varying from  $\text{pK}_a$  to  $\text{pH}_{\text{pzc}}$ .

In addition, we measured the functional groups on the surface of EG@MnFe<sub>2</sub>O<sub>4</sub> with the total acidic groups (carboxylic, lactonic, and phenolic groups) at 0.096 mmol/g and total basic groups at 0.156 mmol/g, while there was no detection of any groups on MnFe<sub>2</sub>O<sub>4</sub> without EG decoration. In fact, the CR adsorption capacity of EG@MnFe<sub>2</sub>O<sub>4</sub> (71.79 mg/g) was found to be higher than that of MnFe<sub>2</sub>O<sub>4</sub> (19.57 mg/g); therefore, these groups can have an important role in improving the adsorption. In general, the surface functional groups can create a wide range of interactions such as the H-bond,  $\pi$ - $\pi$  interaction,  $n$ - $\pi$  interaction, and electrostatic force between CR molecules and adsorbate surface [81–83]. Meanwhile, the adsorption of MnFe<sub>2</sub>O<sub>4</sub> was attributable to the weak forces such as “oxygen-metal” bridge and van der Waals [54].

#### 4. Conclusions

The present study successfully fabricated the EG, MnFe<sub>2</sub>O<sub>4</sub>, and EG@MnFe<sub>2</sub>O<sub>4</sub> materials. The characterization results showed the EG@MnFe<sub>2</sub>O<sub>4</sub> obtained a heterogeneous, highly

defective, amorphous morphology with surface area of 33 m<sup>2</sup>/g. The adsorption results showed the equilibrium time at 240 min, optimal dosage of 0.05 g and solution pH 6 for EG@MnFe<sub>2</sub>O<sub>4</sub> and pH 4 for MnFe<sub>2</sub>O<sub>4</sub>. Moreover, kinetic and isotherm models pointed out that the adsorption of CR over EG@MnFe<sub>2</sub>O<sub>4</sub> at various concentrations adhered to chemisorption mechanism (pseudo-second-order) and monolayer adsorption behaviour (Langmuir equation). In addition, the thermodynamic study confirmed that the nature of adsorption is an endothermic and spontaneous process. The maximum adsorption capacity obtained from the Langmuir model for EG@MnFe<sub>2</sub>O<sub>4</sub> was calculated to be 71.79 mg/g, which was so far higher than that of MnFe<sub>2</sub>O<sub>4</sub> and several previous studies, indicating that EG@MnFe<sub>2</sub>O<sub>4</sub> can be a potential adsorbent for the adsorption of CR dye in water.

#### Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

#### Conflicts of Interest

The authors declare no conflicts of interest.

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## Research Article

# Study on Fire Resistance Ability and Mechanical Properties of Composites Based on Epikote 240 Epoxy Resin and Thermoelectric Fly Ash: An Ecofriendly Additive

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In this study, fly ash was tested as a filler in epoxy with concentrations of 5, 10, and 20 wt.%. Fly ash particles were modified by chemical treatments (using NaOH and HCl) to enhance the compatibility and adhesion, making mechanical properties and flame retardancy of materials better. Flexural strength, tensile strength, and impact resistance decrease as fly ash content increases. The compressive strength is further increased by the addition of fly ash (compressive strength of the materials including 5, 10, 20 wt.% of fly ash modified with NaOH is 176.01, 189.90, and 197.07 MPa, respectively). The interface between fly ash and epoxy matrix plays an important role in determining the mechanical strength and flame retardancy of synthetic materials. The results of UL-94HB and LOI test method for composite materials including 20 wt.% fly ash (modified by NaOH) reached 13.45 mm/min and 22.4%, respectively. These results showed that fly ash is an efficient additive as a flame retardant which decreases the amounts of additives in products and improves their efficiency. Fly ash was also dispersed into epoxy resin to enhance its resistance to oxidation.

## 1. Introduction

Flame retardants (FRs) used as additives in a wide range of production play a very important role in suppressing fire generation and delaying fire spread [1, 2]. A composite material based on epoxy resin and fly ash (a by-product from thermal power plant) with a good fire resistance ability was developed. Fly ash used as a flame retardant instead of current ones (for example, organic halogen compounds) reduces environmental problems when compared to using flame retardant epoxy resin [3]. Some popular commercial flame retardants are not only dangerous to human and environment but they also have negative effects on mechanical properties of materials [4]. For this reason, it is necessary to find an ecofriendly material which is harmless to human. Additives such as clay and fly ash are being paid great attention. Many authors studied the use of ecofriendly additives such as fly ash, multiwalled carbon nanotube, and

nanoclay in enhancing fire resistance of epoxy resin [5–7]. In this study, ultrafine fly ash has been used. Fly ash has been surface-treated with NaOH and HCl acid to improve dispersion in Epikote 240 epoxy matrix. The purpose of this study was to improve fire retardancy and improve some mechanical durability, thereby expanding the application area of fly ash for thermal power plants in Vietnam and reducing the impact on the environment. Methods such as UL 94 and limiting oxygen index (LOI) are used to study the combustibility of composites.

## 2. Materials and Methods

### 2.1. Materials

- (i) Epikote 240 (EP) epoxy resin from Shell Chemicals (USA) with epoxy group content of 24.6%, Mw 5100–5400 mmol/kg, density 1.12 g/cm<sup>3</sup>, and

viscosity at 25°C 007–1.1 Pa·s. Diethylenetriamine (DETA) from Dow Chemicals (USA), with density 0.953 g/cm<sup>3</sup> at 20°C, boiling point 207°C, and Mw 103.2 g/mol<sup>-1</sup>. HCl and NaOH from Dow Chemicals (USA).

- (ii) The fly ash primarily consisted of inorganic materials such as silica, alumina, and calcium oxide. Fly ash taken from the ash waste of Pha Lai Thermal Power Station was collected from Song Da Joint Stock Company 12-Cao Cuong, Vietnam.

## 2.2. Methods

**2.2.1. Sample Preparation.** First, the fly ash was kept in a drier at 100°C for 24 hours to remove the moisture present in it. After 24 hrs, the fly ash was taken out of the drier. Then, the amount of fly ash, epoxy resin (Epikote 240), and hardener (DETA) was calculated for five different composites (0, 5, 10, and 20 w.% fly ash). Curing was performed at room temperature for approx. 24 hrs. After curing, the mould was opened, and the slab was taken out of the mould and cleaned and cured under room temperature for 1 and 7 days.

### 2.2.2. Characterizations

- (i) The morphology of the samples was carried out by scanning electron microscopy (SEM, Evaseq error codes, S-4800, Japan). An ultramicrotome (Leica microsystem) was used to cut ultrathin sections (80 nm) of samples before recovered on a copper grid.
- (ii) The flame retardant properties was tested by the limiting oxygen index (LOI) (Yasuda Seiki Seisakusho Ltd, Japan) according to JIS K720-1976, with sheet dimensions of 120 × 6.5 × 3.2 mm.
- (iii) The UL-94 rating was tested according to the UL-94 (ASTMD635-12) with sheet dimensions of 125 ± 5 mm length by 13.0 ± 0.5 mm width and with the minimum thickness of 3.0 (−0.0 + 0.2) mm.
- (iv) The combustion rate was measured by COMBUSTION RESISTANCE COD 6145000 according to ASTM D757-77 standard. The specimen's dimensions were 3.17 × 12.7 × 121 mm<sup>3</sup>. Mechanical properties were measured on an INSTRON-5582 100 KN (USA) according to ISO 527-1993 at an extension speed of 5 mm/min.
- (v) All data were the average of five independent measurements; the relative errors committed on each data were reported as well. IR spectrum was measured at the Department of Chemistry, University of Natural Sciences (Hanoi National University).

## 3. Results and Discussion

**3.1. Investigation of Characteristics of Fly Ash.** Fly ash from the ash waste of Pha Lai Thermal Power Station was collected in Song Da Joint Stock Company 12-Cao Cuong, Vietnam.

Before the investigation, fly ash was washed by acetone to remove impurities. Scanning electronic microscopy (SEM) was used to determine fly ash particles' morphological structure. The results are shown in Figure 1. As seen in Figure 1, fly ash particles have spherical smooth structure. They are abundant and different in size.

In Figure 2, the IR spectroscopy of fly ash with vibration bands 400–4000 cm<sup>-1</sup> shows that there is a peak at 3649 cm<sup>-1</sup> and 1065 cm<sup>-1</sup> corresponding to -OH (free) and Si-O, respectively, proving the presence of -OH in fly ash's surface, thus making it easier for the modification process to attach silane groups to fly ash's surface to enhance compatibility between inorganic material and polymer substrate. Besides, there are also peaks at 792 cm<sup>-1</sup>, 562 cm<sup>-1</sup> and 480 cm<sup>-1</sup>, and 452 cm<sup>-1</sup> corresponding to the presence of quartz, O-Fe, and O-Al, respectively.

### 3.2. Treatment of Fly Ash's Surface

#### 3.2.1. Treatment of Fly Ash's Surface with NaOH

**(1) IR Spectroscopy of Fly Ash Modified with NaOH.** NaOH is a strong base containing active hydroxide groups. NaOH with concentration of 3 M was used to modify fly ash. In the modification process, fly ash particles were stirred in 3 M solution of NaOH at 80°C for 5 hours. Efficiency of the process is qualitatively evaluated through IR spectroscopy of modified fly ash (Figure 3).

Figure 3 shows that there are new peaks at 3451 cm<sup>-1</sup> and 1653 cm<sup>-1</sup> in IR spectra of modified fly ash in comparison with spectra of initial fly ash. In IR spectra, there is the appearance of a peak at 3451 cm<sup>-1</sup> and 1653 cm<sup>-1</sup> corresponding to the stretching vibrations of -OH groups of NaOH and H<sub>2</sub>O, respectively. On other hand, there is no change in the fingerprint region, indicating that metallic oxides exist on modified fly ash. Therefore, it can be said that the structure of fly ash is quite stable.

**(2) Effects of Alkaline Treatment on Fly Ash's Size and Surface Area.** The surface of initial fly ash is smooth, making it difficult for adhesion between fly ash and polymer substrate. So, it is necessary to treat fly ash surface to increase roughness and surface area or form active groups on the surface.

Fly ash modified with NaOH was filtered, washed, and dried. The contribution of fly ash particles is observed by the SEM method in low resolution.

In Figure 4, the SEM image of fly ash modified with NaOH shows that when the contribution of NaOH is higher, the size of modified fly ash particles is more even in comparison with initial ones. In other words, NaOH makes the size of fly ash particles smaller.

The morphological structure of treated fly ash showed in Figure 4 (fly-NaOH) is rough in comparison with initial ones. There are many cracks and small particles which are aluminum silicate or aluminum sulfate formed from abrasion process on the surface. It was caused by reactions between NaOH and oxides of fly ash. Although the size of fly ash particles of experiments is not similar, there is no

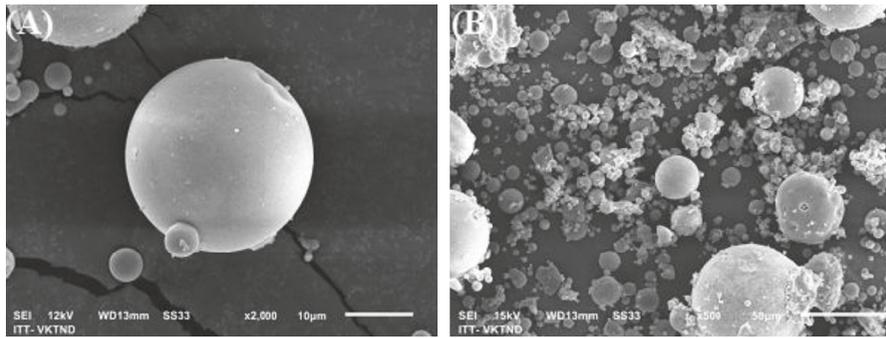


FIGURE 1: SEM image of fly ash/Epikote 240 composites.

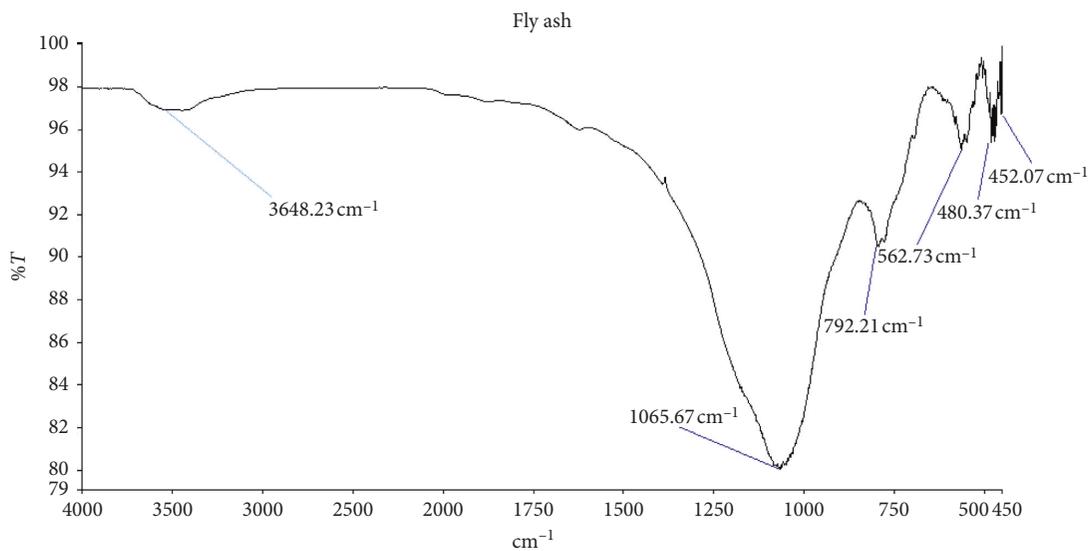


FIGURE 2: IR spectroscopy of the original fly ash sample.

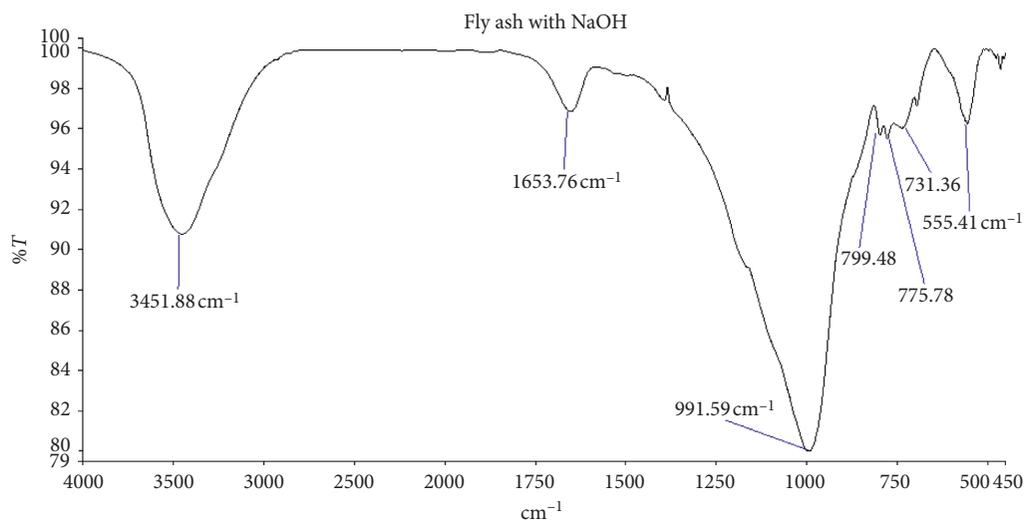


FIGURE 3: IR spectroscopy of the original fly ash-NaOH sample.

difficulty in enhancing properties of fly ash by this method. The surface becomes rough, and the increase of surface area may make the interaction between fly ash and epoxy resin better.

### 3.2.2. Treatment of Fly Ash Surface with HCl Acid

(1) IR Spectroscopy of Fly Ash Modified by HCl Acid. HCl is a strong acid used to corrode metallic oxides included in fly

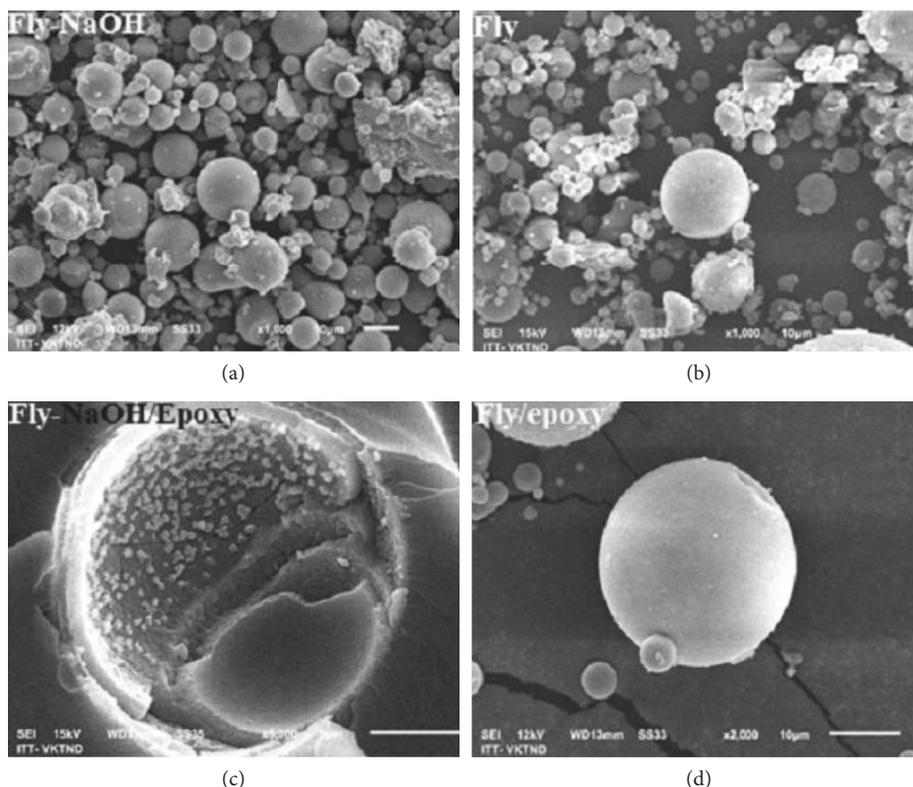


FIGURE 4: SEM image of fly ash modified with NaOH. (a) Fly-NaOH: modified fly ash; (b) fly: not yet counted; (c) fly-NaOH/epoxy: composite epoxy resin surface has modified fly ash; and (d) fly/epoxy: composite epoxy resin substrate has unmodified fly ash surface.

ash. The modification process used 2 M HCl solution. Fly ash particles were stirred in HCl 2 M, at 95°C, for 6 hours to modify. By observing peaks appearing on IR spectroscopy of modified fly ash in Figure 5, efficiency of this method was qualitatively evaluated. There is little difference in IR spectroscopy of modified fly ash in comparison with the initial one. This proves a bad compatibility between acid HCl and fly ash. So, using acid HCl to change the structure of fly ash is ineffective.

(2) *Effects of Acidic Treatment on Fly Ash's Size and Surface Area.* The SEM image in Figure 6 is observed to more clearly understand the change of fly ash particles after modified with HCl. Images in other resolutions of modified fly ash particles show that there are crystals attached to fly ash particles, making fly ash surface area rough, thus increasing contact area between fly ash particles and polymer substrate (see Figure 6).

Besides, the size of modified fly ash particles is more even than that of initial ones, making the dispersion of fly ash particles in resin better (see Figure 6). However, there are only crystals but no cracks on fly ash surface. Therefore, it can be concluded that acid HCl has no strong impact on fly ash and this method is not an optimal one.

### 3.3. Study on Preparation of Fly Ash/Epoxy Composites

#### 3.3.1. Effects of the Amount of Fly Ash Modified by Inorganic Compounds on Mechanical Properties, Flame Retardant Ability, and Structure of the Materials

(1) *Effects on Mechanical Properties.* Effects of the amount of fly ash modified by inorganic compounds (NaOH and HCl) on tensile strength of the materials are shown in Figure 7. As a result, materials' tensile strength follows the order: materials including fly ash modified by NaOH > materials including fly ash modified by HCl > materials including fly ash without modification. Besides, increasing the amount of fly ash makes tensile strength decrease, but it is insignificant. This shows that the compatibility with resin of modified fly ash is better than of initial fly ash, leading to the increase of tensile strength. Concretely, tensile strength of the materials including 5, 10, and 20 wt.% of fly ash modified with NaOH is 82.43, 79.20, and 75.75 MPa, respectively. Tensile strength of the materials including 5, 10, and 20 wt.% of fly ash modified with HCl is 79.98, 78.39, and 75.37 MPa, respectively.

Effects of the amount of fly ash modified by inorganic compounds (NaOH and HCl) on tensile modulus of the materials are shown in Figure 8. As a result, materials' tensile modulus follows the order: materials including fly ash modified with NaOH > materials including fly ash without modification > materials including fly ash modified with HCl. Besides, increasing the amount of fly ash makes tensile modulus decrease, but it is insignificant. This shows that the compatibility with resin of modified fly ash is better than of initial fly ash, leading to the stability of tensile modulus. Concretely, tensile modulus of the materials including 5, 10, and 20 wt.% of fly ash modified with NaOH is 52.27, 49.98, and 47.75 MPa, respectively. Tensile modulus of the

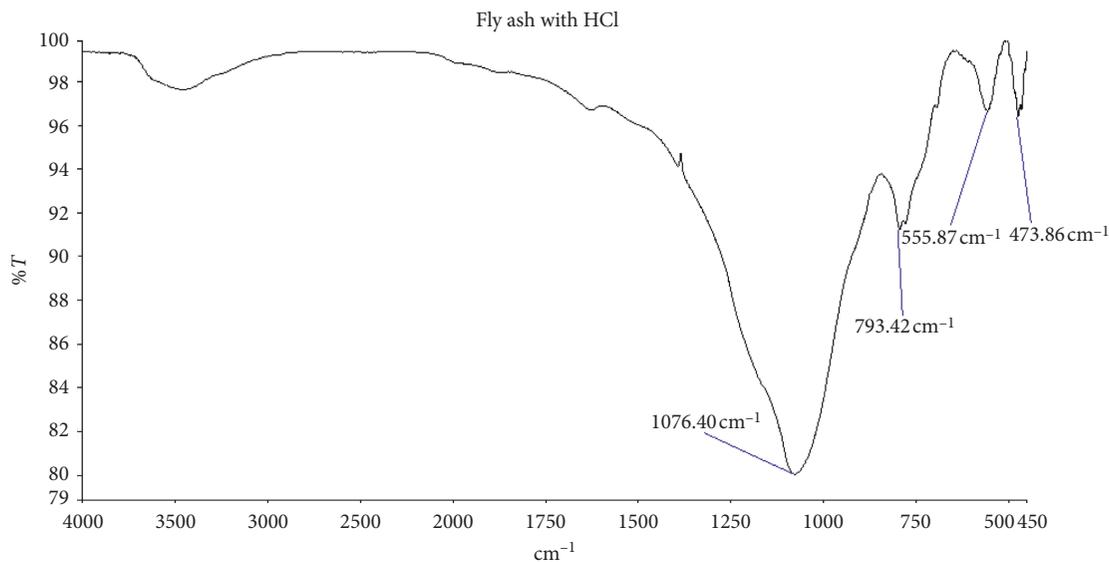


FIGURE 5: IR spectroscopy of the original fly-HCl ash sample.

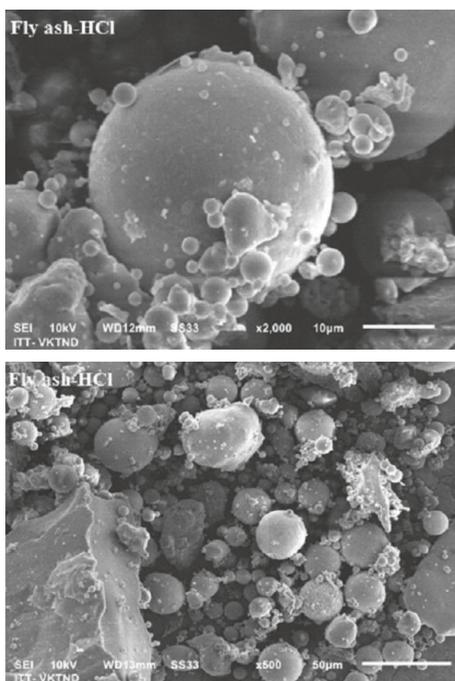


FIGURE 6: SEM image of fly ash modified with HCl.

materials including 5, 10, and 20 wt.% of fly ash modified with HCl is 45.09, 43.79, and 41.08 MPa, respectively.

Figure 9 shows effects of the amount of fly ash modified with inorganic compounds (NaOH and HCl) on compressive strength of the materials. As a result, materials' compressive strength follows the order: materials including fly ash modified by NaOH > materials including fly ash modified by HCl > materials including fly ash without modification. Moreover, impressive strength of the materials significantly increases with the increase of the amount of fly ash. This is caused by the increase in compatibility, adhesion, and filling ability of modified fly ash with resin, thus leading to the improvement of compressive strength. Concretely,

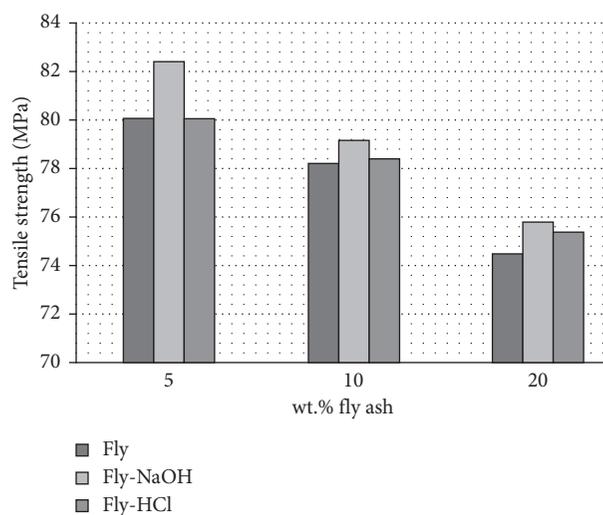


FIGURE 7: Comparison of flexural strength.

compressive strength of the materials including 5, 10, and 20 wt.% of fly ash modified with NaOH is 176.01, 189.90, and 197.07 MPa, respectively. Compressive strength of the materials including 5, 10, and 20 wt.% of fly ash modified with HCl is 145.33, 180.07, and 196.78 MPa, respectively.

When epoxy resin is cured with diethylenetriamine (DETA), cross-linking forms a three-dimensional space circuit. Fly ash acts as an inorganic filler that loses the space between polymer chains, reducing the flexibility of the polymer molecule to increase hardness. Besides, fly ash particles were filled into spaces between polymers in the epoxy matrix, creating pressure on polymers in the vicinity. As a result, the tension was reduced and the hardness was enhanced. In addition, the adhesion of the particle/matrix has a significant influence on the durability of granular polymer composites. A strong interfering link between particles and polymer matrix is important for effective stress transfer resulting in high intensity of synthesis [5].

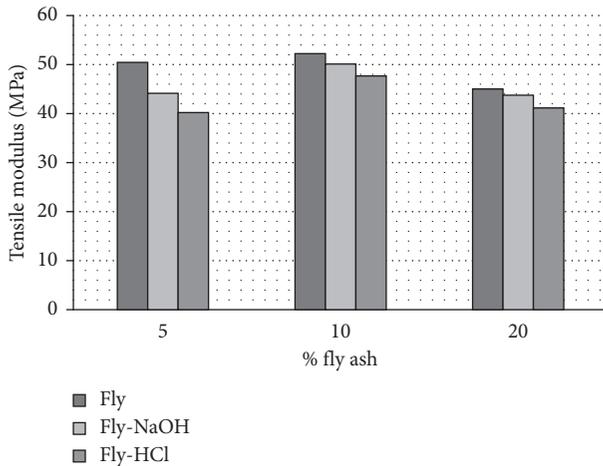


FIGURE 8: Comparison of tensile strength.

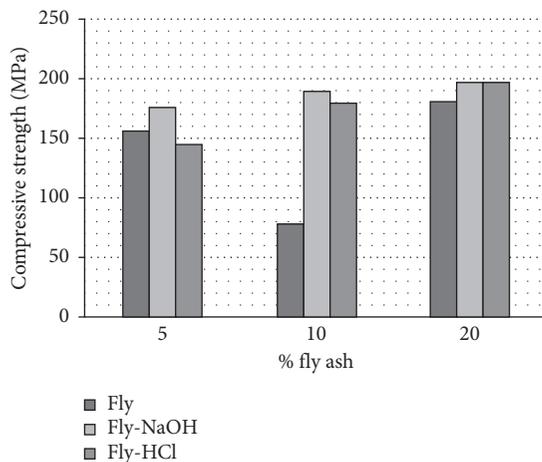


FIGURE 9: Comparison of compressive strength.

Figure 10 shows effects of the amount of fly ash modified with inorganic compounds (NaOH and HCl) on compact strength of the materials. As a result, materials' compact strength follows the order: materials including fly ash modified by HCl > materials including fly ash modified by NaOH > materials including fly ash without modification. Moreover, compact strength of the materials insignificantly decreases with the increase of the amount of fly ash. After modification, compatibility of fly ash with resin is better, leading to the improvement of compact strength. Concretely, compact strength of the materials including 5, 10, and 20 wt.% of fly ash modified with NaOH is 6.89, 6.01, and 5.70 MPa, respectively. Compact strength of the materials including 5, 10, and 20 wt.% of fly ash modified with HCl is 6.54, 6.55, and 5.98 (kJ/m<sup>2</sup>), respectively.

The results show that the amount of fly ash affects mechanical properties of the materials. Like fly ash without modification, there are effects on the materials in the case of modified fly ash such as increasing compressive strength and decreasing tensile modulus, compact strength, and tensile strength. However, effects made by modified fly ash are more significant than by initial fly ash because of good contribution and adhesion of modified fly ash particles with resin.

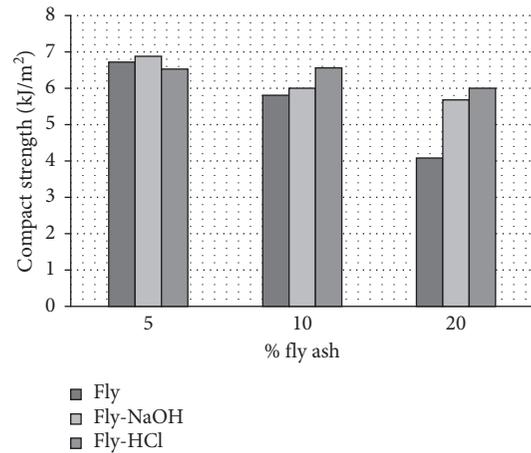


FIGURE 10: Comparison of compact strength.

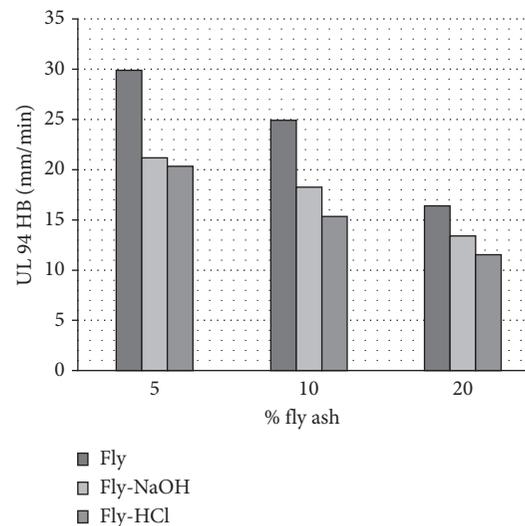


FIGURE 11: Flame retardancy according to the UL 94HB research method.

Thus, fly ash modified with NaOH is better than fly ash modified with HCl.

(2) *Investigation of Effects of the Amount of Fly Ash on Flame Retardancy of the Materials by UL 94 HB Standard.* Figure 11 shows effects of the amount of fly ash modified with inorganic compounds (NaOH and HCl) on the burning rate of the materials following UL 94 HB standard. As a result, the burning rate of the materials follows the order: the materials including fly ash modified with HCl < the materials including fly ash modified with NaOH < the materials including fly ash without modifications. Besides, the higher the amount of fly ash is, the lower the burning rate is or the better the flame retardancy of the materials is. This proves that after modification, fly ash's compatibility with resin is better, making flame retardancy of the materials better. Concretely, the burning rate following UL 94 HB standard of the materials including 5, 10, and 20 wt.% of NaOH is 21.15, 18.22, and 13.45 mm/min, respectively. The burning rate following UL 94 HB standard of the materials

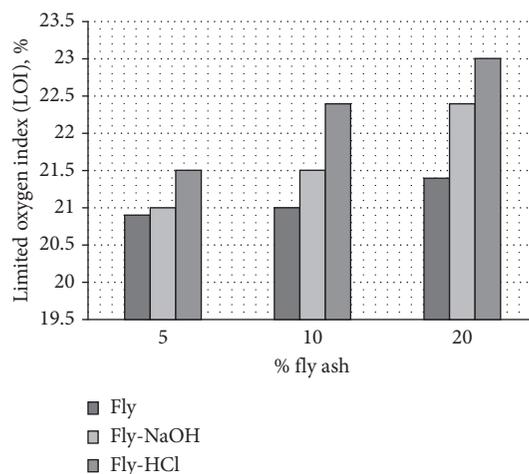


FIGURE 12: Effects of the amount of fly ash on limited oxygen index (LOI).

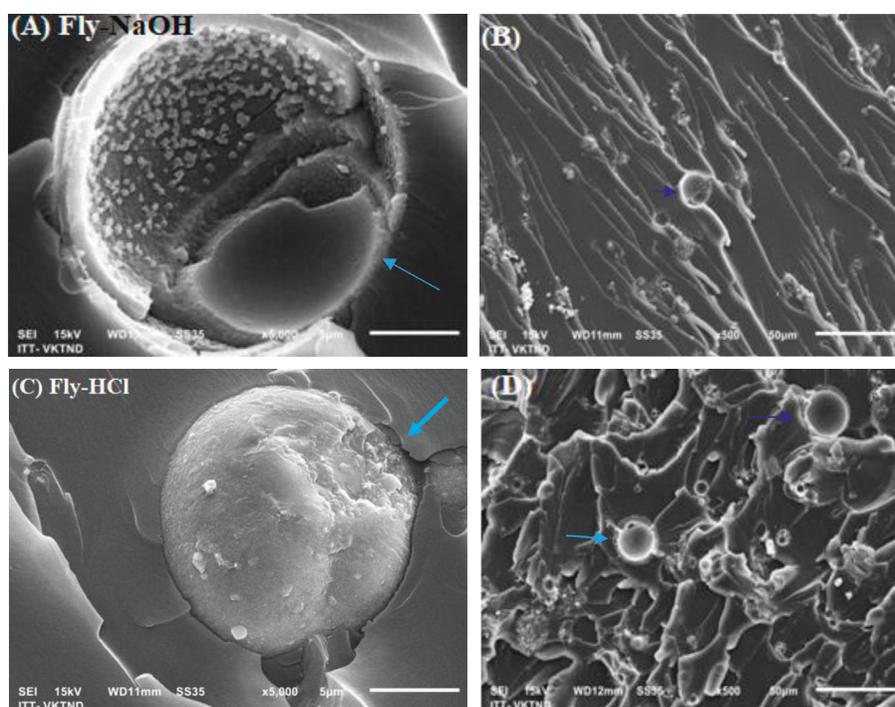


FIGURE 13: SEM image of fly ash modified with HCl (C, D) and fly ash modified with NaOH (A, B).

including 5, 10, and 20 wt.% of HCl is 20.27, 15.37, and 11.51 mm/min, respectively.

Figure 12 shows effects of the amount of fly ash modified with inorganic compounds (NaOH and HCl) on LOI of the materials. As a result, LOI of the materials follows the order: the materials including fly ash modified with HCl > the materials including fly ash modified with NaOH > the materials including fly ash without modifications. Besides, the higher the amount of fly ash is, the higher the LOI is or the better the flame retardancy of the materials is. This proves that after modification, fly ash's compatibility with resin is better, making flame retardancy of the materials better. Concretely, LOI of the materials including 5, 10, and 20 wt.%

of NaOH is 21, 21.5, and 22.4%, respectively. LOI of the materials including 5, 10, and 20 wt.% of HCl is 21.5, 22.4, and 23%, respectively.

Figures 11 and 12 show that modified fly ash makes flame retardancy of the materials better than initial fly ash. This is caused by the good contact and dispersion of modified fly ash. Among them, fly ash modified with HCl is better than with NaOH. However, the difference is insignificant. From the aforementioned results, it can be said that the sample including 20 wt.% of fly ash is the best with stable mechanical properties and good flame retardancy. Therefore, it will be selected for further experiments.

3.3.2. *Effects of the Amount of Fly Ash Modified with Inorganic Compounds on Structure of the Materials.* SEM images in Figure 13 show the dispersion and adhesion of modified fly ash in resin. Figure 13 shows fracture surface of the material including 20 wt.% of fly ash modified with NaOH and HCl.

For fly ash modified with NaOH, it can be seen that fly ash particles have a broken shell to release smaller inside particles which adhere and contact with resin (Figure 13(a)). Therefore, adhesion ability and contact surface area of fly ash modified with NaOH are better than of initial one. Besides, there are high density and good contribution of spherical fly ash particles in resin (Figure 13(b)). For fly ash modified with HCl, it can be seen that there are rough surfaces of fly ash particles (Figure 13(c)) leading to the higher contact surface area of modified fly ash than initial ones. Besides, there are also high density and good contribution of spherical fly ash particles in resin (Figure 13(d)).

#### 4. Conclusions

In this study, fly ash collected from Vietnamese thermal power plants was modified by NaOH and HCl to improve its efficiency and reduce its negative impacts on the environment. The aim is to improve the flame retardant properties and improve some mechanical properties. According to research results, the following conclusions are given:

- (i) High compatibility between fly ash (denatured by NaOH and HCl) and epoxy resin substrate. As a result, the fire resistance of the material has been enhanced.
- (ii) The interface between fly ash and epoxy resin substrate plays a very important role in improving mechanical properties and flame retardancy of materials. SEM images show that fly ash particles are evenly dispersed into epoxy resin substrate.
- (iii) There is an increase in the compressive strength of the material when increasing the fly ash content. Besides, there is decrease in flexural strength, tensile strength, and compact strength but without significant effects on the material.

#### Data Availability

For any questions relating to the data or the original data requirements of the article, contact the corresponding author at anhnt@hau.edu.vn.

#### Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

#### Acknowledgments

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## Research Article

# Mechanical Properties and Flame Retardancy of Epoxy Resin/Nanoclay/Multiwalled Carbon Nanotube Nanocomposites

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This paper reports the improvement of the mechanical properties and flame retardant properties of epoxy Epikote 240/nanoclay I.30E/multiwalled carbon nanotube nanocomposite prepared by mechanical stirring method combined with ultrasonic vibration, nanoclay I.30E content (1; 2; 3 wt.%) and content of MWNT (0.01; 0.02; 0.03 wt.%). When burned, MWCNT reduces degradation speed of epoxy Epikote 240 resin and increases the char yield, and nanoclay acts as an energy storage medium to hinder the heat transfer in epoxy resin. The limiting oxygen index value and UL94 test indicated improvement of flame retardancy of the nanocomposites. The results exhibit the potentiality of these based epoxy Epikote 240 resin/nanoclay I.30E/MWCNTs nanocomposites for multifaceted advanced applications. These fillers can produce environmental friendly products with high thermal and mechanical properties.

## 1. Introduction

Currently, multicarbon carbon nanotubes and nanoclay are the stuffing widely used because they improve both the fire-retardant properties and mechanical properties of epoxy plastic; they do not create toxic fumes or smoke corrosion during burning process, unlike common fire-retardant materials based on halogen compounds [1, 2]. Some studies have investigated the fire resistance of epoxy-based nanocomposite materials in MWCNTs and stated that, for MWCNTs, at the content of 2 and 4%, 5% by weight, the fire resistance of the material increases. It is explained that the formation of coal coating on the surface of the sample separated from oxygen in the environment leads to the prevention of the development of flame [3, 4]. Therefore, the improvement of fire resistance of materials is clearly shown. For nanoclay additives, Cevdet et al. conducted research on mechanical properties, flammability, and structural morphology of epoxy/clay nanocomposite; nanoclay has been prepared with the content of 0.5, 1, 2, and 3% by weight [5].

This work focuses on the study of flammability and mechanical properties of epoxy Epikote 240 substrate nanocomposites materials by adding MWCNT (0.02 wt.%) and nanoclay I.30E (2 wt.%), a small amount compared to the other works announced.

## 2. Materials and Methods

**2.1. Materials.** The epoxy Epikote 240 (EP240) was provided by Shell Chemicals (USA). EP240 is a low viscosity, based on a blend of bisphenol A resin and bisphenol B resin, contented epoxy group of 24.6%, molecular weight (Mw) of 5100–5400 mmol/kg, density of 1.12 g/ml, and viscosity at 25°C to be 0.7–1.1 Pa·s. Diethylenetriamine (DETA) received from Dow Chemical (USA) has a density of 0.95 g/ml boiling point of 207°C and Mw of 103 mmol/kg and is used directly without any further purification. Multiwalled carbon nanotubes (MWCNTs) of Showa Denko (Japan). Synthesized by catalyst deposition method, MWCNTs have an average diameter of 40–45 nm, an average length of 3 μm,

and a density of  $0.08 \text{ g/cm}^3$ . Nanomer® I.30E nanoclay (Nanocor USA) is a surface-changing montmorillonite (MMT) mineral that will disperse into nanoparticles in epoxy resin systems. Dispersion creates a mixture close to the molecule often called nanocomposite. This new composite model shows enhanced strength, heat and barrier properties. I.30E is provided in the form of white powder dispersed into thin particles that are almost transparent in the plastic matrix. Type E raw glass cloth  $600 \text{ g/m}^2$  (China).

## 2.2. Methods

**2.2.1. Sample Preparation and Characterization.** The nanoclay-MWCNT hybrids were prepared according to Table 1. MMT (1, 2, and 3 wt.%) and MWCNT (0.01, 0.02, and 0.03 wt.%) were dispersed in epoxy Epikote 240 resin, stirred at 3500 rpm for 8 h (HS-100T, WiseStir, Korea). In order to break up the MWCNT bundles and disperse the additives, sonication was performed using an ultrasonic bath (Elmasonic S300 H, 37 kHz, Germany) for 6 h,  $65^\circ\text{C}$ . After the mixtures were homogeneously mixed, the curing agent DETA (amount of curing agent was calculated by epoxy content of epoxy resin, stirred for 15 min at 200 rpm/min) was added, and the mixtures were moulded for curing. The mould was coated with a uniform thin film of silicone—a releasing agent for easy removal of cured specimen. The samples were cured at room temperature for about 24 h and further cured at  $80^\circ\text{C}$  in the laboratory oven for 3 h. Then, the samples were removed from the mould, and after 7 days, mixture was analyzed and mechanical properties measured.

Produce glass/epoxy nanomaterials. The glass/epoxy nanomaterials are fabricated using a combination of manual hot and hot compressing techniques. The layers of glass-woven fabrics are stacked into 9 layers, and the orientation of the yarn in the fabric is kept constant.

### 2.2.2. Characterizations

- (i) Limiting Oxygen Index (LOI) according to ASTM D2863-12 and JIS K720 standard (Japan): the sample bars used for the test were  $150 \times 6.5 \times 3 \text{ mm}^3$ .
- (ii) The Horizontal Burning tests (UL-94HB): Standard bar specimens are  $125 \pm 5 \text{ mm}$  in length with  $13.0 \pm 0.5 \text{ mm}$  width and provided with the minimum thickness of  $3.0 (-0.0 + 0.2) \text{ mm}$  (ASTM D635-12).
- (iii) Combustion Resistance: The apparatus is specifically designed for combustion and incandescence resistance of thermoplastics, thermosetting, rigids, and laminates. The apparatus was designed and built to meet the following standards: ASTM D 757; specimen's dimensions  $3.17 \times 12.7 \times 121 \text{ mm}$ ; maximum temperature of  $950^\circ\text{C}$ .
- (iv) The combustion rate was measured by COMBUSTION RESISTANCE COD 6145000 according to the ASTM D757-77 standard. Specimen's dimensions are  $3.17 \times 12.7 \times 121 \text{ mm}^3$ .

TABLE 1: Taguchi orthogonal array of designed experiments based on the coded levels.

Trial	Sample code	MWCNT content (wt.%)	Nanoclay content (wt.%)
1	EP1	0.01	1
2	EP2	0.02	1
3	EP3	0.03	1
4	EP4	0.01	2
5	EP5	0.02	2
6	EP6	0.03	2
7	EP7	0.01	3
8	EP8	0.02	3
9	EP9	0.03	3

Mechanical tests were conducted on at least five specimens by a 100 kN universal testing machine (INSTRON-5582, USA).

- (i) Flexural properties were determined by using three-point bending test specimens with dimensions of  $100 \times 15 \times 4 \text{ mm}$  according to ISO 178.
- (ii) Compressive properties were determined by using three-point bending test specimens with dimensions of  $15 \times 10 \times 10 \text{ mm}$  according to ISO 178-1993.
- (iii) Izod Impact Strength was determined according to the ASTM D265 standard in Tinius Olsen (USA). The standard specimen for ASTM is  $64 \times 12.7 \times 3.2 \text{ mm}$  ( $2(1/2) \times 1/2 \times 1/8 \text{ inch}$ ), Izod Sample Geometry: 2 mm.
- (iv) Tensile properties were determined by using three-point bending test specimens according to ISO 178. Specimen size according to ISO is  $10 \text{ mm} \times 4 \text{ mm} \times 80 \text{ mm}$ .
- (v) The morphology of the samples was carried out by scanning electron microscope (SEM, Evacseq error codes, S-4800, Japan). Structural characterizations were studied by X-ray diffraction (XRD, D8-Advance, Brucker, Germany).

## 3. Results and Discussion

**3.1. Distribution of MMT/MWCNT Additives in the Epoxy Complex.** Morphology of the nanocomposites is as follows: Figure 1 presents cross sections of the EP1, EP2, and EP3 samples to investigate the dispersion.

The fracture surface is so rough, proving high strength of the material lead to it is difficult to destroy. MWCNTs and nanoclay play so important a role in limiting the development of the fracture (Figures 1(a)–1(c); Figures 2(a)–2(c); and Figures 3(a)–3(c)). Therefore, in order to break the material, the force must be higher. Figures 1–3 show that there were rough surfaces in the regions including nanoparticles in comparison to other regions with higher and flatter cracks (Figure 1(c)). For the distribution of nanoparticles, EP5 sample (Figure 2(b)) had the uniform distribution of nanoparticles in epoxy resin E 240 and a so rough fracture surface. FE-SEM images in Figures 1–3

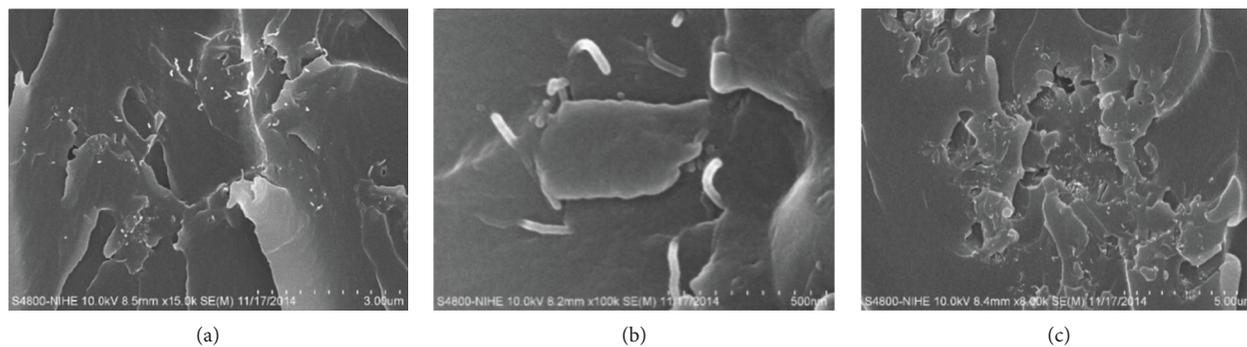


FIGURE 1: Cross-section images of (a) EP1, (b) EP2, and (c) EP3.

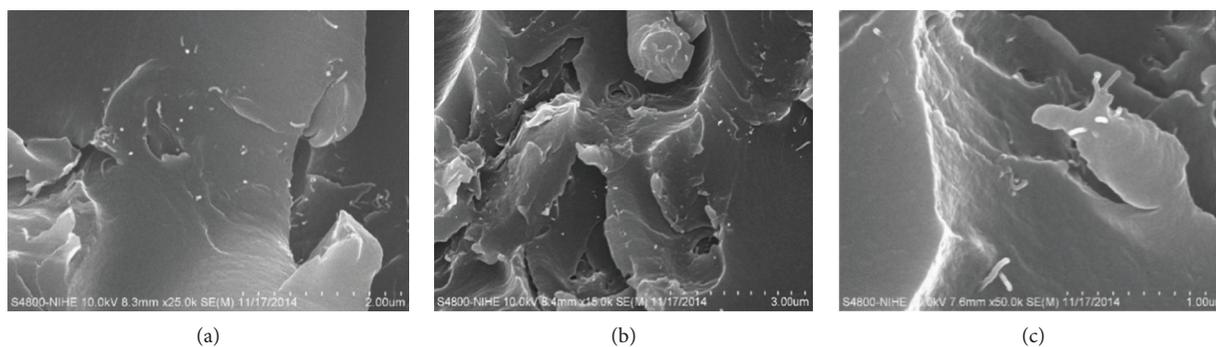


FIGURE 2: Cross-section images of (a) EP4, (b) EP5, and (c) EP6.

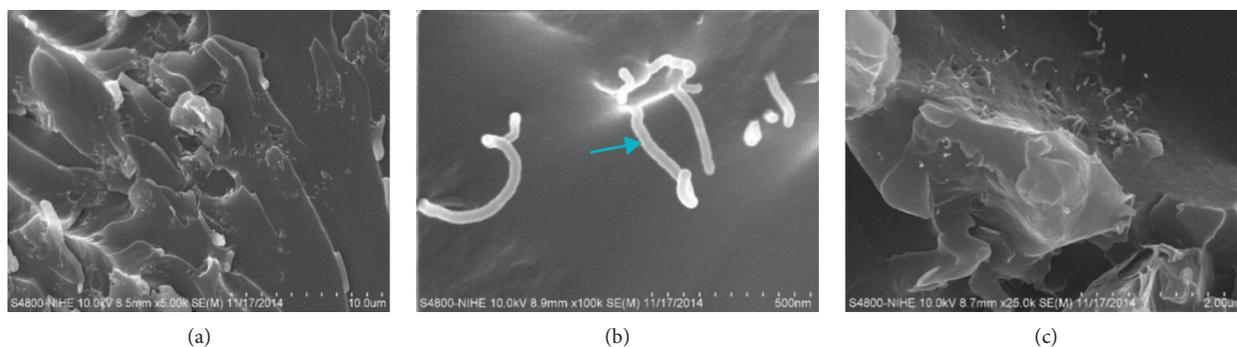


FIGURE 3: Cross-section images of (a) EP1, (b) EP2, and (c) EP3.

indicate that nanoparticles were well stuck on epoxy resin E 240. Because, after breaking the sample, nanoparticles were still maintained on the surfaces and covered by the resin. Moreover, FE-SEM images of the fracture surfaces of tensile samples show that cracks often begun at nanoparticles' agglomeration.

In the magnitude of 100.000 times, the uniform distribution of MWCNTs in epoxy resin E 240 is so clearly observed, and there was no nanoparticles' agglomeration (Figures 4(a) and 4(b)). Figure 4(c) also shows the uniform distribution of nanoclay in epoxy resin. So, MWCNTs and nanoclay were quite well distributed in epoxy resin E 240 by stirring combined with the ultrasonic vibration. The distribution pattern of the nanoclay in the polymer matrix can be identified by the X-ray diffraction patterns of the

nanocomposites (Figure 5). In Figure 4, the captured surfaces not only observe the dispersion of MWCNTs but also nanoclay, though not in any strict order but the thermal conductivity of nanomaterials as well as coal layers. The formation after fire can fully explain to us the flame flammability and heat transfer of composite materials with additives MWCNTs/nanoclay I.30E. The difference in the addition of MWCNTs and nanoclay helped the nanoparticles/epoxy mixtures not easily get melted as for pure epoxy resin samples, even at high temperatures. If a layer of ash can be formed during combustion of the polymer, it can act as an insulating sheet, limiting heat transfer from the source to the polymer. Therefore, the number and texture of the ash layers is important to limit the combustion of the polymer. In Figure 4(b), it can be seen that the MWCNTs are evenly

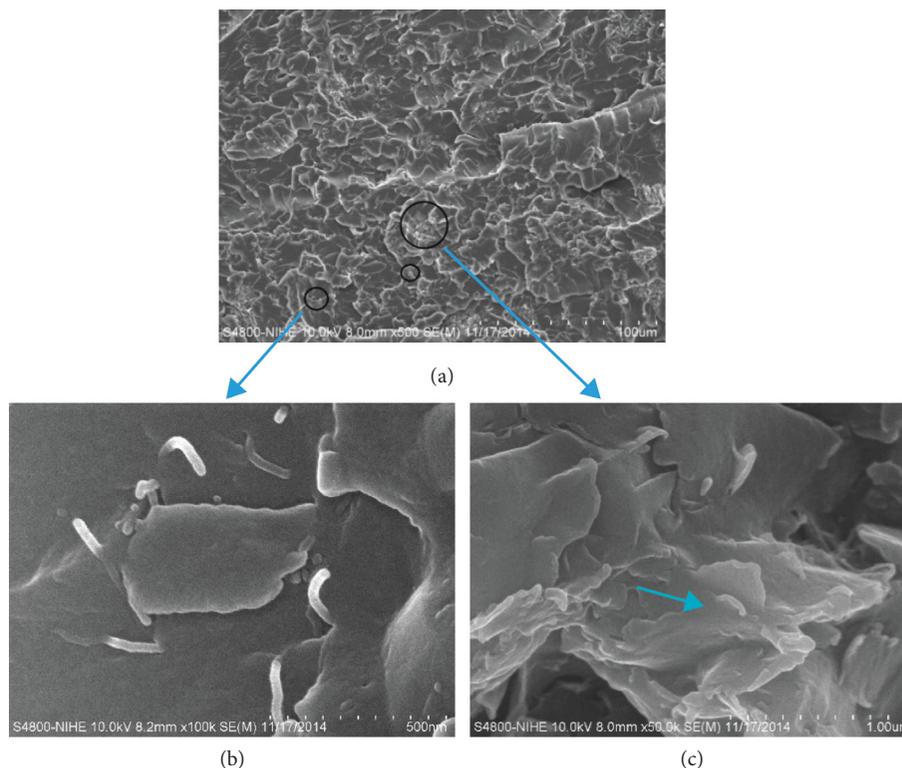


FIGURE 4: FE-SEM image of broken surface material MWCNTs/nanoclay I.30E/epoxy E 240. (a) 500 times, (b) 100,000 times, and (c) 50,000 times.

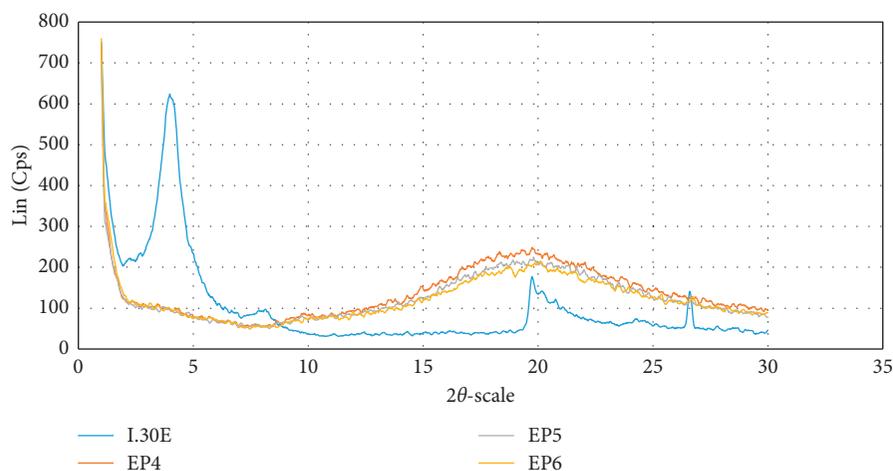


FIGURE 5: XRD patterns for I.30E: nanoclay (MMT), EP4: nanocomposite of epoxy resin with 2 wt.% MMT/0.01 wt.%, EP5: nanocomposite of epoxy resin with 2 wt.% MMT/0.02 wt.%, EP6: nanocomposite of epoxy resin with 2 wt.% MMT/0.03 wt.%; nanoclay (MMT) shows a basal reflection at  $4.1^\circ$  (d-spacing = 6.4 nm) corresponding to [0 0 1] plane. It also shows another peak at  $20.1^\circ$ . The nanocomposites with 1, 2.5, and 5 wt.% clay exhibit no Bragg's scattering, indicating that silicate layers of organoclay may be exfoliated as they do not have any regular repeating distance.

dispersed in epoxy; besides, nanoclay layers (Figure 4(c)) are also dispersed evenly [6–8].

**3.2. Mechanical Properties.** Presence of multiwalled carbon nanotubes in epoxy base materials reduces partial free volume and fills in the gaps and defects formed from the

epoxy resin curing process [9]. Thus increasing thermal stability, fire retardation as well as mechanical durability. Because if there are gaps in the epoxy material (defects), it is the higher flare of combustion.

Uniform dispersion and perfect adhesion of MWCNTs in epoxy plastic is the main reason to increase the mechanical properties of epoxy resin. In this work, multiwalled

carbon nanotubes were relatively uniformly dispersed, with no cumulative contraction observed in FE-SEM images. Cracks start from interface, and then, the MWCNTs are affected by the outside [10]. Improved mechanical properties are shown in this work. MWCNTs increase the ability to withstand external forces. MWCNTs in the epoxy material matrix have prevented the development of microscopic cracks, altering the movement trajectory of the crack [11]. The spread of cracks is prevented, clearly displayed in Figure 6 (results of our research related to this work).

Mechanical strength of samples was increased with the contents of nanoclay and MWCNTs of 2% and 0.02% by weight, respectively. For other contents, mechanical strength was less increased, due to limiting of the contribution (Table 2). If there are layers of ash formed from burning polymers, they can play as heat-isolation layers, restricting the heat transfer from heat resources to polymers. Thus, the number and structure of ash layers play an important role to restrict the combustion of polymers.

The degree of dispersion of MWCNTs and nanoclay in epoxy E 240 is a decisive factor for fire resistance and mechanical properties of nanocomposites. At other ratios, mechanical properties tend to decrease because of the limited dispersion capacity, so the mechanical strength is slightly reduced. Particularly, for the level of distribution of nanoparticles, sample MWCNTs/nanoclay = 0.02/2 (EP5) has nanoparticles distributed evenly in epoxy E 240 resin. This can be explained by the blending level of MWCNTs/nanoclay = 0.02/2 (EP5), the material achieves high compatibility, and the structure is more compact than the rest. Therefore, the mechanical properties and the fire retardancy increase. As for other mixing ratios, it may be due to the residual mass of MWCNTs or nanoclay remaining after fabrication. This leads to the creation of a lower compatibility structure so that when there is a high-temperature impact, the material is easily destroyed at the points, the structure area is unstable, the combustion rate is high, and the mechanical strength is reduced.

**3.3. Flame Retardancy.** The LOI, representing the lowest oxygen volume content for sustaining the flame in an environment, was used for quantifying the flame retardancy of epoxy resin. The oxygen volume content in ambient atmosphere is about 21%. Therefore, a material exhibiting its LOI above 21 might show flame-retardant property. Generally, materials with LOI values higher than 26 might show self-extinguishing behavior and were considered to be highly flame-retardant. The results of LOI and UL-94 for epoxy resin and its composites are listed in Table 3. Table 3 shows that the best results were achieved with 0.02% and 2% by weight of MWCNTs and nanoclay, respectively. The result was LOI of 25%, the burning rate of 20.5 mm/min, and UL 94HB of 18.6 mm/min. The quality of flame-protecting layers of materials and characteristics of burned material's surfaces was evaluated by FE-SEM method (Figures 1(a) and 2–4).

With epoxy resin, oxidizing agents are easy to attack, and therefore, this plastic sample will easily ignite. MWCNTs have formed a thin film covering the outside of the material.

Although thin, it is interwovenly complicated by MWCNTs with the ability to conduct heat along the pipe as well as the heat resistance in the middle of the tubes very well. This leads to the fact that the oxidizing agents are difficult to penetrate and help the material's fire resistance, especially when the protective coal layer is formed [4].

When MWCNTs are well dispersed in the substrate, the coal layer produced will be more evenly spread over the surface. Also, this barrier will minimize the ability to catch fire as well as exposure to air oxygen. At the same time, the tendency to reignite is reduced, making the fire impossible to spread and fade [4]. The compact structure also increases the fire resistance of the material.

A barrier-like barrier is created by nanoclay elements that are heat-resistant and heat-retaining, which slows down the diffusion of oxygen and prevents flammable substances from burning in the material. The process of heat transfer to the material has therefore reduced the time to sustain the combustion. The formation of a silicate ash layer evenly spread on the surface of nanocomposite has prevented the penetration of the flame to help the combustion process be extinguished.

In the case of MWCNTs/nanoclay/epoxy resin materials, there was no crack in flat surfaces (Figure 7(b)), in which when the epoxy material is burned, the surface of the burning gas has many cracks (Figure 7(a): neat epoxy). The ash layers formed from burning MWCNTs and nanoclay in surfaces play an important role like heat shields to prevent the heat transfer. If there are layers of ash formed from burning polymers, they can play as heat-isolation layers, restricting the heat transfer from heat resources to polymers. Thus, the number and structure of ash layers play an important role to restrict the combustion of polymers. It can delay the heat transfer from heat resources, leading to more slow increase temperature. A phenomenon observed in experiments with the presence of MWCNTs was the dripping of samples when burned, proving the important role of MWCNTs in improving the fire-retardant properties of materials. It can delay the heat transfer from heat resources, leading to more slowly increase temperature. A phenomenon observed in experiments with the presence of MWCNTs was the dripping of samples when burned, proving the important role of MWCNTs in improving the fire-retardant properties of materials.

If the nanocontent increases, the viscosity increases and affects dispersion. If the nanocontent exceeds the threshold leading to a decrease in the compatibility with epoxy base resin and the accumulation of nanoparticles (Figures 8 and 9), the amount of residual nanomaterial creates holes (Figure 10) inside. Whether these factors are responsible for the reduction of mechanical strength and fire resistance. In the case of small nanoadditives, the mechanical strength and fire resistance are not met.

On the other hand, if the dispersion technique is not suitable, there will be nanoparticles aggregation in some places right above the interface of nano-epoxy E 240. There are residual nanoparticles, forming a separate phase of breaking down, where cracks are formed and grown,

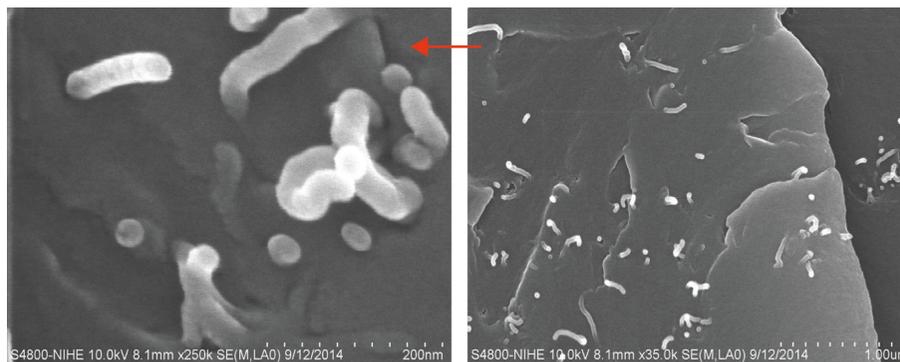


FIGURE 6: FE-SEM micrographs of MWCNTs 0.02 wt.%/nanoclay 2 wt.%/epoxy Epikotre 240 nanocomposites.

TABLE 2: Optimum mechanical properties of epoxy/nanoclay/MWNT nanocomposites from fine tuning experiments.

Trial	Sample code	MWCNT content (wt.%)	Nanoclay content (wt.%)	Tensile strength (MPa)	Flexural strength (MPa)	Compressive strength (MPa)	Impact strength (kJ/m <sup>2</sup> )
1	Neat epoxy resin	0.00	0	55.90 ± 0.6	86.75 ± 0.5	156.08 ± 0.3	7.11 ± 0.45
2	EP1	0.01	1	87.56 ± 0.5	93.70 ± 0.5	205.99 ± 0.4	10.60 ± 0.50
3	EP2	0.02	1	88.34 ± 0.6	93.60 ± 0.4	195.23 ± 0.3	12.70 ± 0.45
4	EP3	0.03	1	90.42 ± 0.4	94.26 ± 0.5	216.08 ± 0.2	19.70 ± 0.60
5	EP4	0.01	2	93.43 ± 0.6	98.56 ± 0.3	203.76 ± 0.5	21.54 ± 0.70
6	EP5	0.02	2	95.50 ± 0.5	115.45 ± 0.5	219.10 ± 0.3	22.30 ± 0.45
7	EP6	0.03	2	92.12 ± 0.8	108.60 ± 0.3	203.51 ± 0.6	19.70 ± 0.60
8	EP7	0.01	3	93.45 ± 0.6	108.90 ± 0.6	212.08 ± 0.4	20.27 ± 0.50
9	EP8	0.02	3	90.67 ± 0.4	103.60 ± 0.4	202.13 ± 0.2	18.13 ± 0.40
10	EP9	0.03	3	90.67 ± 0.5	102.78 ± 0.2	200.10 ± 0.3	16.04 ± 0.70

TABLE 3: Results of flammability tests (reaction to small flame): oxygen index (OI) and UL 94 for nanocomposites.

Trial	Material	MWCNT content (wt.%)	Nanoclay content (wt.%)	LOI (vol.% O <sub>2</sub> ± 2σ)	Combustion rate (mm/min)	UL94 HB (mm/min)
1	Neat epoxy resin	0.00	0	20.6 ± 0.3	28.41	Not rated (NR)
2	EP1	0.01	1	22.8 ± 0.3	24.25	25.78 (HB)
3	EP2	0.02	1	24.2 ± 0.5	23.01	22.35 (HB)
4	EP3	0.03	1	24.6 ± 0.4	22.45	22.03 (HB)
5	EP4	0.01	2	24.2 ± 0.3	22.34	20.01 (HB)
6	EP5	0.02	2	25.0 ± 0.3	20.05	18.60 (HB)
7	EP6	0.03	2	24.6 ± 0.5	19.03	18.85 (HB)
8	EP7	0.01	3	24.2 ± 0.4	20.45	19.65 (HB)
9	EP8	0.02	3	24.6 ± 0.6	21.43	18.68 (HB)
10	EP9	0.03	3	24.6 ± 0.3	20.80	18.76 (HB)

reducing mechanical properties and fire resistance of the materials (Figures 10 and 11).

**3.4. E-Glass/Epoxy Nanocomposites.** Figures 12(a)–12(d) show the magnified SEM micrographs of fractured fibers. Evident from these micrographs, the fiber in e-glass/epoxy composites sample contains considerable amount of epoxy resin residue and rougher fracture surface in comparison to control samples. Similarly, in 2 wt.% nanoclay/e-glass/epoxy composites samples, distributed resin residue and rougher fracture surface were observed but not as profound as in

0.02 wt.% MWCNTs/e-glass/epoxy composites counterpart. In 2 wt.% nanoclay/0.02 wt.% MWCNTs/e-glass/epoxy composite samples, there are mixed regions of dispersed and agglomerated MWCNTs. The interfacial bonding in a well-dispersed region may have improved the interfacial bonding, whereas the agglomerated region contributed to the initiation of fracture. As a result, a distributed residue of resin, rougher fracture surface (Figure 12(d)), and several cracks (Figure 12(d)) were observed in 2 wt.% nanoclay/0.02MWCNTs/e-glass/epoxy composites sample.

The purpose of the research team is to manufacture epoxy E 240 substrates based on MWCNTs and nanoclay

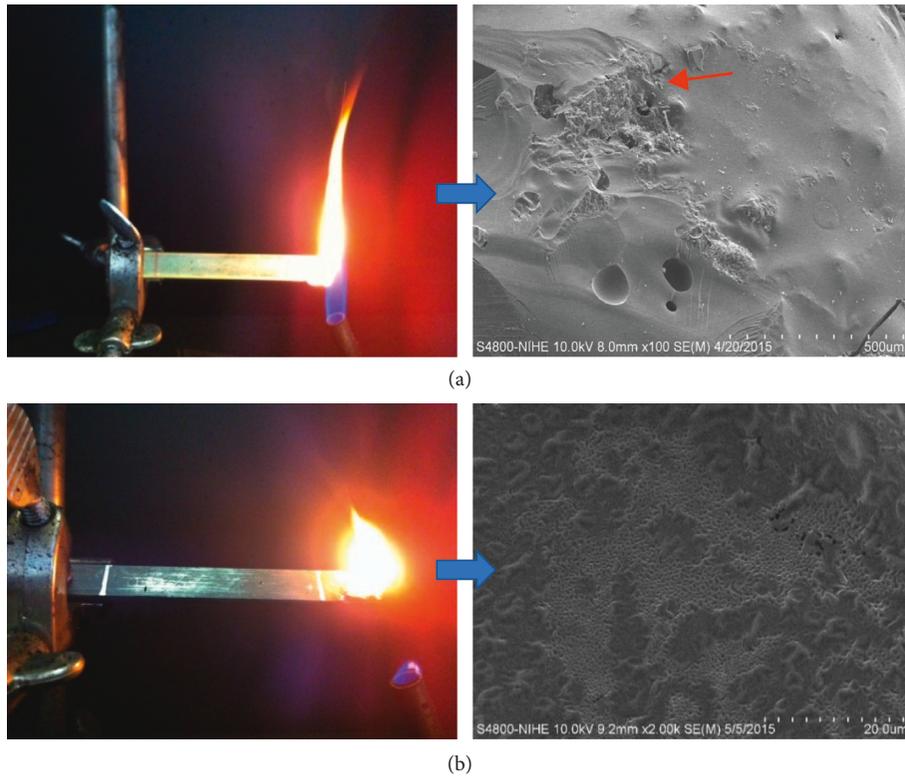


FIGURE 7: SEM images of the residual of (a) neat epoxy and (b) composites MWCNTs 0.02 wt.%/nanoclay 2 wt.%/epoxy resin (UL-94HB).

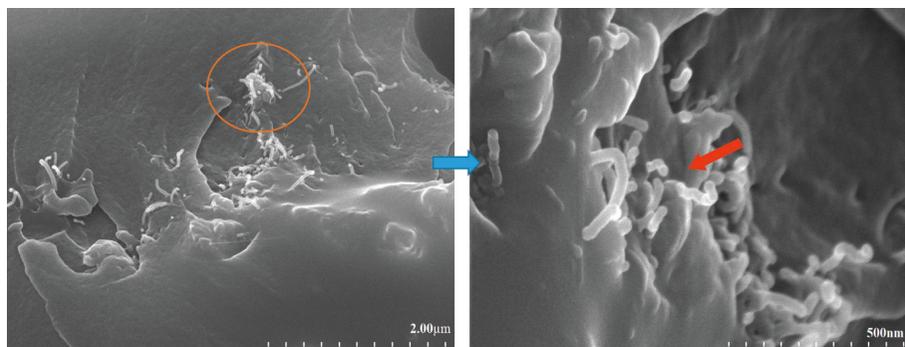


FIGURE 8: FE-SEM image of nanocomposite material MWCNTs/nanoclay mixing ratio: 0.03/2 (percentage mass).

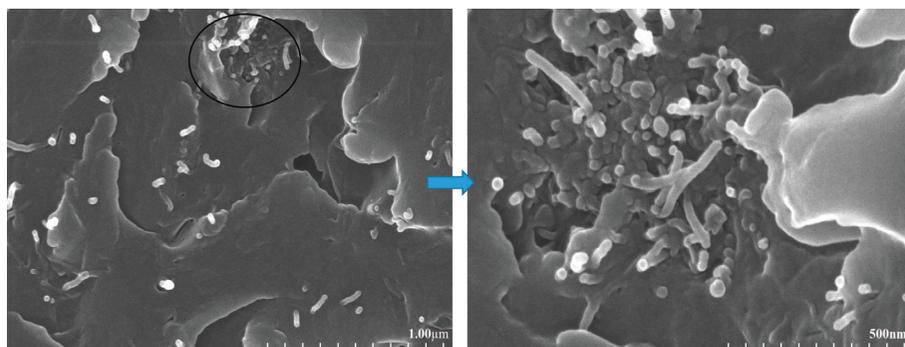


FIGURE 9: FE-SEM image of nanocomposite material MWCNTs/nanoclay mixing ratio: 0.03/3 (percentage mass).

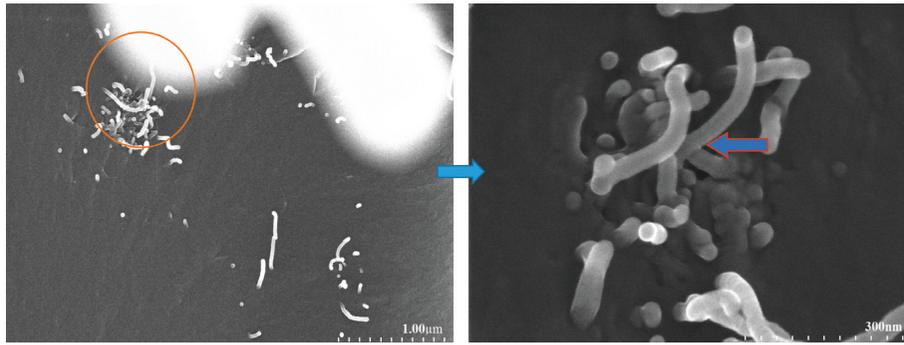


FIGURE 10: FE-SEM of MWCNTs/epoxy Epikote 240 nanocomposites.

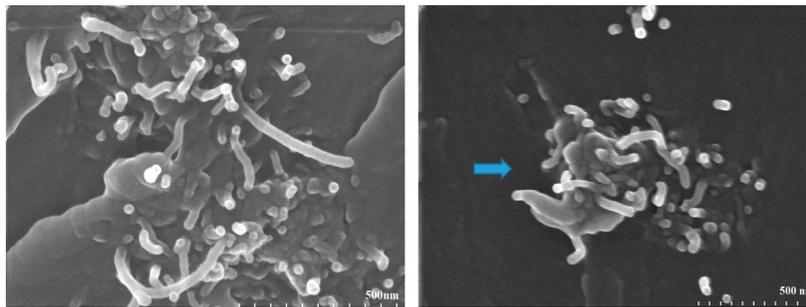


FIGURE 11: FE-SEM of MWCNTs/epoxy Epikote 240 nanocomposites.

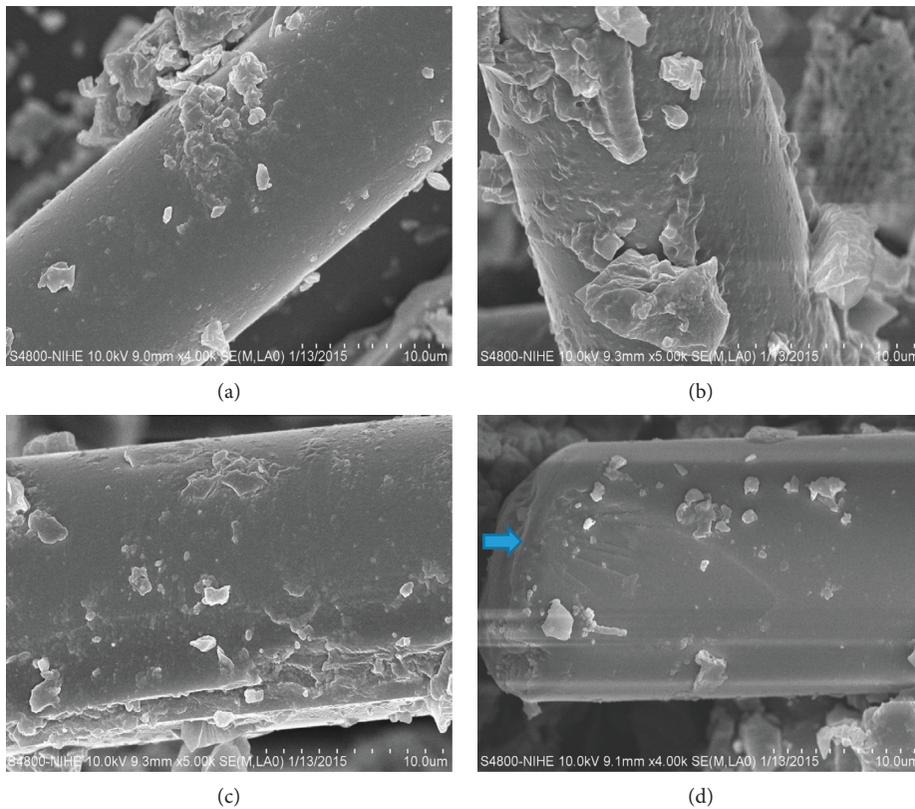


FIGURE 12: FE-SEM micrographs of fractured fiber of (a-e) glass/epoxy composites; (b) 2 wt.% nanoclay/e-glass/epoxy composites; (c) 0.02 wt.% MWCNTs/e-glass/epoxy composites; and (d) 2 wt.% nanoclay/0.02MWCNTs/e-glass/epoxy composites.

I.30E reinforced with glass cloth. Evaluate adhesion between epoxy base material (dispersed MWCNTs and nanoclay) and glass fiber-reinforced substance. The adhesion between substrate and reinforcement (MWCNTs, nanoclay, and glass fiber) plays an important role for the mechanical strength and fire resistance of nanocomposite-reinforced fiberglass materials. It may be directly related to the roughness of the fracture surface where crack development occurs [10].

#### 4. Conclusions

Results show that epoxy resin with an improved flame-retardant property was prepared by addition of nanoclay I.30E and MWCNT. In conclusion, mechanical properties and flame retardancy of epoxy resin were significantly improved by nanoclay I.30E/MWCNT additives. MWCNT and nanoclay I.30E uniformly distributed in epoxy resin form ash layers covering in material surface and preventing the contact between oxygen and the materials, limiting the development of flame. It can be said that the distribution ability of retardants in binders is more uniform, mechanical and retardant properties of materials are more improved. Thus, better dispersion and enhanced interfacial bonding between epoxy, MWCNT, nanoclay I.30E, and e-glass fibers leads to the improvement in thermomechanical and flexural properties of epoxy and consequently of glass/epoxy composites.

#### Data Availability

For any questions relating to the data or the original data requirements of the article, contact the corresponding author at anhnt.hau@gmail.com (anhnt@hau.edu.vn).

#### Conflicts of Interest

The authors declare that they have no conflicts of interest.

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## Research Article

# Preparation and Characterization of a Hydrophilic Polysulfone Membrane Using Graphene Oxide

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In general, the polysulfone (PSf) membranes are popular choices for water treatment because they have high thermal stability and good chemical resistance. On the other hand, the filtration capacity of the polysulfone membrane is limited because of its low water flux and poor antifouling ability, which are caused by the low surface hydrophilicity of the membranes. In this research, blending of graphene oxide (GO) or graphene oxide-titanium dioxide (GO-TiO<sub>2</sub>) mixture into the polysulfone matrix had been carried out through the phase inversion method to enhance the hydrophilic and antifouling properties. Methods such as energy-dispersive X-ray spectroscopy, scanning electron microscopy, Fourier transform infrared spectroscopy, and water contact angle measurement were used to examine the surface properties of the prepared membranes. Experimental results have led to a conclusion that graphene oxide can be stabilized into prepared membranes, and then, by reducing the water contact angle values, the surface of these membranes becomes hydrophilic, which increases the permeability and the water flux of methylene blue from the aqueous feed solution, improving the membrane's antifouling resistance.

## 1. Introduction

Today, membranes and membrane processes have been applied in cleaning technology and the environmental field [1, 2]. Efficiency and utility from membrane applications have led to the need for new membrane materials with properties suitable for their applications. Therefore, the type of material selected and the method of membrane preparation are the determining factors for the properties of the membrane.

Polysulfone (PSf) is the preferred choice in membrane fabrication, and its prominence is derived from chemical resistance, wide operating temperature and pH, and high mechanical strength [2–5]. However, at present, the operating costs of PSf membrane processes are still quite high

because of fouling, limitations on filtering capacity, and longevity, which are due to their high hydrophobic properties [2–4, 6, 7]. Recently, the increase in hydrophilicity and the minimization of fouling of PSf membranes have been tested through a variety of solutions including modifying the surface [8, 9], coating onto the membrane surface [10–14], and blending the hydrophilic materials into the membrane casting solution before fabricating the membrane [2, 5, 15–20]. Among the aforementioned methods, the method of blending PSf with some hydrophilic polymers or inorganic nanoparticles to increase the surface hydrophilic and antifouling properties has proven remarkably effective [2, 5, 20–23].

Zodrow et al. [21] blended nanosilver particles into the matrix of the PSf membrane to increase the membrane

hydrophilicity and reduce the biofouling and virus penetration. By using the phase inversion method, Kang et al. [2] prepared more hydrophilic PSf/SGO (sulfonated graphene oxide) membranes. After conducting the tests, the researchers found that mixing 1.5 w/w% SGO into the PSf matrix made this membrane reach a water flux higher than 125% compared to that of the PSf membrane. Prabhu et al. [5] blended the chitosan derivative 1H-pyrazole-4-carbaldehyde into the PSf matrix by the wet coagulation method. These observations indicate that hydrophilic groups (such as hydroxyl, amine, and imine) improved the hydrophilicity of the blended membrane as they cause a decrease in the contact angle (from  $70 \pm 1^\circ$  of the PSf membrane down to  $62 \pm 1^\circ$  of blended membranes) and the improvement in water flux (from 24 of the PSf membrane to  $351 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$  of the blended membrane at 0.8 MPa). Ravishankar et al. [20] blended graphene oxide (GO) nanoparticles into the PSf matrix to prepare PSf/GO membranes. The results showed that the PSf/GO membrane has a better hydrophobicity than the PSf membrane (the contact angle of water is  $34.2^\circ$  and the permeability is  $52.1 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ ).

Recently, graphene oxide (GO) has been one of the most common hydrophilic inorganic particles that are used for preparing blended membranes [3, 20]. It has been proven that the appearance of oxygen-containing groups including hydroxyl, epoxy, and carboxyl when fabricating a graphene oxide-blended membrane has shown that the membrane possess high effective flux and better antifouling capacity [20]. The strong hydrogen network with the water molecules is made up of oxygen functionalities, so it creates a strong hydrophilicity [22, 24]. The combination (blend) of GO into the membrane is prominent in increasing the permeability [25, 26] and antifouling [7] and antibacterial [23, 25–30] properties for membrane applications as have been recorded in many previous studies. All results show that GO-blended polymer membranes are more hydrophilic and antifouling than unblended membranes, and it means that GO membranes are hydrophilic [26–28].

To enhance the membrane-blending properties, titanium dioxide ( $\text{TiO}_2$ ) or other hydrophilic nanoparticle materials are integrated into the polymer membrane by modifying these nanoparticles with GO by the surface hydrothermal method [29, 31]. Safarpour et al. [32] prepared the reverse osmosis membrane by incorporating the reduced graphene oxide (rGO)/ $\text{TiO}_2$  material onto its surface. The researchers found that the separation efficiency and the antifouling capacity of the membranes increased compared to unblended membranes (water flux improved from 34.3 to  $51.3 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ , and antifouling resistance increased from 49% to 75% after 180 minutes filtering bovine serum albumin solution). In another article, Faria et al. [33] showed that the growth of bacteria and biofilm on membranes has been prevented by adding silver and graphene oxide to TFC-PA membranes. The reason for the decline in the flux is due to biofilm development, which has decreased by 30% after incorporating GOAg nanocomposites onto the TFC membrane.

Most polysulfone membranes are prepared by the phase inversion method as other polymer membranes. To begin the membrane forming process, the researchers dissolve the

polymer in the solvent or in an organic solvent mixture. Then, the coating solution is spread in the form of a thin layer onto the plate or on a rotating disc, and the next membrane is coagulated in a solvent-free medium to form a porous membrane [33, 34]. A spin coating method is a technique for making a highly homogeneous membrane [34].

In general, the coating of hydrophilic layers such as GO and  $\text{TiO}_2$  onto the membrane matrix is an effective method for improving the membrane separation performance.

However, very little information on the preparation of the polysulfone membranes with GO and  $\text{TiO}_2$  has been known.

In this study, graphene oxide nanoparticles and graphene oxide/titanium dioxide were blended into the polysulfone matrix to prepare polysulfone/GO (PSf/GO) and polysulfone/GO- $\text{TiO}_2$  (PSf/GO- $\text{TiO}_2$ ) membranes using the phase inversion method. Effects of GO and  $\text{TiO}_2$  on the hydrophilic and antifouling properties of the blended membranes were also compared by determining permeability, retention, flux, and fouling resistance of methylene blue in aqueous solution.

## 2. Experimental Methods

**2.1. Materials.** Graphene oxide (GO) prepared from graphite powder (Merck) by Hummers' method [35] and  $\text{TiO}_2$  prepared from tetrachloride  $\text{TiCl}_4$  (Merck) titanium by the sol-gel method were used as additives in the coating solution. Polysulfone (molecular weight:  $22,000 \text{ g}\cdot\text{mol}^{-1}$ ) was used as the original polymer supplied by Sigma-Aldrich in the casting solution. *N,N*-Dimethyl formamide (DMF) purchased from China Science Co., Ltd. was used as a solvent. Methylene blue (MB) (China) has been used to prepare feed solutions for membrane filtration experiments.

**2.2. Preparation of PSf, PSf/GO, and PSf/GO- $\text{TiO}_2$  Membranes.** The PSf, PSf/GO, and PSf/GO- $\text{TiO}_2$  membranes were prepared through phase inversion with DMF used as a solvent, GO and GO-modified  $\text{TiO}_2$  as additives to prepare PSf/GO and PSf/GO- $\text{TiO}_2$  membranes, and deionized water as the nonsolvent in the coagulation bath.

Polysulfone and a different amount of GO (0.0, 1.0, and 2.0% by weight of PSf) were added to DMF and dissolved for 24 hours at  $60^\circ\text{C}$  by sonication to obtain a homogeneous mixture, and then to allow the mixture to release all the bubbles, it was left overnight.

To prepare PSf/GO- $\text{TiO}_2$  membranes, a different amount of  $\text{TiO}_2$  (10, 15, and 20% by weight of GO) and GO were added to DMF and dissolved for 24 hours at  $60^\circ\text{C}$  by sonication to obtain a homogeneous mixture and then left overnight.

Using the spin coating method, the solutions are then dripped on clean glass supports (coating speed in the range of 1400 to 2400 rpm). Then, the solvent is evaporated in 30 seconds, and this solution is soaked in a freezer. After that, the membrane that was formed was peeled off and deionized water was used to wash it in order to remove any

remaining solvents. Before testing, the blended membranes must be kept carefully in deionized water.

**2.3. Characteristics of Materials and Membranes.** A D8 Advanced Bruker anode X-ray diffractometer with CuK $\alpha$  ( $\lambda = 0.154$  nm) radiation using the scanning step of  $0.02^\circ \cdot \text{s}^{-1}$  in the range of  $2^\circ$  to  $80^\circ$  was used to analyze X-ray diffraction (XRD). An electron microscope (SEM-EDX, Nova Nano SEM 450) and a transmission electron microscope (TEM, JEOL 2100F) were used to determine the morphology, size, and elemental mapping of the samples to be summed; the case is characterized by energy-dispersive X-ray spectroscopy. The results of the Fourier transform infrared (FTIR-ATR) spectroscopy method used for samples were recorded on a PerkinElmer spectrophotometer. Water contact angle measurement was used to calculate the moisture content of the unblended and blended membranes via CAM 101/KSV Instruments (Finland), which was used to capture ionized water drops located on the dry surface of the membrane at  $25^\circ\text{C}$ .

**2.4. Assessment of Membrane Filtration Properties.** Membrane separation tests are performed in a terminal filtration system, including  $200\text{ cm}^3$  stainless steel cylindrical cells and a paddle impeller; working pressure in all experiments is 0.87 bar. The filtrate was collected every 5 minutes, and the average throughput was calculated after 90 minutes of filtration. In all experiments, we carefully washed membrane cells with pure water (both before and after use).

Membrane filtration properties are determined through permeability  $J_w$  ( $\text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$ ) =  $[V_w/(AtP)]$ , where  $V_w$  is the volume of water through the membrane area of  $A$  during the pressure determination of  $P$ . Ratio of permeability normalization ( $J_w/J_{w0}$ ), where  $J_w$  and  $J_{w0}$  are the permeabilities of the blended and unblended membranes, was used to examine the improved permeability of the membrane. The flux ( $J$ ,  $\text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ ) is evaluated by  $J = [V/(At)]$ , where  $V$  is the volume of the filtrate. The normalized flux ratio ( $J/J_0$ ) has been used to determine the enhancement of flux of blended membranes, in which  $J$  and  $J_0$  are the flux of the blended and unblended membranes, respectively. The retention ( $R$ ) of methylene blue is calculated by  $R = [(C_0 - C)/C_0] * 100$  (%), where  $C_0$  and  $C$  are methylene blue concentrations in feed and filtrate, respectively.

**2.5. Assessment of Membrane Antifouling Property.** The antifouling property was determined via the maintained flux ratios (FM, %) during filtration. The maintained flux ratio was evaluated by  $\text{FM} = (J_t/J_{t0}) * 100$  (%), where  $J_t$  and  $J_{t0}$  are the fluxes of membranes at  $t$  time and initial time ( $\text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ ).

### 3. Results and Discussion

**3.1. Characteristics of GO and GO-TiO<sub>2</sub> Nanoparticles.** The successful synthesis of GO, TiO<sub>2</sub>, and GO-TiO<sub>2</sub> materials has been confirmed through X-ray diffraction (XRD) spectroscopy, scanning electron microscopy (SEM), energy-

dispersive X-ray spectroscopy-mapping (EDX-mapping), transmission electron microscopic (TEM) image, and Fourier transform infrared (FTIR) spectral analysis.

**3.1.1. X-Ray Diffraction (XRD) Spectrum.** Figure 1 shows the XRD spectrum of GO, TiO<sub>2</sub>, and GO-TiO<sub>2</sub>. The diffraction peak at a lower angle of about  $11.4^\circ$  GO implies the introduction of oxygen-containing functional groups of GO [36, 37]. However, two broad peaks at about  $26^\circ$  and  $44^\circ$  assigned to graphite can clearly see the complete non-oxidation of graphite. Also, Figures 1(a) and 1(b) shows the appearance of a titanium element in the TiO<sub>2</sub> and GO-TiO<sub>2</sub> nanoparticles, respectively. We can see that the TiO<sub>2</sub> materials appeared in the anatase phase (based on the standard library JCPDS 21-1272), with the occurrence of sharp peaks (101), (004), (105), (211), and (204) at  $2\theta$   $25.5^\circ$ ,  $37.0^\circ$ ,  $54.0^\circ$ ,  $56.5^\circ$ , and  $62.5^\circ$ . Besides, rutile phase also appeared (according to the standard library JCPDS 65-0190) along (110) and (111) at  $2\theta$   $27.5^\circ$  and  $41.2^\circ$ . In Figure 1(b), the characteristic peaks of GO and TiO<sub>2</sub> appeared. Therefore, GO and GO-TiO<sub>2</sub> were synthesized successfully.

**3.1.2. SEM, EDX Mapping, and TEM Images.** Figures 2 and 3 display the SEM, EDX-mapping, and TEM images of GO and GO-TiO<sub>2</sub> nanoparticles. The results showed that GO had a wrinkled surface with some small pieces. This indicated the successful exfoliation of the GO sheet from graphite during graphite oxidation. As can be seen more clearly via the TEM image, there were many layers of GO onto the graphite surface. Thus, the GO material was synthesized successfully from graphite.

SEM images (Figure 3(a1) and 3(a2)) of synthesized GO-TiO<sub>2</sub> materials showed that the aggregated TiO<sub>2</sub> nanoparticles appeared with GO particles. TEM image of GO-TiO<sub>2</sub> materials showed that the average particle size of TiO<sub>2</sub> particles dispersed onto the GO sheet was 10 nm (Figure 3). Thus, the GO-TiO<sub>2</sub> material was synthesized successfully. EDX-mapping images were used to check the components in the synthesized material. Figures 3(b)–3(d) show that there is a homogeneous distribution of the C, O, and Ti elements in the materials.

**3.1.3. FTIR Spectra.** The FTIR-ATR spectra of GO, TiO<sub>2</sub>, and GO-TiO<sub>2</sub> are shown in Figure 4. The peaks of GO (Figure 4(a)) were observed via the appearance of C-O stretching, C=O stretching, and O-H stretching, which include the bands at  $1050\text{ cm}^{-1}$ ,  $1720\text{ cm}^{-1}$ , and  $3350\text{ cm}^{-1}$  after oxidizing graphite into GO. These groups are hydrophilic. Thus, GO is also hydrophilic. Moreover, the spectrum of TiO<sub>2</sub> (Figure 4(b)) and GO-TiO<sub>2</sub> (Figure 4(c)) showed peaks at approximately  $580\text{--}1000\text{ cm}^{-1}$  attributed to Ti-O-Ti stretching [38], showing the successful synthesis of TiO<sub>2</sub> particles into the GO-TiO<sub>2</sub> material.

**3.2. Membrane Characteristics.** After preparation of unblended and blended membranes with GO and GO-TiO<sub>2</sub>, the hydrophilic ability of membranes was evaluated through

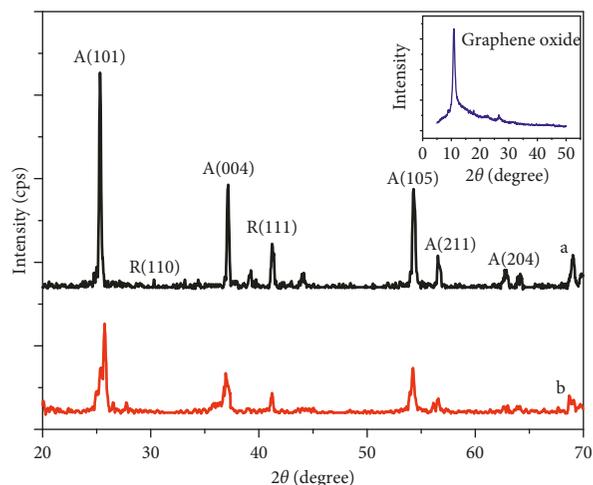


FIGURE 1: XRD spectrum of GO (inset), TiO<sub>2</sub> (a), and GO/TiO<sub>2</sub> (b).

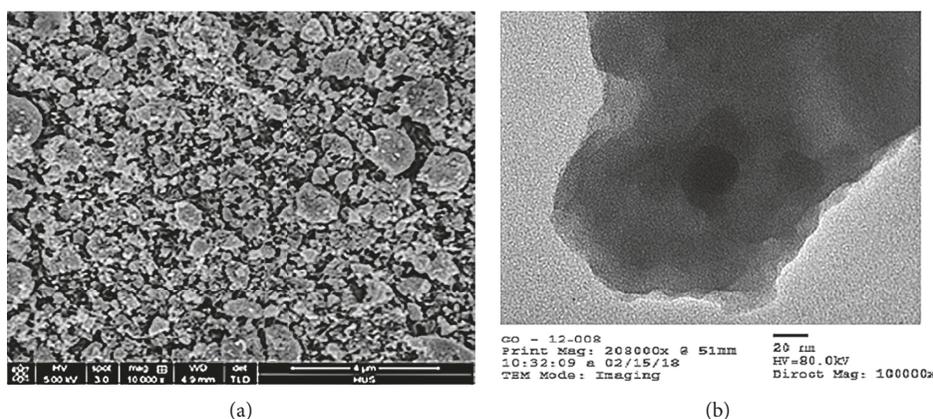


FIGURE 2: SEM and TEM images of GO.

scanning electron microscopy (SEM), energy-dispersive X-ray (EDX) spectroscopy analysis, Fourier transform infrared (FTIR) spectroscopy analysis, and water contact angle (WCA) measurement.

**3.2.1. SEM Images.** SEM images of PSf, PSf/GO, and PSf/GO-TiO<sub>2</sub> membranes with various amounts of TiO<sub>2</sub> (10, 15, and 20 wt.% based on the weight of GO) are displayed in Figure 5.

Following the cross-sectional images, the PSf membrane has a porous structure with the dense skin layer and the membrane thickness was 64 μm. Adding GO to the membrane leads to a dramatic change in the PSf membrane structure. Figure 5 shows that GO is deposited onto the membrane surface, and the dispersed grain structure appeared smooth. GO particles make the membrane thickness higher (79 μm). With the increased addition of TiO<sub>2</sub> to the polymer matrix, surface roughness and membrane thickness increase continuously (from 87.0 to 96.7 μm). It is clear that GO and TiO<sub>2</sub> nanoparticles are uniformly dispersed in the PSf matrix. In the higher content of TiO<sub>2</sub>, the holes have disappeared; the surface of the

blended membrane becomes thicker than that of the unblended membrane.

The formations of materials containing both hydrophilic GO and TiO<sub>2</sub> can lead to changes in chemical functionality and separation performance of the membrane.

**3.2.2. FTIR-ATR Spectrum.** Characteristics of the membrane surface were investigated by FTIR spectroscopy, and FTIR-ATR technique was used to demonstrate the successful incorporation of GO and TiO<sub>2</sub> into the polymer matrix of membranes.

Absorptions of the polysulfone layer are characterized by O=S=O (1000–1300 cm<sup>-1</sup>) and C=C (1400–1600 cm<sup>-1</sup>) for the polysulfone membrane (Figure 6(a)). The appearance of oxygen-containing groups of GO such as C-O stretching (1674 cm<sup>-1</sup>) and C=O stretching (1101 cm<sup>-1</sup>) was observed using spectroscopy (Figure 6(b)) for the blended PSf/GO membrane. With the existence of oxygen-containing groups of GO, the spectroscopy (Figure 6(c)) exhibits a new peak at 600–1000 cm<sup>-1</sup> for the blended PSf/GO-TiO<sub>2</sub> membrane, which attributes to the Ti-O-Ti stretching [39, 40]; it shows the successful

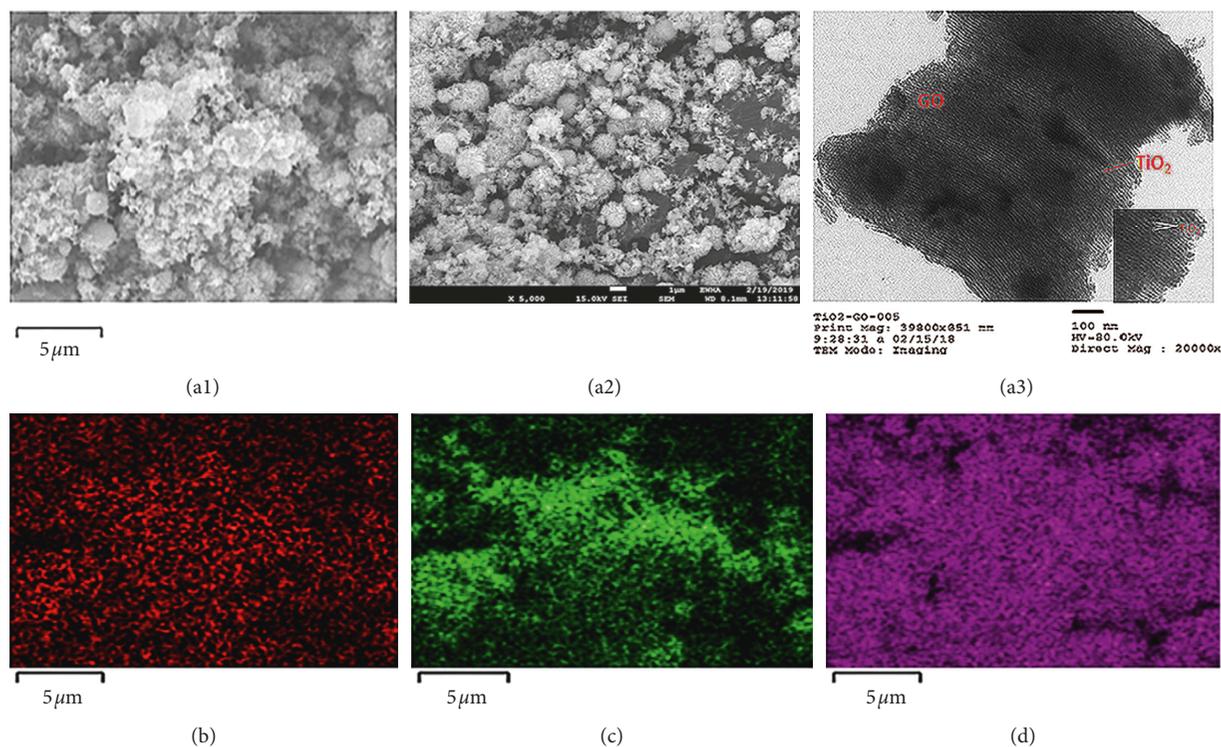


FIGURE 3: SEM (a1, a2), TEM (a3), and EDX-mapping images of C K series (b), O K series (c), and Ti K series (d) elements of GO-TiO<sub>2</sub> materials.

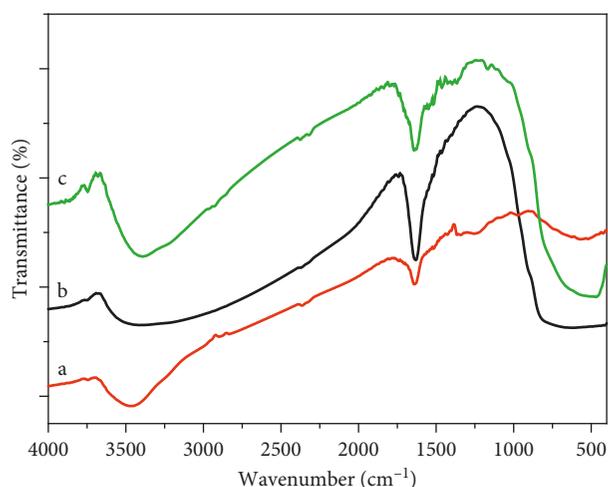


FIGURE 4: FTIR spectra of GO (a), TiO<sub>2</sub> (b), and GO-TiO<sub>2</sub> (c) materials.

blending of TiO<sub>2</sub> and GO particles into the PSf membrane. Thus, the reason why the membrane becomes hydrophilic is the presence of GO and TiO<sub>2</sub>.

**3.2.3. EDX Analysis.** To study the amount of elements of membranes, EDX had been conducted. Figure 7 shows the EDX spectra of unblended and blended membranes and the changes in the proportion of each element.

As can you see, compared to the PSf membrane (Figure 7(a)), the PSf/GO membrane (Figure 7(b)) increased

oxygen (from 9.76% to 19.26%) atomic ratio, but carbon and sulfur ratios were decreased (with a sharp decrease of C atoms from 87.85% to 79.34% and a sharp decrease of S atoms from 2.39% to 1.40%). For the PSf/GO-TiO<sub>2</sub> membrane (Figure 7(c)), the oxygen atomic ratio increased to 33.99% and carbon atomic ratio decreased to 64.79%; meanwhile, the Ti atomic ratio was 0.08%. These results proved that GO and TiO<sub>2</sub> nanoparticles exist on the PSf membrane.

**3.2.4. Water Contact Angle Measurement.** Changes in the water flux of membranes as a result of blending of hydrophilic materials (GO and TiO<sub>2</sub>) were investigated via the water contact angle (WCA) measurements. Figure 8 shows the WCAs of the unblended and blended membranes. The results indicated that, by adding GO and TiO<sub>2</sub> into the PSf matrix, the blended membranes became more hydrophilic with a significant decrease of the WCA (Table 1), reducing from 83.4° for the unblended membrane to around 60.2° for the blended ones, which is because of the formation of the hydrophilic material on the blended membrane. Thus, the increase of the hydrophilic groups on the membrane reduced the water contact angle values. The obtained results imply that the presence of the GO and TiO<sub>2</sub> improves the hydrophilicity of the membrane.

**3.3. Membrane Filtration Property.** Indeed, with the appearance of the oxygen-containing groups of GO and TiO<sub>2</sub>,

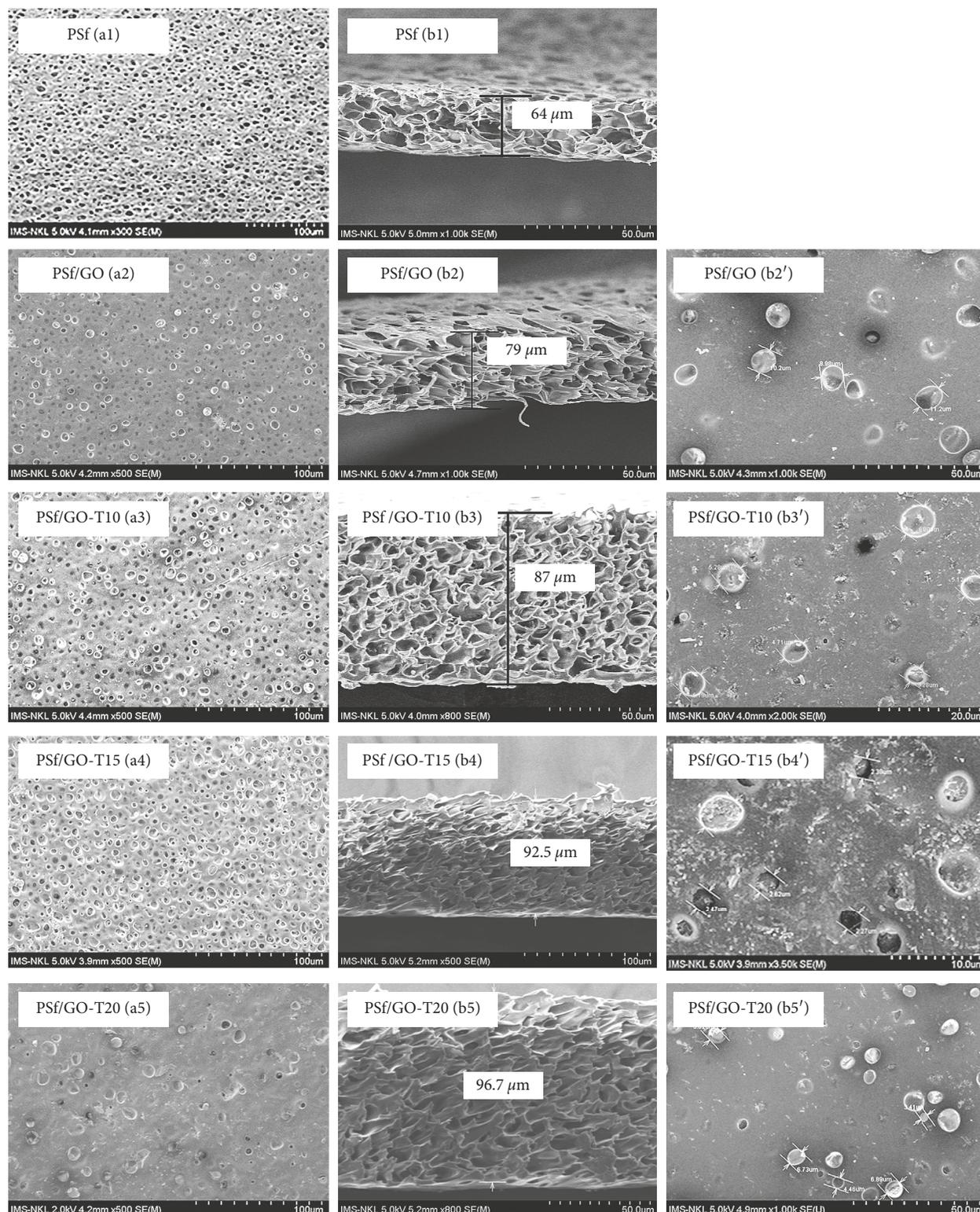


FIGURE 5: SEM images of the surface (a1, a2, a3, a4, a5; b2', b3', b4', b5') and the cross-sectional images (b1, b2, b3, b4, b5) of PSf, PSf/GO, and PSf/GO-TiO<sub>2</sub> membranes.

the blended membranes became more hydrophilic, and the obtained experimental results related to membrane separation performance are shown below.

**3.3.1. Permeability.** The permeability can be selected to characterize the changes in the hydrophilic property of the membrane surface. The permeability of the membrane will

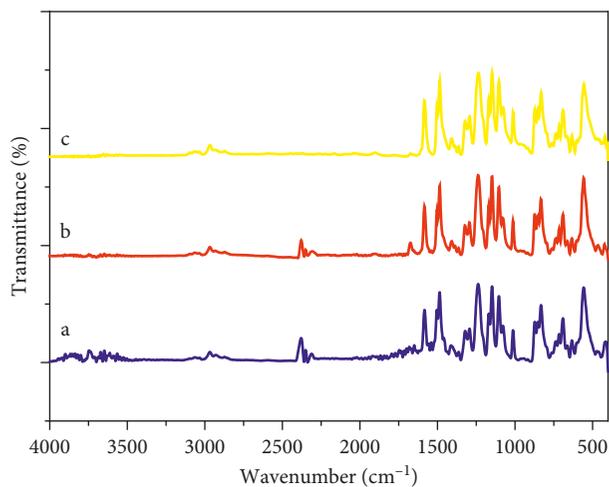


FIGURE 6: FTIR-ATR spectra of PSf (a), PSf/GO (b), and PSf/GO-Ti15 (c) membranes.

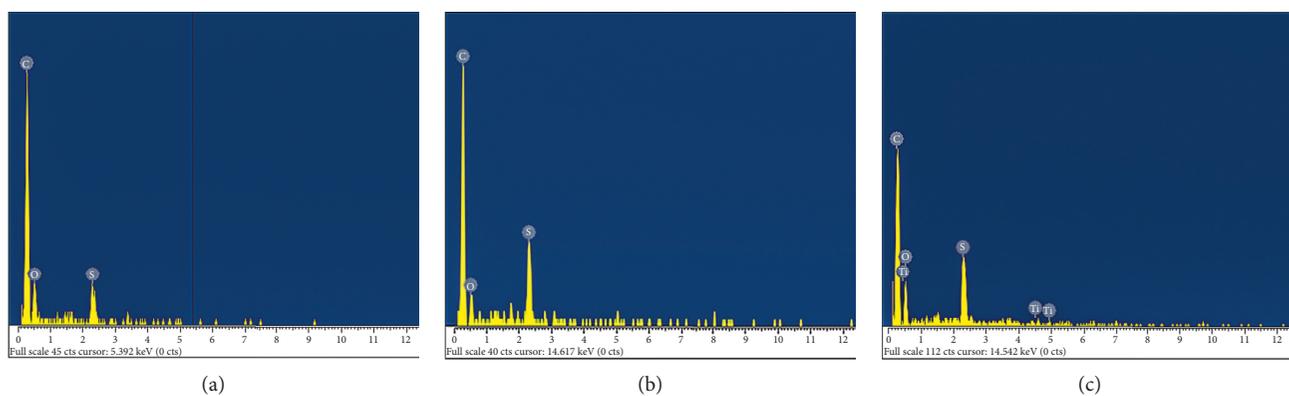


FIGURE 7: EDX spectra of PSf (a), PSf/GO (b), and PSf/GO-Ti15 (c) membranes.

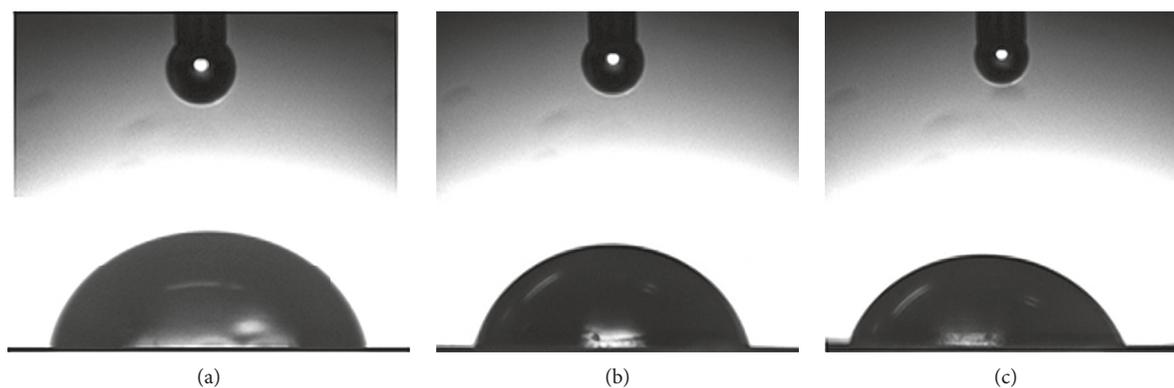


FIGURE 8: Water contact angle images of (a) PSf, (b) PSf/GO, and (c) PSf/GO-Ti15 membranes.

TABLE 1: Water contact angle values of PSf, PSf/GO, and PSf/GO-Ti15 membranes.

Membranes	PSf	PSf/GO	PSf/GO-Ti15
WCA (°)	83.4	76.2	60.2

be increased if the membrane becomes hydrophilic, which can be achieved by blending GO and  $\text{TiO}_2$  into the membrane [22]. The normalized permeability between the unblended membrane and the blended membrane at different conditions of  $\text{TiO}_2$  is shown in Figure 9. There is an increase

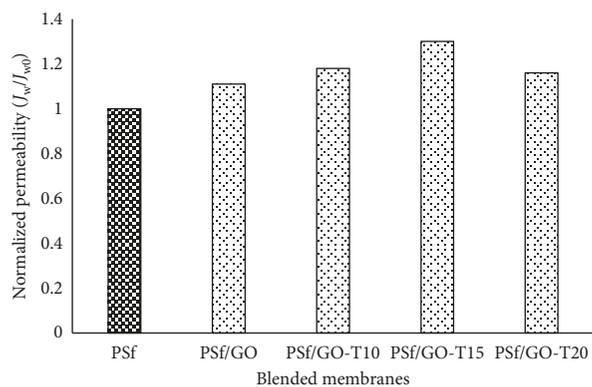


FIGURE 9: Normalized permeability of unblended and blended membranes.

(about 11 to 30%) in the permeability in membranes blended with GO and  $\text{TiO}_2$  compared to unblended membranes. Thus, the presence of GO and  $\text{TiO}_2$  functional groups that contain oxygen caused changes in water permeability. This also corresponds to the results of the WCA.

**3.3.2. Separation Performance.** Figure 10 shows the experimental results about the separation property of unblended and blended membranes at different conditions of  $\text{TiO}_2$ .

These results show that the flux in the filtrate of the blended membranes could increase dramatically (from 20 to 40%) compared to that of the unblended ones. These results are similar to the result of Badrinezhad et al. [1]. By increasing the amount of titanium dioxide, the separation performance of blended membranes is also higher, approximately 20% higher than unblended ones. This improvement is due to a thin layer of hydration formed on the surface of the membrane caused by hydrogen bonding between water molecules under the influence of oxygen-containing groups. This layer makes the water flux higher. In addition, the retention improves from 38% to 59% for the blended membranes. The increase in the retention is due to a hydrophilic thin layer formed, making the membrane surfaces compact.

**3.3.3. Antifouling Property.** The hydrophilicity also helps mitigate adhesion of foulants and increase the membrane antifouling ability. Figure 11 shows the comparison of the maintained flux ratios of unblended and blended membranes. The results indicate that the flux degradation of the blended membrane is greatly reduced compared to that of the unblended membrane. However, the time required to keep the flow stable is shortened. After 90 min of filtration of the methylene blue feed solution, the flux maintaining ratio of the unblended membrane was about 41%; meanwhile, it was higher than 45% that of the blended one.

## 4. Conclusions

In this research, the PSf, PSf/GO, and PSf/GO- $\text{TiO}_2$  composite membranes with different ratios of  $\text{TiO}_2$  are fabricated

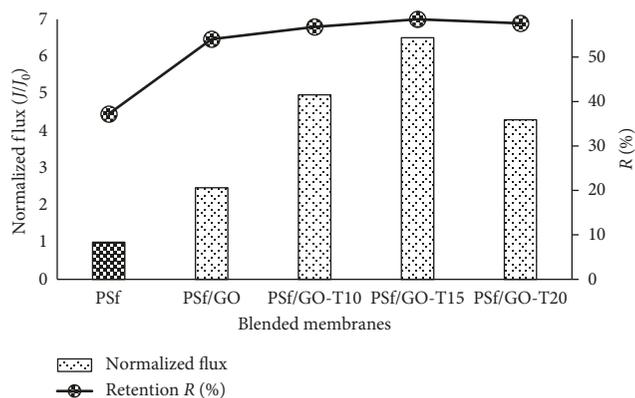


FIGURE 10: Normalized flux and retention of unblended and blended membranes.

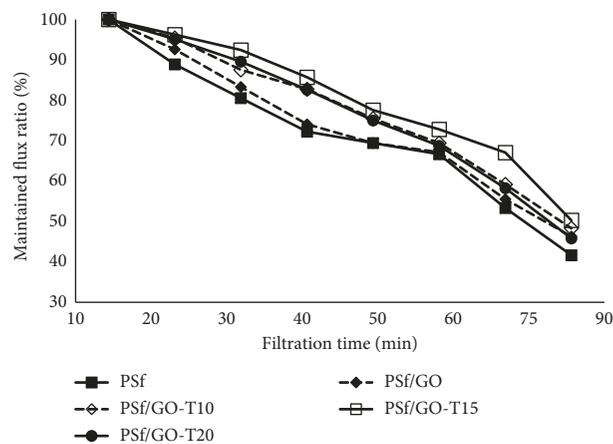


FIGURE 11: Maintained flux ratio of unblended and blended membranes.

and characterized. The presence of graphene oxide and titanium dioxide in the polysulfone polymer matrix is confirmed by SEM images, EDX spectra, FTIR-ATR spectroscopy, and WCA. The obtained results confirm the appearance of oxygen-containing groups of GO and  $\text{TiO}_2$ . This makes the blended membrane more hydrophilic with the increase of permeability, retention, flux, and antifouling capacity.

## Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

## Conflicts of Interest

The authors declare that they have no conflicts of interest.

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## Research Article

# Platinum Nanoflower-Modified Electrode as a Sensitive Sensor for Simultaneous Detection of Lead and Cadmium at Trace Levels

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We introduce the fabrication and electrochemical application of platinum nanoflower-modified glassy carbon electrode (PtNFs/GCE) for the trace level determination of lead and cadmium using differential pulse anodic stripping voltammetry (DPASV). The modified electrodes have been characterized by EDX, XRD, SEM, and AFM techniques to confirm chemical and physical properties. The effect of potential electrodeposition on the properties of the electrode was investigated. At  $-0.2$  V of potential, platinum developed with a nanoflower shape and dispersed densely all over the glassy carbon surface. In this condition, the highest of lead and cadmium electrochemical signals was clearly observed. The sensor showed wide linearity in the concentration range of  $1-100 \mu\text{g}\cdot\text{L}^{-1}$  with detection limits of  $0.408 \mu\text{g}\cdot\text{L}^{-1}$  and  $0.453 \mu\text{g}\cdot\text{L}^{-1}$  for lead and cadmium ions, respectively. The produced electrodes have good reproducibility with relative standard deviations of 4.65% for lead and 4.36% for cadmium ions. The results demonstrate that this simple, stable, and sensitive sensor is suitable for the simultaneous electrochemical determination of  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  at trace levels.

## 1. Introduction

One of the crucial factors leading to worldwide environmental pollution is the presence of heavy metal ions. Among heavy metals, cadmium is one of the most toxic heavy metals found in some surface and subsurface waters. A number of acute and chronic illnesses such as emphysema, hypertension, and skeletal malformation in the fetus have been attributed to the harmful properties of cadmium [1]. Another frequently encountered toxic contaminant in the environment is lead due to its application for car batteries, paints, and gasoline [2]. In detail, lead can disturb the metabolism of calcium and other critical nutrients by competing for binding sites [3]. Lead poisoning causes a variety of symptoms such as digestive, neurological, cardiac, and abdominal pain [4]. Several critical health problems have been

attributed to lead and most of the effects are observed in children, infants, and unborn individuals [5]. The significant environmental and biological damages caused by cadmium and lead call for rapid, sensitive, and simple analytical methods for their detection and monitoring.

Among analytical methods, electrochemical methods are the most efficient techniques for the determination of heavy metal ions because of their simple operation, low cost, high sensitivity, and capability to analyze elemental speciation. The efficiency of electrochemical analysis is strongly affected by the properties of the working electrode. Platinum has been commonly used as the electrode material. The major advantages of platinum in electrochemistry are chemical inertness, stability, easy fabrication, high conductivity, high reactivity, low background current [6], and high catalytic activity for a wide variety of reactions. The catalytic activity

of platinum depends on the size and orientation of platinum particles [7–9]; platinum nanoparticles (PtNPs) are over 100 times more active than microsized platinum powder and 1000 times more active than macrosized platinum [10]. Besides the high catalytic activity, nanoplatinum shows the fast electron exchange and the high ratio of surface area to volume [11]. Thus, the nanostructured electrode could help significantly increase the sensitivity in the analysis at trace levels.

So far, platinum nanostructured electrodes have been used for substrate modification and applied in detection of various organic compounds such as glucose [12], cholesterol [13], ascorbic acid [14], dopamine, uric acid [15], and granisetron [16]. In these research studies, the electrochemical signals of targets observed on the modified electrodes increased dramatically compared with those observed on the substrate that demonstrates the faster electron transfer and a larger electroactive surface of the nanostructured electrodes. However, there are a few authors studying Pt nanostructured electrodes for heavy-metal determination. In [17], Yoon et al. blended Pt nanoparticles with carbon powder and organic binder for electrode manufacturing to investigate the catalytic activity of platinum nanoparticles in the copper analysis. This modified electrode improved the copper peak current which is three times higher than that measured on the nonmodified electrode. Besides, almost fabricated Pt nanoelectrode for determination of organic compounds and heavy metals were at the construction of the sphere [17] or cube [14]. The platinum nanothorn with sharp tips and edges was electrochemically prepared; however, this material was used as a platform in surface-enhanced Raman scattering (SERS) measurement with high activity [18]. Besides, Pt nanoflowers, that is, nanostructures of Pt with flower-like shape, were prepared by using different methods such as chemical method [19, 20] and electrochemical method with cyclic voltammetric technique [12]. These electrodes exhibited a high electrochemically active surface area, thus leading to a high electrocatalytic activity.

In the present work, we developed a nanoflower-shaped platinum on a glassy carbon electrode by a one-step electrochemical deposition method and used it as a sensing probe in the simultaneous measurement of  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  ions at trace levels. The modified electrode was characterized by cyclic voltammetry (CV), field-emission scanning electron microscope (FE-SEM), energy dispersive X-ray (EDX), atomic force microscopy (AFM), and X-ray diffraction (XRD). The electrochemical behavior of lead and cadmium has been investigated with a sensitive, fast, and simple different pulse anodic stripping voltammetry (DPASV) method. In addition, the enhancement of the sensibility in Pb and Cd analysis has been evaluated when using the fabricated platinum nanoflowers electrodes.

## 2. Experimental

**2.1. Reagents.** All reagents necessary for the construction of Pt nanoflowers and subsequent measurements, hexachloroplatinic (IV) acid hexahydrate, potassium hexacyanoferrate (III),

sodium dihydrogen phosphate, disodium hydrogen phosphate, potassium chloride, sodium acetate, sulfuric acid, hydrochloric acid, acetic acid, lead stock solution (1000 ppm), and cadmium stock solution (1000 ppm), were purchased from Merck (KGaA, 64271 Darmstadt, Germany).

**2.2. Apparatus.** All electrochemical measurements were performed at room temperature. A three-electrode system with platinum nanoflower-modified glassy carbon electrode (PtNFs/GCE) as a working electrode, an Ag/AgCl reference electrode, and a platinum wire counter electrode were used to perform electrochemical measurements. The three-electrode system was connected to a custom-made multifunction potentiostat/galvanostat manufactured at the Vietnam Academy of Science and Technology (Hanoi, Vietnam). It was equipped with 12-bit analog-digital, digital-analog converters (ADC-DAC) with two operational amplifiers, which can provide ultrasensitive measurements with current resolution down to 0.008 nA. A field-emission scanning electron microscope (FE-SEM, S-4800, Hitachi Company, Japan) was employed to evaluate the morphologies of the PtNFs/GCE. The crystal phase was determined by D8 ADVANCE, Bruker, using  $\text{CuK}\alpha$  ( $\lambda = 1.54060$  nm) and scanning degree  $2\theta = 20\text{--}70^\circ$ . Energy dispersive X-ray spectroscopy (EDX) was performed with a JSM-6510LV, JEOL Ltd. Company, Japan. Atomic force microscopy (AFM) was performed with a Solver PRO SPM, NT-MDT Company, Russian.

**2.3. Preparation of Modified Electrode.** The glassy carbon electrode ( $d = 3.0$  mm) was washed with water and ethanol, then polished with a water slurry of  $0.05\ \mu\text{m}$  size of alumina powder to get a smooth and shiny surface, then electrodes were rinsed with double-distilled water and placed in an ultrasonic bath for a few minutes to remove any residual polishing material on the electrode surface, and then the electrode was dried at room temperature. The electrodeposition of platinum nanoparticles on the bare glassy carbon electrode was carried out in  $0.1\ \text{M}\cdot\text{H}_2\text{SO}_4$  solution containing  $1.0\ \text{mM}\cdot\text{H}_2\text{PtCl}_6$ . The effect of deposition potential ( $E_{\text{Pt}}$ ) on properties of the fabricated Pt layer was investigated. The effect of deposition time ( $t_{\text{Pt}}$ ) was evaluated in our previous study and herein we used the optimal value of  $t_{\text{Pt}}$ , that is, 150 s for further experiences. Following that, the Pt/GCE was gently cleaned with distilled water before use.

**2.4. Electrochemical Measurements.** The electrochemical measurements of the proposed sensor were carried out at room temperature ( $25 \pm 1^\circ\text{C}$ ) by the cyclic voltammetry (CV) and different pulse anodic stripping voltammetry (DPASV) methods. The electrochemical properties of the PtNFs/GCE were investigated by the cyclic voltammetric (CV) method in  $0.5\ \text{M}\cdot\text{H}_2\text{SO}_4$  solution from  $-0.1$  V to  $1.4$  V and solution of  $0.2\ \text{M}\cdot\text{PBS}$  pH 7 containing  $5\ \text{mM}\ [\text{Fe}(\text{CN})_6]^{3-}$  from  $-0.3$  V to  $0.8$  V at a scan rate of  $0.1\ \text{V}\cdot\text{s}^{-1}$ . The DPASV studies were carried out with preconcentration time 120 s, pulse amplitude

0.060 V, pulse time 0.050 s, step potential 0.007 V, step time 0.03 s, and sweep rate  $0.25 \text{ V}\cdot\text{s}^{-1}$ . The  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  ions were stripped of the electrode surface in the scan range  $-1.2$  to  $0.2 \text{ V}$ , and the peak currents were measured.

### 3. Results and Discussion

**3.1. Formation and Properties of PtNFs/GCE.** Platinum nanoflowers (PtNFs) were electrochemically deposited on GC by chronoamperometry in  $1.0 \text{ mM}\cdot\text{H}_2\text{PtCl}_6/0.1 \text{ M}\cdot\text{H}_2\text{SO}_4$  solution. An overview of the electrochemical behavior of this system is provided in Figure 1(a), which is a current-potential curve obtained from a cyclic voltammetric experiment at a polished GC electrode in  $0.1 \text{ M}\cdot\text{H}_2\text{SO}_4$  and in  $0.1 \text{ M}\cdot\text{H}_2\text{SO}_4$  solution containing  $10.0 \text{ mM}\cdot\text{H}_2\text{PtCl}_6$ . This wave exhibits three potential regions: the hydrogen region (from  $-0.2$  to  $+0.15 \text{ V}$ ) corresponds the adsorption/desorption of hydrogen with different energies, a broad oxidation peak for the Pt-oxide formation (commences at  $0.7 \text{ V}$  and extends up to  $1.2 \text{ V}$ ), and a single reduction peak at  $0.5 \text{ V}$  corresponding to the reduction of Pt(IV) to Pt(0) on the electrode surface. The result is in agreement with previous studies [21–23]. Therefore, in order to deposit Pt onto the GCE by chronoamperometry, the applied potential must be lower than  $0.3 \text{ V}$ .

Typical CV measured in  $0.5 \text{ M}\cdot\text{H}_2\text{SO}_4$  solution on the prepared Pt electrode is presented (Figure 1(b)). After the oxidation of Pt in the scanning at the anodic direction from  $-0.1$  to  $1.5 \text{ V}$ , in the reverse direction, the clear cathodic peak is observed at  $0.5 \text{ V}$  presented for the reduction of Pt (IV) on GC. These observations are in agreement with the data of other authors [23, 24]. This means that Pt had been deposited on glassy carbon platforms at the studied potential.

**3.2. Characterization of Platinum Nanoparticles.** In order to study the surface morphology, chemical characterization, and structure of the platinum particles, the field-emission scanning electron microscopy, X-ray diffraction, energy dispersive X-ray spectroscopy, and atomic force microscopy techniques were used in the next experiment.

**3.2.1. EDX Study.** The presence of Pt nanoparticles on the glassy carbon electrode surface is verified by the EDX analysis (Figure 2). The spectrum contained two peaks which were assigned to C, Pt.

The major peaks are around  $0.28, 2.10 \text{ keV}$ , which correspond to the binding energy of C, Pt. This also confirms that no other impurities have been identified. The weight ratios of prepared Pt on the electrodes increase as  $E_{\text{Pt}}$  changes from  $0.2 \text{ V}$  to  $-0.3 \text{ V}$  then decrease at  $-0.5 \text{ V}$ . This can be concluded that the amount of platinum deposited on the GCE strongly depends on the electrodeposition potential. These data show that platinum was successfully deposited on the surface of the glassy carbon with the highest amount at the applied potential of  $-0.3 \text{ V}$ .

**3.2.2. XRD Study.** Figure 3 shows the X-ray diffraction patterns of platinum nanoparticles deposited on the glassy

carbon electrode. There were three well-defined characteristic diffraction peaks at  $39.9^\circ, 46.2^\circ,$  and  $67.5^\circ$  respectively, indexed to reflections from (111), (200), and (220) planes of the face-centered cubic (fcc) crystal structure of metallic platinum. This result evidently exhibits that Pt exists on the GCE surface. The result is in agreement with previous studies [25–27].

**3.2.3. SEM Study.** The surface morphology of the Pt/GCE was investigated by microscopic imaging analysis. Figure 4 shows the typical SEM images of the GCE (Figure 4(a)) and Pt layer electrodeposited on the GCE under different electrodeposition potentials. The size of individual PtNF piece rises up to exceed the nanoscale. According to the SEM images, Pt was formed separately in nanoparticles shape at the deposition potential of  $0.2 \text{ V}$  and  $0.0 \text{ V}$  (Figures 4(b) and 4(c)) and in nanoflowers shape at the deposition potential of  $-0.2 \text{ V}$  and  $-0.3 \text{ V}$  (Figures 4(d) and 4(e)), and at the deposition potential of  $-0.5 \text{ V}$ , Pt developed into a film on the GCE (Figure 4(f)). This can be explained that at a negative potential, both hydrogen bubble release and Pt formation occur simultaneously, which resulted in the flower shape of Pt, while a positive potential represented the potential range at which only Pt formation occurred. At the deposition potential of  $-0.3 \text{ V}$ , the flower-shaped form is still maintained; however, large Pt clusters are observed due to the formation of Pt particles between flowers. It is observed in Figure 4(e) that there are some defects at which no Pt occupied resulting from the attachment of large  $\text{H}_2$  bubble at those sites. At the deposition potential of  $-0.5 \text{ V}$ , the Pt flower pieces developed slapping whereby they aggregated into a film, they had not been single, free flower-shaped structures at nanoscale any longer. In addition, the stronger hydrogen bubble release at that potential should significantly prevent the formation of Pt on the electrode surface; thus, many sites of glassy carbon surface (black spots) that have no Pt occupying can be seen in Figure 4(f). This structure would lead to a decrease of electrochemically active surface area of an electrode. This result will be reaffirmed in the next section.

**3.2.4. AFM Study.** The surface morphology of the GCE, platinum nanoparticle-modified GCE with deposition potential of  $0.2 \text{ V}$  (Pt0.2/GCE), and  $-0.2 \text{ V}$  (Pt-0.2/GCE) was examined by atomic force microscopy (AFM). The main goal was to determine and characterize a possible difference between the surface morphologies of the electrodes. A set of typical AFM images obtained for electrode surfaces tested in our study is shown in Figure 5. The images clearly reveal that the electrodes are used in different surface morphology.

The surface of the glassy carbon electrode appears to be smooth, atomically flat terraces (Figure 5(a)). To describe the electrode surface more quantitatively and to provide a quantitative comparison of the surface quality among the tested electrodes, we employed the root-mean-square (RMS) roughness [28]. RMS has been established as a rigorous quantitative measure of the surface roughness, and the

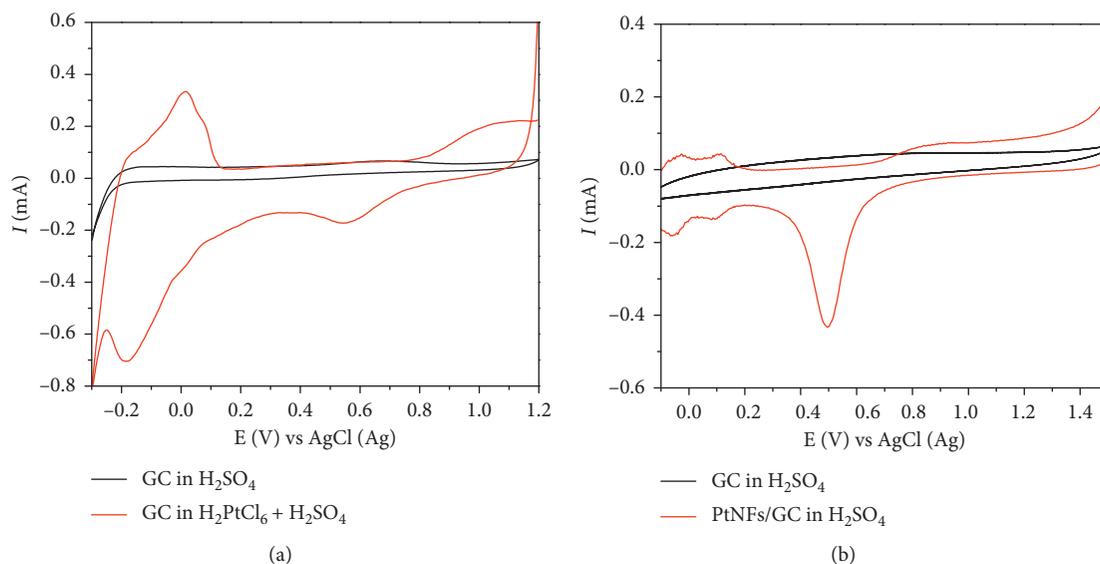


FIGURE 1: The cyclic voltammograms of a glassy carbon electrode in 0.1 M- $H_2SO_4$  solution and in 0.1 M- $H_2SO_4$  solution containing 10.0 mM- $H_2PtCl_6$  solution (a); a glassy carbon electrode and Pt/GCE in 0.1 M- $H_2SO_4$  solution (b), scanning rate of 0.1 V/s.

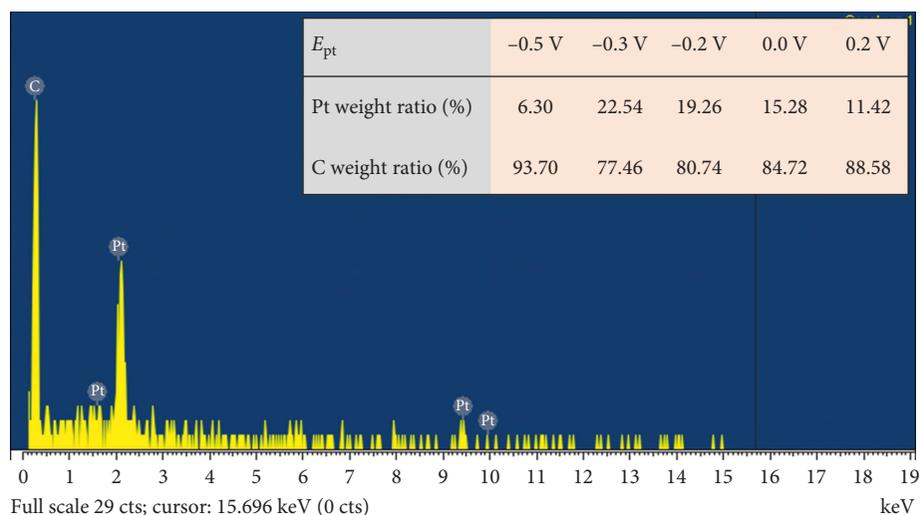


FIGURE 2: EDX spectra for the Pt/GCE prepared at the deposition potential of  $-0.3$  V and the weight ratio of Pt element on the GCE at the different deposition potential ( $E_{pt}$ ) (inset).

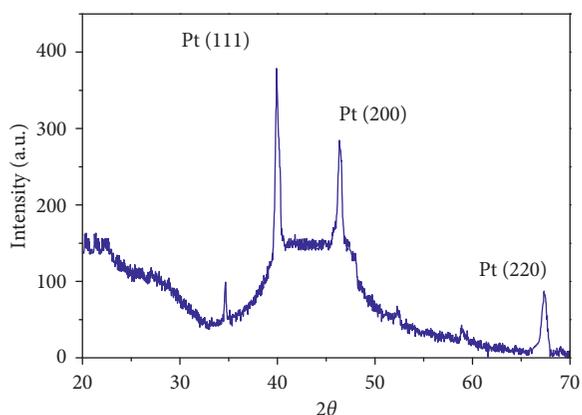


FIGURE 3: The X-ray diffraction pattern of platinum nanoparticles showing the face-centered cubic (fcc) crystal structure.

surface quality has often been used for such purpose. Apparently, it is one of the simplest morphology parameters that can be used for the surface quality description. For the GC electrode, we found that the average RMS is 672.82 nm. Contrary to the smooth and homogeneous surface of the GC electrode, the AFM image in Figure 5(b) reveals numerous features distributed all over the Pt-0.2/GC electrode surface. Typical morphology of Pt-0.2/GC electrode surface is shown in Figure 5(c). The AFM images of the electrode surface reveal mainly nodular features. However, they appear to be of a different shape and a lower height than those observed at the Pt-0.2/GC electrode surface. As expected, the Pt-0.2/GC electrode surface possessed a lower RMS value (730.53 nm) than that of the Pt-0.2/GC electrode surface (777.09 nm). In comparison with other electrodes, it is obvious that the Pt-0.2/GC electrode surface has the most

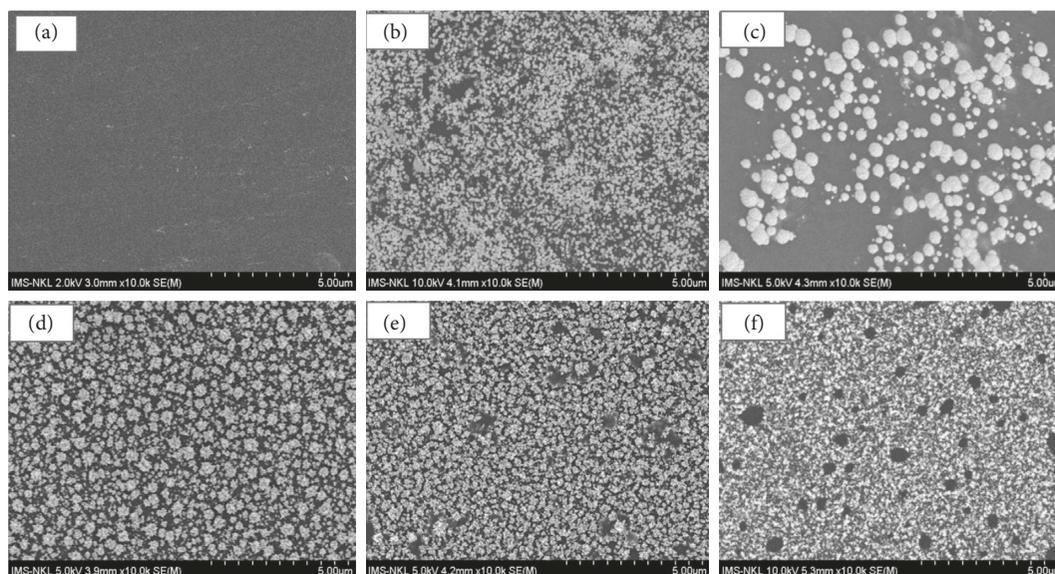


FIGURE 4: SEM images of GCE (a); PtNFs/GCE deposited at potential of 0.2 V (b), 0.0 V (c), -0.2 V (d), -0.3 V (e), and -0.5 V (f). Solution of 0.1 M·H<sub>2</sub>SO<sub>4</sub> containing 1.0 mM·H<sub>2</sub>PtCl<sub>6</sub>; stirring at 50 rpm.

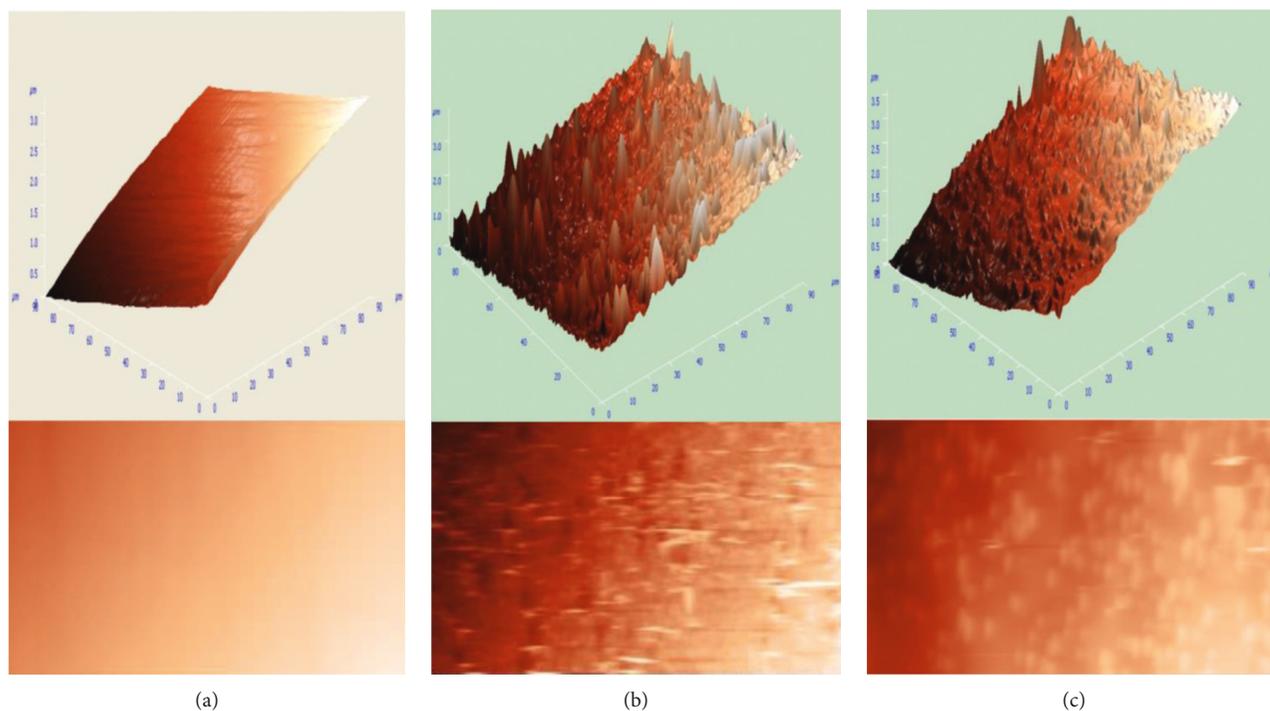


FIGURE 5: AFM images show the characteristic surface morphology form GCE (a); PtNFs/GCE deposited at the potential of -0.2 V (b); 0.2 V (c).

roughness and which consequently leads to an increase of electrochemically active surface area of the electrode. This result will be reaffirmed in the next section.

**3.3. Electrochemical Characterization of PtNFs/GCE.** Electrochemical characterization of Pt/GC electrodes prepared at different electrodeposition potentials of -0.5 V, -0.3 V, -0.2 V, 0.0 V, and 0.2 V was carried out by cyclic

voltammetry in two solutions which are 0.5 M·H<sub>2</sub>SO<sub>4</sub> and 5 mM K<sub>3</sub>[Fe(CN)]<sub>6</sub>. The electrochemically active surface areas of electrodes are calculated from the charge of hydrogen desorption peaks in 0.5 M·H<sub>2</sub>SO<sub>4</sub> solution and [Fe(CN)<sub>6</sub>]<sup>3-</sup> reduction peaks in K<sub>3</sub>Fe(CN)<sub>6</sub> solution through Randles-Sevcik equation [29–31]. As can be seen from the obtained results (Figure 6), the variation of surface areas of Pt electrodes estimated from both methods vs. deposition potential has the same trend in general. However, the data

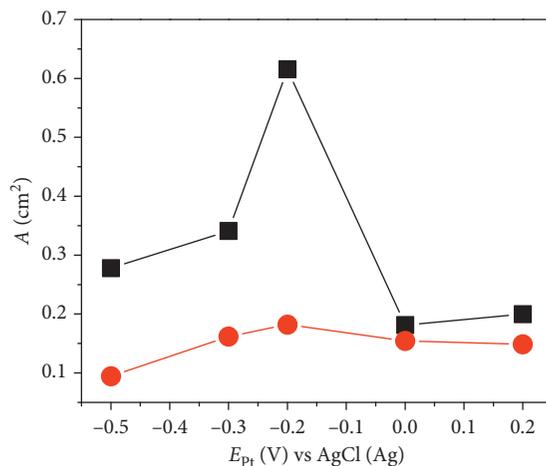


FIGURE 6: Effect of Pt electrodeposition potential on active surface area obtained from hydrogen desorption peaks (■) and ferricyanide reduction peaks (●).

calculated from hydrogen desorption peaks are higher than that obtained from ferricyanide reduction peaks. This could be explained by the fact that the size of the hydrogen atom is much smaller than that of the ferricyanide complex. As a result, the number of hydrogen is higher than the number of ferricyanide on the same electrode surface, especially on the Pt electrodes having a complex structure (flower-shaped nanostructure) that were prepared at  $-0.2$  V,  $-0.3$  V, and  $-0.5$  V. Obviously, surface areas calculated from charge of hydrogen desorption as well as from the ferricyanide peak current are directly proportional to the number of active species on the surface. Therefore, the surface areas of Pt electrodes calculated from the former method are higher than those obtained from the latter one. The data reveal that the largest area is reached at  $-0.2$  V of electrodeposition potential for both methods.

**3.4. Effect of Pt Electrodeposition Potential on Cadmium and Lead Signals.** As mentioned above, Pt deposition potential had a significant influence on the surface structure as well as the active surface area of the electrodes. Therefore, it certainly affects the electrochemical signal of cadmium and lead on these modified electrodes. Figure 7 shows DPASVs using GCE and the modified electrodes prepared at different electrodeposition potentials (E<sub>Pt</sub>) in acetate buffer solution pH 4.5 containing  $10 \mu\text{g}\cdot\text{L}^{-1}\cdot\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$ . The higher peak signal on the PtNFs/GCE compared with the one on the GCE confirms the ability to detect cadmium and lead of the modified electrodes with higher sensitivity. It is observed that the peak height raises as  $E_{Pt}$  decreases and reaches a peak at  $E_{Pt}$  of  $-0.2$  V, suggesting the amount of  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  preconcentrated onto the Pt/GCE depends on the surface morphology of this modified electrode. At more negative electrodeposition potential, the surface area of the electrode significantly decreases. This can be explained by the fact that the stronger generation of hydrogen at lower potential can damage the aggregation of metal crystals [32]. In addition, the formation of larger hydrogen bubble prevented the deposition of Pt on the electrode surface,

resulting in the exposure of large areas of GC substrate which can be clearly observed on the SEM image.

**3.5. Repeatability, Reproducibility, and Selectivity of PtNFs/GCE.** In this section, the repeatability, reproducibility, and selectivity of the PtNFs/GCE were studied. The repeatability of the modified electrode was evaluated by measuring the  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  ( $10 \mu\text{g}\cdot\text{L}^{-1}$ ), respectively, in acetate buffer (pH 4.5) at the same electrode (Figure 8(a)). The relative standard deviation (RSD) values were calculated to investigate the repeatability of the PtNFs/GCE as 1.59% for  $\text{Cd}^{2+}$  and 1.45% for  $\text{Pb}^{2+}$ , showing the good stability of cadmium and lead signal at the electrode. The reproducibility of the PtNFs/GCE was calculated through the  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  ( $10 \mu\text{g}\cdot\text{L}^{-1}$ ) signals from measurements of five different electrodes (Figure 8(b)). The RSD value of reproducibility was calculated to be 4.36% for  $\text{Cd}^{2+}$  and 4.65% for  $\text{Pb}^{2+}$  indicating that the fabrication procedure was reliable.

In order to evaluate the selectivity of the modified electrode, some common interferences were tested under optimized conditions. The effects of  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Fe}^{3+}$  were studied by recording the stripping peak current of  $20 \mu\text{g}\cdot\text{L}^{-1}\cdot\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  in the presence of interferences. The obtained results indicate that the presence of a 100-fold excess of  $\text{Zn}^{2+}$  and  $\text{Fe}^{3+}$  does not influence the  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  signals. The interference of  $\text{Cu}^{2+}$  on the stripping peaks of Pb and Cd on the PtNFs/GCE was obtained even at Cu(II)-to-Pb(II) or Cu(II)-to-Cd(II) concentration ratios 10:1 and was more severe as the Cu(II)-to-metal concentration ratio increased. In terms of the effects of organic compounds, especially surfactants could be absorbed on the electrode surface and so that they could influence the electrochemical responses of the  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  stripping peak current.

**3.6. Calibration and Detection Limit.** The linear range and detection limit were evaluated by using the optimal PtNFs/GCE in acetate buffer solution (pH 4.5). The DPASVs of increased amounts of metal ion species in the

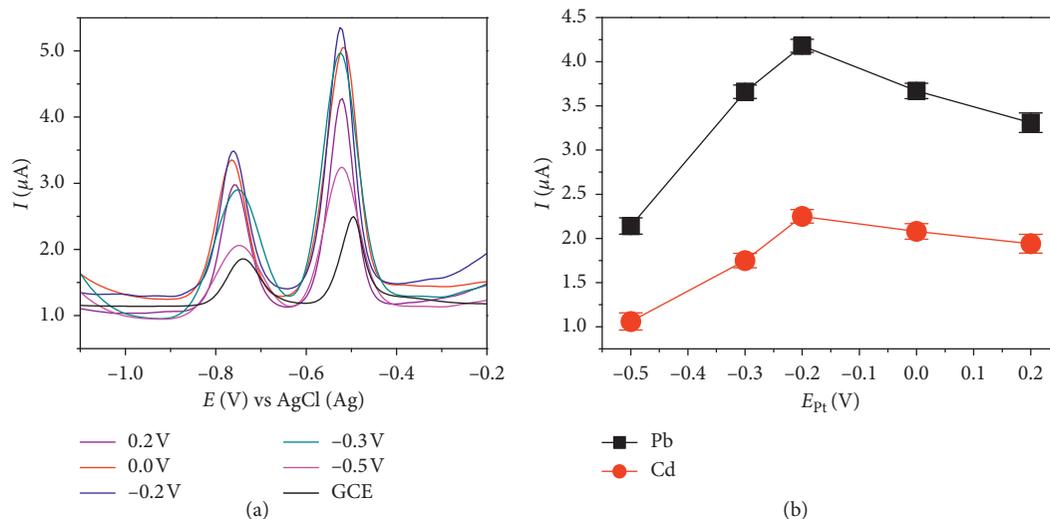


FIGURE 7: DPASVs at GCE and PtNFs/GCE prepared at different electrodeposition potentials ( $E_{Pt}$ ) in acetate buffer solution pH 4.5 containing  $10 \mu\text{g}\cdot\text{L}^{-1}\cdot\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  (a); the influence of  $E_{Pt}$  of electrode fabrication on peak current of  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  (b).

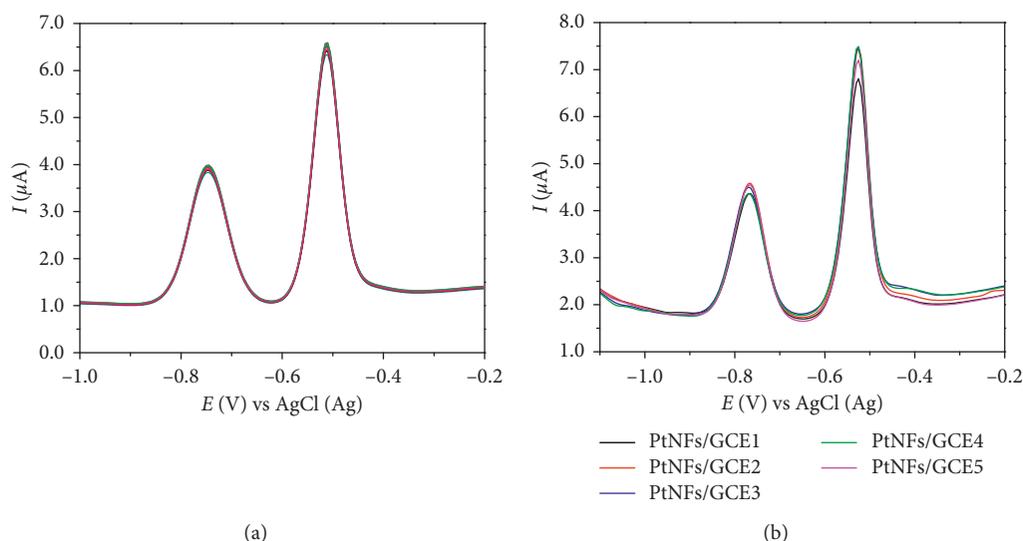


FIGURE 8: The DPASVs of  $10 \mu\text{g}\cdot\text{L}^{-1}\cdot\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  in acetate buffer (pH 4.5) at one PtNFs/GCE with ten successive measurements (a) and at five different electrodes (b).

concentration range of  $1\text{--}100 \mu\text{g}\cdot\text{L}^{-1}$  are illustrated in Figure 9(a). The corresponding calibration curves are shown in Figures 9(b) and 9(c) for lead and cadmium ions, respectively. Each point on these curves is an averaged value of three repeated measurements. The correlation equations were  $I = (1.754 \pm 0.479) + (0.366 \pm 0.0095) C$  with a correlation coefficient of 0.998 for  $\text{Pb}^{2+}$  and  $I = (0.463 \pm 0.302) + (0.203 \pm 0.006) C$  with a correlation coefficient of 0.997 for  $\text{Cd}^{2+}$ , where  $C$  is the concentration of metal ions ( $\mu\text{g}\cdot\text{L}^{-1}$ ) and  $I$  is the peak current ( $\mu\text{A}$ ). The detection limits of  $0.408$  and  $0.453 \mu\text{g}\cdot\text{L}^{-1}$  of  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  were estimated from 10 replicate determination of blank solution under optimum conditions, respectively. The comparison results of the proposed sensor with previously reported voltammetric procedures for lead and cadmium

ions determination are presented in Table 1. This compares the sensing characteristics such as the linear range and the detection limit of some developed platforms based on different modified electrode materials. The limit of detection (LOD) of this our electrode is much lower than that of some sensors reported in Table 1. The results confirm that the proposed sensor had an acceptable utility for the simultaneous detection of  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  with high sensitivity and accuracy, low cost, and fast and simple operation.

#### 4. Conclusions

Electrodeposition of platinum nanoflowers on GC electrodes was achieved by controlling the electrochemical

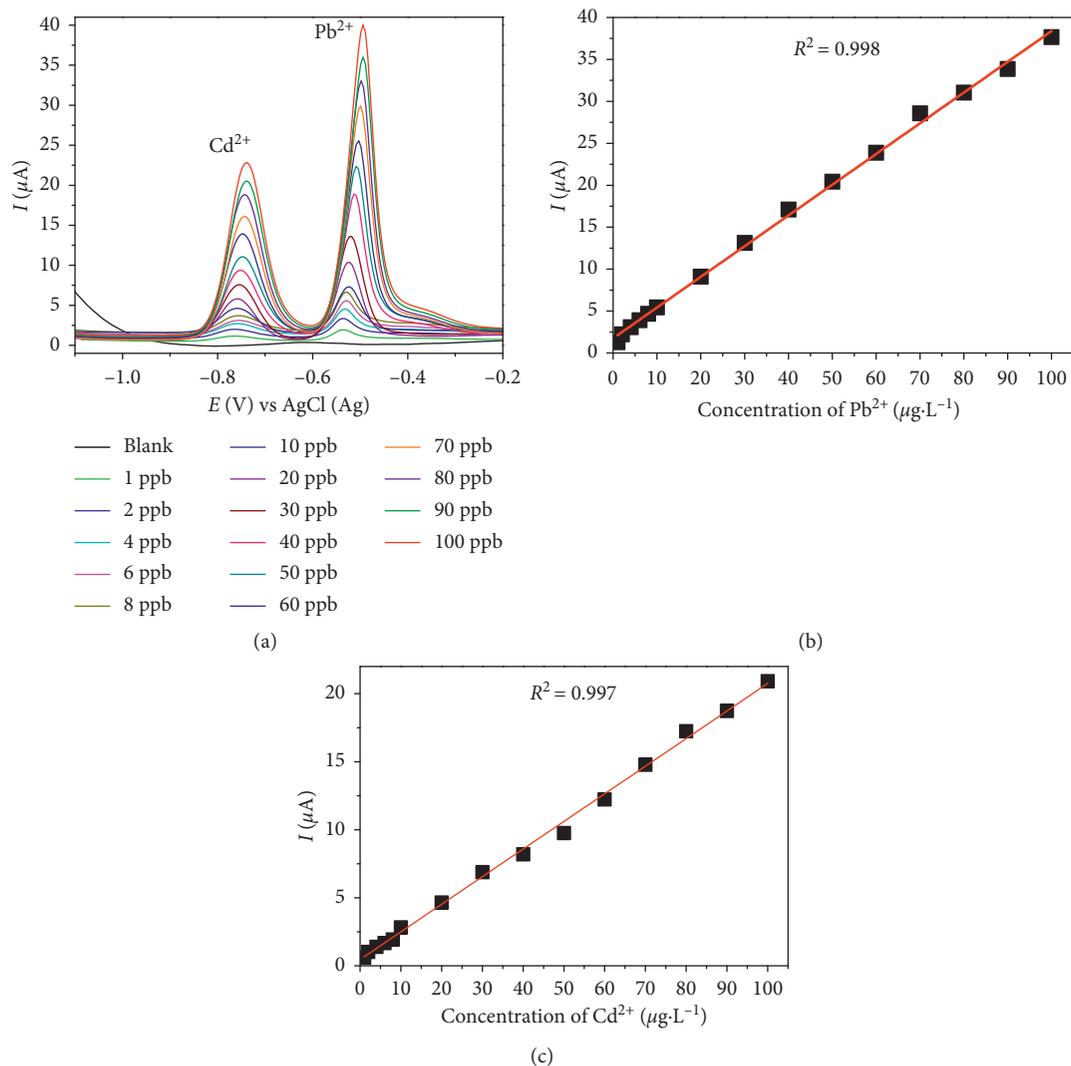


FIGURE 9: DPASVs at different concentrations of  $Pb^{2+}$  and  $Cd^{2+}$  ions at the PtNFs/GCE (a) and relationship between  $Pb^{2+}$  and  $Cd^{2+}$  concentrations with corresponding peak currents (b, c).

TABLE 1: Comparison of the proposed sensor with other reported methods.

Electrodes	Linear range ( $\mu g \cdot L^{-1}$ )		Detection limit ( $\mu g \cdot L^{-1}$ )		Reference
	$Pb^{2+}$	$Cd^{2+}$	$Pb^{2+}$	$Cd^{2+}$	
ZnFe <sub>2</sub> O <sub>4</sub> /GCE	10–130	10–130	0.6	1.3	[33]
Polyaniline/GCE	0–414	0–224	20.7	14.6	[34]
CB-15-crown-5/GCE	10.9–186.5	15.7–191.1	3.3	4.7	[35]
GSH@Fe <sub>3</sub> O <sub>4</sub>	0.5–100	0.5–100	0.2	0.2	[1]
Sb-BDDE	50–500	100–500	25.4	38.1	[36]
PtNFs/GCE	1–100	1–100	0.4	0.5	This work

GCE: glassy carbon electrode; CB-15-crown-5: 4-carboxybenzo-15-crown-5; GSH@Fe<sub>3</sub>O<sub>4</sub>: glutathione functionalized magnetic nanocomposite; Sb-BDDE: antimony nanoparticle-modified boron-doped diamond electrode.

deposition time and potential. Our results show that the total active surface area of Pt, as well as density and surface construction, can be controlled by adjusting deposition conditions. The composition and the microstructure of the modified PtNFs/GCE were characterized by XRD, EDX, SEM, and AFM techniques. Application of PtNFs/GCEs for

the simultaneous electrochemical determination of  $Pb^{2+}$  and  $Cd^{2+}$  is reported for the first time. The proposed sensor showed good analytical signal response and exhibited very low detection limits of 0.408 and 0.453  $\mu g \cdot L^{-1}$  for  $Pb^{2+}$  and  $Cd^{2+}$ , respectively. The RSD of reproducibility of the PtNFs/GCE of 4.36% for  $Cd^{2+}$  and 4.65% for  $Pb^{2+}$  demonstrated

that the PtNFs/GCE is stable in sensing  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  and the procedure of preparation of PtNFs/GCE is reliable.

## Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

## Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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## Supplementary Materials

Platinum nanoflowers modified glassy carbon electrodes (PtNFs/GCE) was prepared by electrodeposition. The modified electrodes have been characterized by EDX, SEM and AFM techniques to confirm chemical and physical properties. The electrochemical properties of PtNFs/GCE were investigated by cyclic voltammetry method (CV). Application of PtNFs/GCE for the simultaneous electrochemical determination of Pb and Cd were performed by anodic stripping voltammetry method (ASV). (*Supplementary Materials*)

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## Research Article

# An Initial Evaluation on the Adsorption of SO<sub>2</sub> and NO<sub>2</sub> over Porous Fe<sub>3</sub>O<sub>4</sub> Nanoparticles Synthesized by Facile Scalable Method

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In this study, Fe<sub>3</sub>O<sub>4</sub> nanoparticles used as an adsorbent for the removal of toxic gases were successfully synthesized via the facile coprecipitation method. The Fe<sub>3</sub>O<sub>4</sub> nanoparticles displayed a well-defined morphology with the size of ~10 nm and a porous structure with a specific area of 115.90 m<sup>2</sup>/g and a wide range of pore sizes. These nanoparticles exhibited effective adsorption abilities upon the exposure to toxic gases. In particular, the amount of 40.5 mg SO<sub>2</sub> and 108.5 mg NO<sub>2</sub> was adsorbed in 1 g of Fe<sub>3</sub>O<sub>4</sub> nanoparticles after 60 minutes of exposure, making the Fe<sub>3</sub>O<sub>4</sub> nanoparticles become a promising adsorbent for the removal of toxic gases.

## 1. Introduction

Toxic gases that are present during the fires are one of the main causes of fire deaths [1]. Depending on the materials that are burning, some kind of different toxic gases might be produced. These gases may include carbon monoxide (CO), nitrogen dioxide (NO<sub>2</sub>), sulfur dioxide (SO<sub>2</sub>), and hydrogen cyanide (HCN) [2]. They prevent cellular respiration, leading these cells to death or causing irritation, and are toxic for the body, at a higher level causing death quickly [3]. In addition to carbon monoxide, the main agent of deaths in the fire, nitrogen dioxide and sulfur dioxide are also known as dangerous agents for the humans' life. Hence, the removal of these gases from the fire is necessary to protect humans. Nanoparticle powders with a large specific surface area have been proposed for adsorption and cleaning up of fumes and toxic gases generated in fires [4]. The hydroxide, carbonate,

bicarbonate, and oxides of metal have attracted wide attention for that because they can be decomposed to CO<sub>2</sub> and H<sub>2</sub>O to extinguish the fire or can be resistant to the fire flame improving the isolating ability of flammable materials with fire and oxygen [5–8]. Among them, the Fe<sub>3</sub>O<sub>4</sub> nanostructured material is a potential candidate due to its stability, high surface area, and easy synthesis [9]. Some researchers have pointed out that Fe<sub>3</sub>O<sub>4</sub> can be an efficient adsorbent for the removal of heavy metal ions [9–11] and inorganic anions [12] from aqueous solutions. However, there have been very few reports using Fe<sub>3</sub>O<sub>4</sub> as an adsorbent for the removal of nitrogen dioxide and sulfur dioxide.

The removal of SO<sub>2</sub> and NO<sub>2</sub> has been also investigated in the field of environment because the amount of these gases released in atmosphere can induce acid rain which is harmful to humans [13, 14]. Active carbon has been known as an effective adsorbent in processes of removing stack

gases [15]. Nevertheless, it is difficult to apply active carbon for the removal of SO<sub>2</sub> and NO<sub>2</sub> in fires due to its flammable nature.

In this work, Fe<sub>3</sub>O<sub>4</sub> nanoparticles were prepared by a facile scalable method and applied as an adsorbent for the adsorption of NO<sub>2</sub> and SO<sub>2</sub>. The material was characterized by a number of analytical techniques. The Fe<sub>3</sub>O<sub>4</sub> nanoparticles exhibited good adsorption abilities in the removal of SO<sub>2</sub> and NO<sub>2</sub>.

## 2. Experimental Section

**2.1. Synthesis of Fe<sub>3</sub>O<sub>4</sub> Nanoparticles.** All chemicals were of analytical grade. Iron(III) chloride hexahydrate (FeCl<sub>3</sub>·6H<sub>2</sub>O), iron(II) chloride tetrahydrate (FeCl<sub>2</sub>·4H<sub>2</sub>O), ammonia solution 25% (NH<sub>3</sub>·H<sub>2</sub>O), sulfur dioxide (99.9%), nitrogen dioxide (99.5%), and nitrogen (99.999%) were purchased from Sigma-Aldrich and used without any further purification. The magnetite (Fe<sub>3</sub>O<sub>4</sub>) nanoparticles were prepared by the following coprecipitation method [16–18].

In brief, FeCl<sub>3</sub>·6H<sub>2</sub>O (0.05 mol, 13.52 g) and FeCl<sub>2</sub>·4H<sub>2</sub>O (0.03 mol, 5.96 g) were dissolved in 100 mL DI water with a Fe<sup>2+</sup>/Fe<sup>3+</sup> molar ratio of 0.6. Then, the ammonium solution was added dropwise into the solution until pH = 11.0 over a period of 2 h, under vigorous stirring to achieve Fe<sub>3</sub>O<sub>4</sub> nanoparticles with high purity. The obtained precipitate was filtered, washed with DI water, and dried in vacuum at 60°C for 24 h.

**2.2. Material Characterization.** The specific surface area was determined from N<sub>2</sub> adsorption/desorption at 77 K by the Brunauer–Emmett–Teller (BET) method using a Micromeritics surface area analyzer (TriStar II Plus, Micromeritics Instrument Corp, USA). The morphology and particle size were determined by field emission scanning electron microscope (FE-SEM, S-4800, Hitachi, Japan) and particle-size distribution measurement (Litesizer™ 500, Anton Paar Instrument Co. Ltd., Austria). The structure of adsorbents was characterized by high-resolution XRD (D/max Ultima III, Rigaku, Japan). The thermogravimetric analysis (TGA) was determined on TGA-50, Shimadzu, Japan, in an air atmosphere with a heating rate of 5°C·min<sup>-1</sup> from room temperature to 700°C. Temperature-programmed reduction (TPR) was carried out under 5% CO in Ar flow (100 cc/min) at a heating rate of 10°C/min, from room temperature to about 900°C using AutoChem™ II 2920 (Micromeritics Instrument Corp, USA).

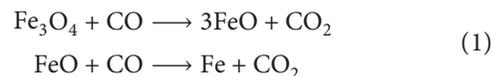
**2.3. Adsorption Experiments.** For the adsorption study, 1 g of Fe<sub>3</sub>O<sub>4</sub> nanoparticles were exposed to dried SO<sub>2</sub> and NO<sub>2</sub> at a particular time in the fixed bed reactor under ambient temperature. These gases were mixed with nitrogen as a carrier gas (5% SO<sub>2</sub> or NO<sub>2</sub> in the N<sub>2</sub> atmosphere). The Fe<sub>3</sub>O<sub>4</sub> nanoparticles were pretreated under an Ar flow at 400°C during 2 h and then cooled to the room temperature. After that, the gas stream was supplied with a flow rate of 200 cc/min. The uptake quantities were recorded as a function of time based on a mass change of samples. The

presence of the gas phase in contact with the materials was monitored by the FTIR measurement (Thermo Fisher, USA) at 8 cm<sup>-1</sup> resolution. In addition, energy-dispersive X-ray spectroscopy (SEM-EDX) (HORIBA-EMAX80; Hitachi High-Technology) was used to evaluate the presence as well as the adsorbed quantity of SO<sub>2</sub> and NO<sub>2</sub>.

## 3. Results and Discussion

**3.1. Characterization of Fe<sub>3</sub>O<sub>4</sub> Nanoparticles.** The porous, interconnected Fe<sub>3</sub>O<sub>4</sub> nanoparticles were synthesized using a facile scalable method. The mixture solution of FeCl<sub>3</sub> and FeCl<sub>2</sub> was prepared with a Fe<sup>2+</sup>/Fe<sup>3+</sup> molar ratio of 0.6. The used Fe<sup>2+</sup>/Fe<sup>3+</sup> molar ratio is higher than the Fe<sup>2+</sup>/Fe<sup>3+</sup> molar ratio in Fe<sub>3</sub>O<sub>4</sub> because a part of Fe<sup>2+</sup> oxidized to Fe<sup>3+</sup> will lead to the lower Fe<sup>2+</sup>/Fe<sup>3+</sup> molar ratio. The increase of Fe<sup>2+</sup> concentration can attain the ideal Fe<sup>2+</sup>/Fe<sup>3+</sup> molar ratio of ~0.5. Then, the ammonium solution was added dropwise into the solution until pH = 11.0 to achieve Fe<sub>3</sub>O<sub>4</sub> nanoparticles with high purity. Figure 1 shows the X-ray diffraction (XRD) patterns of the synthesized Fe<sub>3</sub>O<sub>4</sub>. All peaks were indexed to cubic Fe<sub>3</sub>O<sub>4</sub> (JCPDS: 01-088-0315) without any impurity phase. However, γ-Fe<sub>2</sub>O<sub>3</sub> has the same crystal structure and a lattice spacing as Fe<sub>3</sub>O<sub>4</sub>. To distinguish Fe<sub>3</sub>O<sub>4</sub> from γ-Fe<sub>2</sub>O<sub>3</sub>, the *d* value of lattice spacing of (311) was calculated by Bragg's equation. The *d*-spacing value (311) of Fe<sub>3</sub>O<sub>4</sub> was calculated to be 2.5249 Å, similar to the value of 2.52516 Å (standard cubic Fe<sub>3</sub>O<sub>4</sub>: 01-088-0315). As reported by Iida et al. [18], the standard *d*-spacing value (311) of γ-Fe<sub>2</sub>O<sub>3</sub> is 2.5177 Å (γ-Fe<sub>2</sub>O<sub>3</sub>, JCPDS: 00-039-1346). It can infer that the phase of the obtained material is completely matched with the phase of the standard cubic Fe<sub>3</sub>O<sub>4</sub>.

Moreover, TPR<sub>CO</sub> profiles of synthesized Fe<sub>3</sub>O<sub>4</sub> further proved that the obtained material was pure Fe<sub>3</sub>O<sub>4</sub>. As shown in Figure 2, TPR<sub>CO</sub> profiles illustrated two distinct peaks of the reduction process, corresponding to two-step reduction of Fe<sub>3</sub>O<sub>4</sub> → FeO and FeO → Fe. There was no peak of the Fe<sub>2</sub>O<sub>3</sub> → Fe<sub>3</sub>O<sub>4</sub> reduction process, referring that there was no presence of Fe<sub>2</sub>O<sub>3</sub> in the synthesized material. The reduction temperature of the two-step reduction was approximately 285°C (Fe<sub>3</sub>O<sub>4</sub> → FeO) and 595°C (FeO → Fe). These reduction reactions can be described as follows [19–21]:



According to these reports [19–21], the reduction of Fe<sub>3</sub>O<sub>4</sub> by carbon monoxide starts in the temperature range of ~509–807°C, which was higher than the reduction temperature of Fe<sub>3</sub>O<sub>4</sub> in our study. The lower reaction temperature can be explained due to nanometer-sized Fe<sub>3</sub>O<sub>4</sub>, reacting with carbon monoxide more easily than crystalline Fe<sub>3</sub>O<sub>4</sub>.

The morphology of Fe<sub>3</sub>O<sub>4</sub> was observed using FE-SEM. As shown in Figure 3(a), Fe<sub>3</sub>O<sub>4</sub> exhibited a uniform granular shape with nanoparticles interconnected to each other. The Fe<sub>3</sub>O<sub>4</sub> nanoparticles have a diameter of ~10 nm. Besides, the

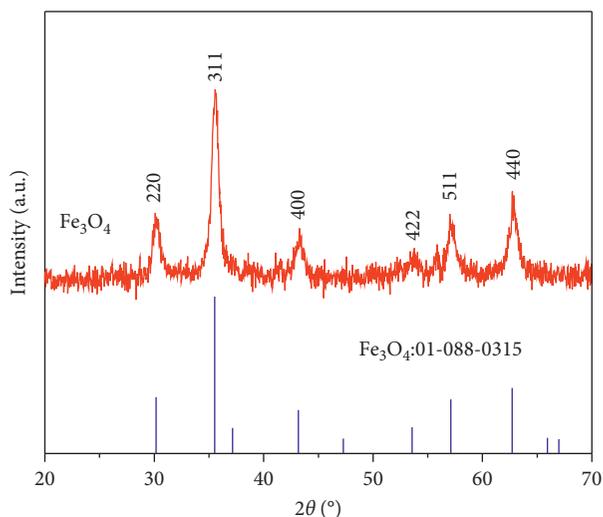


FIGURE 1: XRD patterns of synthesized  $\text{Fe}_3\text{O}_4$  nanoparticles.

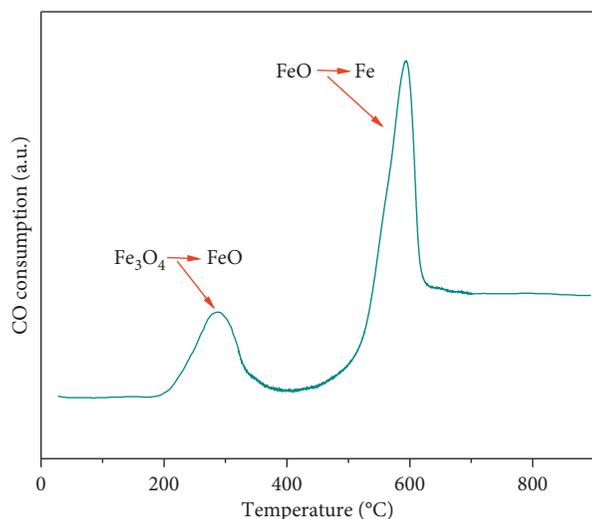
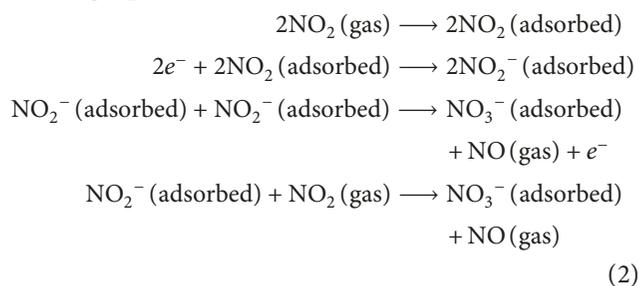


FIGURE 2:  $\text{TPR}_{\text{CO}}$  profile for  $\text{Fe}_3\text{O}_4$  nanoparticles, a heating rate of  $5^\circ\text{C}/\text{min}$ .

interconnected  $\text{Fe}_3\text{O}_4$  nanoparticles formed void spaces which intercalated among  $\text{Fe}_3\text{O}_4$  nanoparticles as a porous structure. This unique structure plays an important role: it enables better the access of toxic gases to the inside of material, which can improve the adsorption capacity of materials [22]. Furthermore, using Scherrer's equation, the size of  $\text{Fe}_3\text{O}_4$  particles was calculated to be  $\sim 9.8$  nm based on the XRD results (Figure 1), suggesting the similar results between XRD and FE-SEM measurement. Figure 3(b) further affirmed the uniform of  $\text{Fe}_3\text{O}_4$  nanoparticles with the narrow particle-size distribution and the nanosize of  $\text{Fe}_3\text{O}_4$  [23]. The particle-size distribution of  $\text{Fe}_3\text{O}_4$  changes from 7 to 13 nm, revealing the good uniform of  $\text{Fe}_3\text{O}_4$  nanoparticles. The nanometer-sized  $\text{Fe}_3\text{O}_4$  was expecting to achieve a high specific area. The porous structure of  $\text{Fe}_3\text{O}_4$  was characterized using  $\text{N}_2$  adsorption-desorption isotherms. As shown in Figure 3(c), isotherm adsorption of  $\text{Fe}_3\text{O}_4$  depicted typical type-IV (multilayer adsorption) that

has a broad range of pore sizes and the Barrett-Joyner-Halenda (BJH) pore size distribution (inset) of the  $\text{Fe}_3\text{O}_4$ . Via BET and BJH analysis, the specific area, average pore diameter, and pore volume of  $\text{Fe}_3\text{O}_4$  were determined to be approximately  $115.90 \text{ m}^2/\text{g}$ ,  $10.63 \text{ nm}$ , and  $0.30 \text{ cm}^3/\text{g}$ , respectively. The relatively high pore size of the  $\text{Fe}_3\text{O}_4$  particles allow the access of toxic gases inside materials easily. Moreover, the large surface area can facilitate the adsorption of stack gases at the material surface/gases interface [24]. The TGA has proceeded in an air atmosphere with a heating rate of  $5^\circ\text{C}/\text{min}$  from room temperature to  $700^\circ\text{C}$  to evaluate the purity of  $\text{Fe}_3\text{O}_4$  materials again, as shown in Figure 3(d). The weight gain near  $100^\circ\text{C}$  was attributed to the oxidation of  $\text{Fe}_3\text{O}_4$  to  $\gamma\text{-Fe}_2\text{O}_3$ . Interestingly, the oxidation temperature in our study is lower than the previous study [25]. This behaviour might be due to the high surface area of the nanometer-sized  $\text{Fe}_3\text{O}_4$ , making them react with oxygen more easily than crystalline  $\text{Fe}_3\text{O}_4$ . Nevertheless, the temperature near  $100^\circ\text{C}$  was also the evaporation temperature of moisture from the sample. Because the loss weight owing to the removal of moisture was lower than the weight gain due to the oxidation, the mass change in TG data just shows the mass gain. The content of moisture and  $\text{Fe}_3\text{O}_4$  in the obtained sample was estimated to be 2.21 and 97.79%, respectively (Figure 3(d)).

**3.2. Adsorption Ability of  $\text{Fe}_3\text{O}_4$  Nanoparticles.** Figure 4 shows the adsorption abilities of  $\text{Fe}_3\text{O}_4$  after exposing to  $\text{NO}_2$  in conditions of the study. As shown in Figure 4(a), the intensities of the IR features after 15 minutes exposure to  $\text{NO}_2$  start to change, suggesting that the amount of  $\text{NO}_2$  was adsorbed on the surface of  $\text{Fe}_3\text{O}_4$ . The adsorption of  $\text{NO}_2$  at room temperature leads to an intensity increase of the  $1386 \text{ cm}^{-1}$  band, corresponding to the band of nitrate ( $\text{NO}_3^-$ ) [26]. The adsorption mechanism of  $\text{NO}_2$  on the  $\text{Fe}_3\text{O}_4$  surface was reported by Eltouny et al. [27] via the following equations:



The intensity of this peak increases as the time exposing to  $\text{NO}_2$  gas increases, suggesting that the larger amount of  $\text{NO}_2$  was adsorbed. The uptake of  $\text{NO}_2$  by the  $\text{Fe}_3\text{O}_4$  nanoparticles was shown in Figure 4(b). The amount of  $\text{NO}_2$  adsorbed by the  $\text{Fe}_3\text{O}_4$  reached the saturation level after 60 minutes of exposure. The mass of  $\text{NO}_2$  adsorbed by the  $\text{Fe}_3\text{O}_4$  after 60 minutes of exposure was recorded at  $108.5 \text{ mg}/\text{g}$  of  $\text{Fe}_3\text{O}_4$ . The high adsorption values of the  $\text{Fe}_3\text{O}_4$  sample were owing to its larger pore volume and high surface area. Furthermore, the presence and mass of  $\text{NO}_2$  in the  $\text{Fe}_3\text{O}_4$  sample were also measured by SEM-EDX

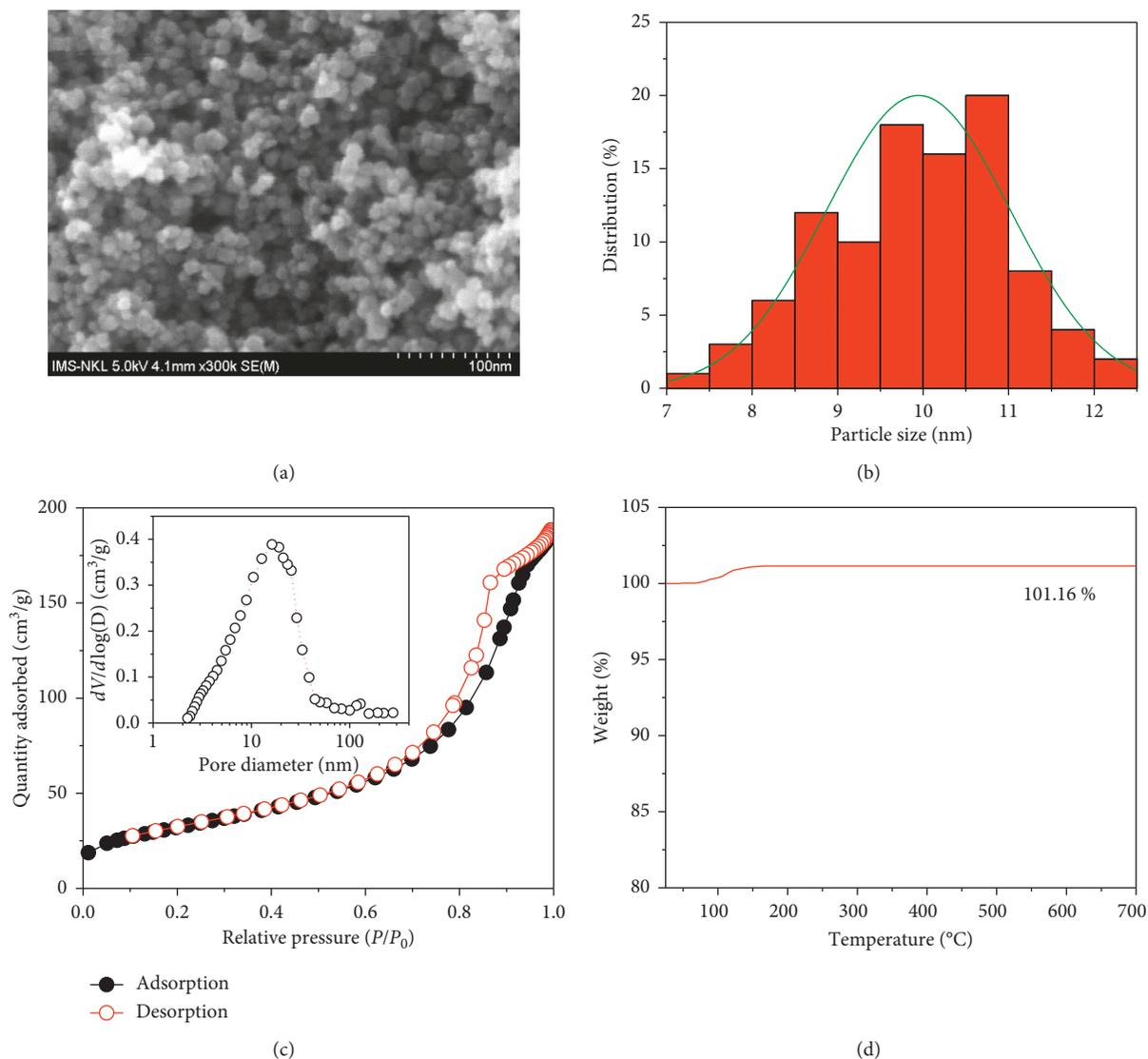
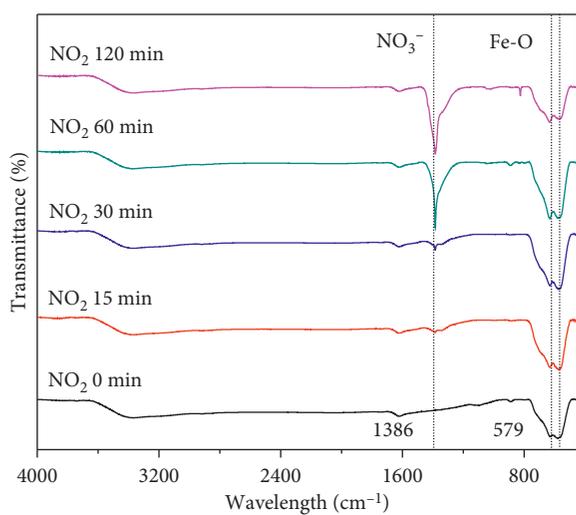


FIGURE 3: (a) FE-SEM image; (b) particle-size distribution; (c)  $N_2$  adsorption/desorption isotherms; (d) thermogravimetric analysis (TGA) of synthesized  $Fe_3O_4$ . Inset in Figure 3(c) shows the pore size distribution calculated from the Barrett-Joyner-Halenda (BJH) formula of synthesized  $Fe_3O_4$ .

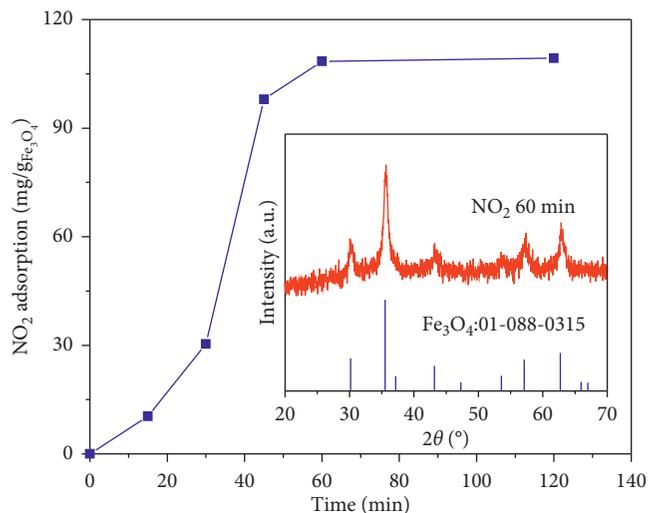
analysis. As shown in Figure 4(c), the signal of N, Fe, and O elements was detected in the  $Fe_3O_4$  sample exposing to  $NO_2$  after 60 minutes. Based on the intensity of the N element in the sample, %wt.  $NO_2$  in the sample can be, respectively, calculated to be  $\sim 9.79$  %wt., corresponding to the  $NO_2$  adsorption of  $\sim 108.6$  mg/g of  $Fe_3O_4$ . This result was similar to the adsorption mass of  $NO_2$  by the  $Fe_3O_4$  in Figure 4(b). The morphology of the  $Fe_3O_4$  sample after 60 minutes of exposure to  $NO_2$  was analyzed using the FE-SEM measurement. There was no change in the morphology of  $Fe_3O_4$  nanoparticles before (Figure 3(a)) and after (Figure 4(d)) exposing to the  $NO_2$  gas environment, referring to the stable structure of the  $Fe_3O_4$  sample. Furthermore, the XRD pattern of  $Fe_3O_4$  after exposing with  $NO_2$  (Figure 4(b) inset) did not show any change, compared with the XRD pattern of  $Fe_3O_4$  (Figure 1). The good stable structure can retain the adsorption ability after the

regeneration and repeating the  $NO_2/Fe_3O_4$  adsorption many times.

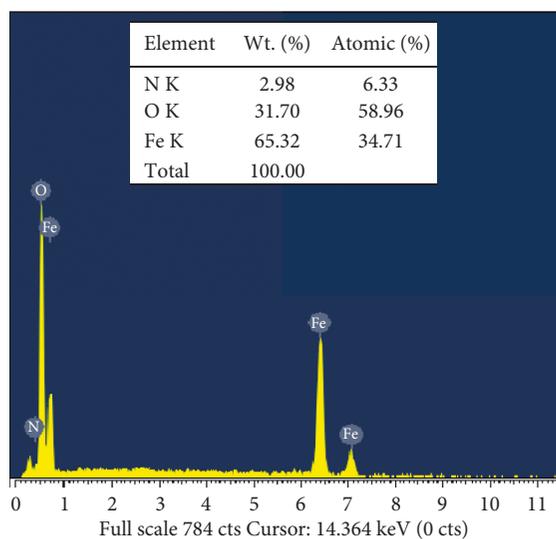
The adsorption abilities of  $Fe_3O_4$  were further examined with the  $SO_2$  gas. Figure 5 shows the adsorption ability of  $Fe_3O_4$  with  $SO_2$ . Figure 5(a) shows the FTIR spectra obtained after exposing the  $Fe_3O_4$  sample to  $SO_2$  at different times. The signal at the band of  $\sim 1400$  and  $\sim 1120$   $cm^{-1}$ , corresponding to the species of physical adsorption of  $SO_2$ , was detected [15]. However, the intensities of  $SO_2$  species were low, suggesting that the small amount of  $SO_2$  was adsorbed on the surface of the  $Fe_3O_4$  sample. The adsorbed amount of  $SO_2$  was displayed in Figure 5(b). The mass of  $SO_2$  adsorbed by the  $Fe_3O_4$  at the saturation level after 60 minutes of exposure. Moreover, the presence and the adsorption mass of  $SO_2$  in the  $Fe_3O_4$  sample was evaluated by SEM-EDX analysis (Figure 5(c)). The signal of the S element was found to be



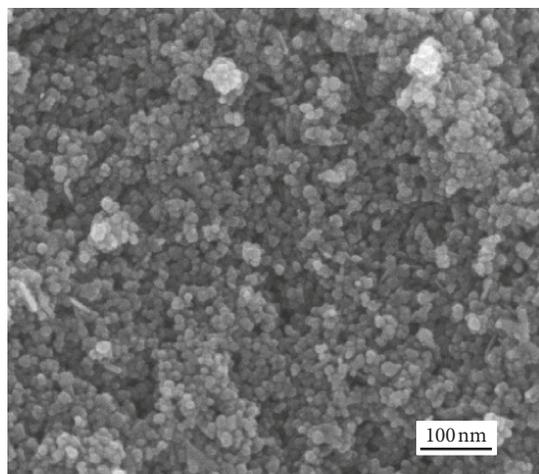
(a)



(b)

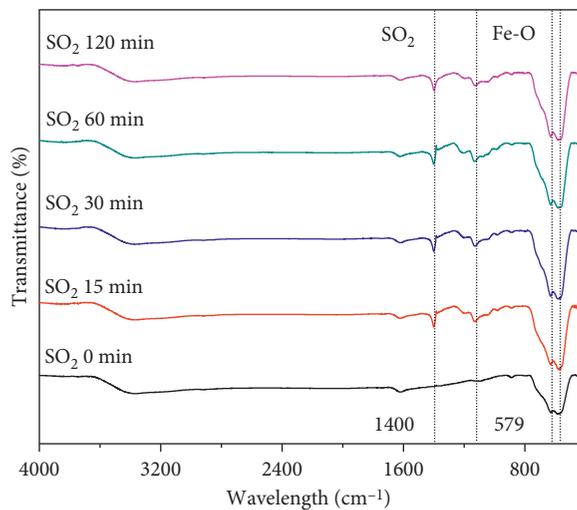


(c)

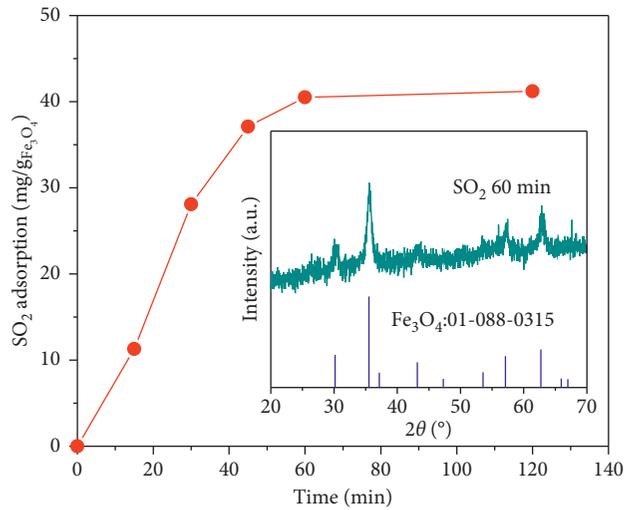


(d)

FIGURE 4: (a) FTIR of  $\text{Fe}_3\text{O}_4$  samples after exposing to  $\text{NO}_2$  gas at the particular time; (b)  $\text{NO}_2$  adsorption on  $\text{Fe}_3\text{O}_4$  samples; (c) SEM-EDX spectra; (d) FE-SEM image of  $\text{Fe}_3\text{O}_4$  after 60 min of exposure to  $\text{NO}_2$ . Inset in Figure 4(b) shows the XRD pattern of  $\text{Fe}_3\text{O}_4$  after 60 min of exposure to  $\text{NO}_2$ .



(a)



(b)

FIGURE 5: Continued.

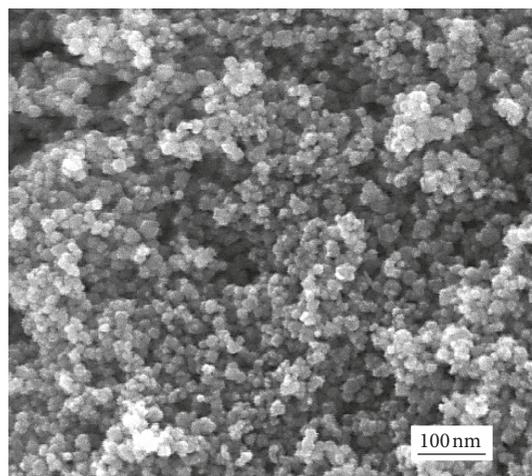
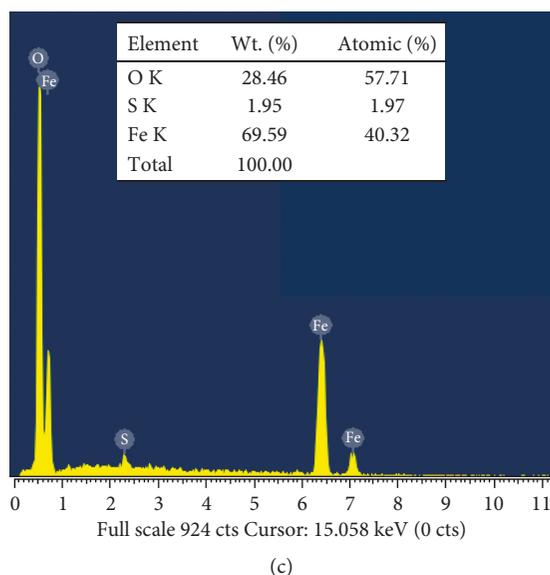


FIGURE 5: (a) FTIR of  $\text{Fe}_3\text{O}_4$  samples after exposing to  $\text{SO}_2$  gas at the particular time; (b)  $\text{SO}_2$  adsorption on  $\text{Fe}_3\text{O}_4$  samples; (c) SEM-EDX spectra; (d) FE-SEM image of  $\text{Fe}_3\text{O}_4$  after 60 min of exposure to  $\text{SO}_2$ . Inset in Figure 5(b) shows the XRD pattern of  $\text{Fe}_3\text{O}_4$  after 60 min of exposure to  $\text{SO}_2$ .

1.95 %wt. of  $\text{SO}_2$  in the sample, corresponding to 3.90  $\text{SO}_2$  %wt. in the sample after 60 minutes of exposure. This quantity was calculated to  $\sim 40.6$  mg/g of  $\text{Fe}_3\text{O}_4$ , similar to the obtained adsorption of  $\text{Fe}_3\text{O}_4$  in Figure 5(b). The surface of the  $\text{Fe}_3\text{O}_4$  sample after 60 minutes of exposure with  $\text{SO}_2$  was analyzed using FE-SEM measurement. As shown in Figure 5(d), the highly porous structure of  $\text{Fe}_3\text{O}_4$  was sustained, and no significant change was realized (compared with Figure 3(a)). Moreover, the phase state of  $\text{Fe}_3\text{O}_4$  (Figure 5(b) inset) after the adsorption also remains, demonstrating the stable-phase state and porous structure. This structure was promising to be recycled and continuously adsorbs gases many times.

#### 4. Conclusions

$\text{Fe}_3\text{O}_4$  nanoparticles have successfully been synthesized via the facile scalable method, in which  $\text{Fe}_3\text{O}_4$  nanoparticles well achieved a porous structure with the high specific area and purity. The  $\text{Fe}_3\text{O}_4$  nanoparticles exhibited good adsorption with toxic gases. The surface of the  $\text{Fe}_3\text{O}_4$  nanoparticles adsorbed high amounts of  $\text{SO}_2$  and  $\text{NO}_2$  of 40.5 mg/g of  $\text{Fe}_3\text{O}_4$  and 108.5 mg/g of  $\text{Fe}_3\text{O}_4$ , respectively, at a saturation state after 60 minutes of exposure. The high adsorption performance was attributed to the high porosity and specific areas, which enabled the better diffusion and adsorption of toxic gases to the surface of the porous material. The resultant structure of  $\text{Fe}_3\text{O}_4$  after exposing to the toxic gases would be the good adsorbent, which can be regenerated and adsorb gases many times.

#### Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

#### Conflicts of Interest

The authors declare that there are no conflicts of interest.

#### Authors' Contributions

Xuan-Manh Pham and Duy Linh Pham contributed equally to this work.

#### Acknowledgments

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## Research Article

# Synthesis of Acidic Heterogeneous Catalysts with High Stability Based on Graphene Oxide/Activated Carbon Composites for the Esterification of Lactic Acid

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In this article, acidic heterogeneous catalysts based on graphene oxide and sulfonated biochar were prepared, characterized, and used for lactic acid esterification to form ethyl lactate. Graphene oxide was supported on activated carbon (GO/AC) to more easily filter the catalyst from the reactants. The catalysts were characterized by such methods as XRD, FT-IR, SEM, BET, and the acid-base titration. Catalytic activity was evaluated through the esterification of lactic acid. As a result, the activity of the catalysts decreased in the following order: graphene oxide > sulfonated biochar ≈ GO/AC >> activated carbon. In addition, the GO/AC catalyst showed good stability with an unchanged yield from the 3<sup>rd</sup> to the 6<sup>th</sup> recycling test. These results suggest potential applications for new acidic heterogeneous catalysts based on graphene oxide and sulfonated biochar that could replace homogeneous acids in the future.

## 1. Introduction

Ethyl lactate is an ecofriendly solvent with valuable properties such as low volatility, high biodegradability, and low toxicity. Ethyl lactate is used as a “green” solvent in different fields such as organic synthesis, pharmaceuticals, coatings, printing, food, and perfume additives [1]. Ethyl lactate has many positive characteristics and can replace traditional solvents originating from petroleum.

Ethyl lactate is a product of lactic acid esterification in the presence of an acidic catalyst. Acidic homogeneous catalysts, such as H<sub>2</sub>SO<sub>4</sub> and HCl, have been used for esterification. However, acidic homogeneous catalysts cannot be recycled and have to be neutralized, thereby complicating the process. To overcome their disadvantages, heterogeneous catalysts have been used in esterifications despite them having lower activity than homogeneous catalysts.

Over the years, many solid acid catalysts for lactic acid esterification such as Preysler [2], K<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> [3], and Amberlyst ionic resins [4–7] have been investigated. Among

these catalysts, solid acid catalysts based on sulfonated carbon have attracted the attention of many scientists. These catalysts are synthesized by the sulfonation of carbonated products such as starch, cellulose, and glucose [8]. With the abundance of such acidic functional groups as -SO<sub>3</sub>H and -COOH on their surface, these catalysts have been applied in esterification [9–11] and transesterification [12, 13] reactions. However, during the reaction, -SO<sub>3</sub>H groups leach into the reactive medium, reducing catalytic activity [14].

Recently, graphene and graphene oxide (GO) have earned more attention from researchers due to their high stabilities in the liquid phase and their high resistance in the acidic medium. Moreover, many of their applications have been implemented, such as energy storage, electronic devices, optoelectronics, sensors, and catalysis [15–17]. Graphene oxide was synthesized by the oxidation of graphite forming acidic functional groups such as -SO<sub>3</sub>H and carboxylic acid on the surface of the material. Due to these functional groups, graphene oxide has been used as an acidic catalyst in organic synthesis, such as in the cellulose

hydrolysis reaction [18]; the dehydration and etherification of fructose, xylose, and inulin [19, 20]; the etherification of HMF [21]; the esterification of levulinic acid with alcohol [22]; the esterification of glycerol and acetic acid [23]; and biodiesel synthesis [24]. The results showed that the catalytic activity of graphene oxide was good for these reactions. For example, using graphene oxide as catalyst, Wei et al. reported that the yield of forming ethyl acetate was 93.5% for esterification between acetic acid and ethanol, higher than the yield when using the homogeneous catalyst  $\text{H}_2\text{SO}_4$  [25]. Samir Kundu and Basudeb Basu used and reused GO as a catalyst for 2-aminopyridine, acetophenone, and thiophenol synthesis. The conversion was quite stable with a value of 84% and 80% for the 1<sup>st</sup> and 4<sup>th</sup> cycles, respectively [26].

Graphene oxide is a potentially acidic heterogeneous catalyst with good solubility in aqueous solutions (or polar solvents) because it includes many oxygen-rich functional groups (-OH, -COOH, -CHO, etc.), which are very highly hydrophilic [17]. However, this property makes it difficult to separate the graphene oxide catalyst from the reaction mixture. Therefore, the separation of graphene oxide from the reaction mixture usually requires a high-speed centrifugation process instead of normal filtrations or vacuum extractions [17, 21, 23, 24].

To solve this problem, graphene oxide should be supported on a solid with a high surface area, not only limiting its "high solubility" but also avoiding the "leaching" of graphene oxide into the reaction medium. In this article, the synthesis of solid catalysts based on sulfonated biochar and graphene oxide was studied. Graphene oxide was supported on activated carbon to more easily filter the catalysts from the reactants. Their catalytic activities were tested by demonstrating lactic acid esterification from ethyl lactate.

## 2. Materials and Methods

**2.1. Materials.** Pine sawdust, taken from Ninh Binh province, Vietnam, was crushed, sieved, and collected. All sawdust particles are in the range of 0.5 to 0.85 mm in diameter. Then, the collected sawdust was dried at 105°C for 2 h. Commercially activated carbon, made from coconut shells in Vietnam, was washed with distilled water, dried at 105°C, and finally crushed. Expanded graphite powder (<45  $\mu\text{m}$ , 99.9995%),  $\text{NaNO}_3$  ( $\geq 99\%$ ),  $\text{KMnO}_4$  ( $\geq 99\%$ ),  $\text{H}_2\text{O}_2$  (30%), HCl (37%),  $\text{H}_2\text{SO}_4$  (95–98%), lactic acid 85%, and ethanol (99.95%) were all purchased from Sigma-Aldrich (Singapore). All experiments were conducted using deionized water.

**2.2. Synthesis of Graphene Oxide Supported on Activated Carbon (GO/AC).** Graphene oxide synthesis was conducted using the modified method of Hummers [27]. GO after synthesis is dispersed in water with a concentration of 5.0  $\text{mg}\cdot\text{mL}^{-1}$ . GO is dispersed on AC support by the dry impregnation method: 100 mL of the suspension was stirred into 5.000 g of 85°C-dried AC in a 250 mL glass beaker at room temperature for 5 h. Then, the mixture was dried at 85°C for 48 h. Then, it was cooled off in a desiccator. Finally,

we obtained 5.495 g of GO/AC catalyst with a weight ratio of GO to AC of 1 : 10. The efficiency on the supporting process was at 99.91%.

**2.3. Synthesis of Sulfonated Biochar.** The synthesis followed two processes:

- (i) Carbonation: 40 g of pine sawdust was carbonated in a furnace under an  $\text{N}_2$  environment, at 400°C for 5 h (heating rate of 10°C/min). The product obtained was denoted as biochar.
- (ii) Sulfonation: 15 g of obtained biochar was stirred at 150°C in 300 ml of 98%  $\text{H}_2\text{SO}_4$  solution in a three-neck glass flask of 500 ml for 15 h. The reaction system was cooled and slowly diluted with 1 L of distilled water. Then, hot distilled water (80°C) was used to wash the filtered mixture until the sulfate ion disappeared (checked by 10%  $\text{BaCl}_2$  solution). The solid was dried at 105°C for 8 h to obtain the final product—sulfonated biochar catalyst.

**2.4. Catalyst Characterization.** Sample morphology was observed by scanning electron microscopy (SEM) using an S-4800 microscope (Hitachi, Japan). The specific surface area of the catalysts was measured by BET Micromeritics 201-A. The infrared spectrum of the samples, in the wavelength range of 400–4000  $\text{cm}^{-1}$ , was measured on a Tensor 27-Bruker FTIR Spectrometer. XRD patterns of the catalysts were measured on a D8 Advance (Bruker) apparatus. A shaker and pH meter were used for titration. The acidic content (- $\text{SO}_3\text{H}$ ) of all catalysts was determined by an acid-base titration method [28]. For example, a suspension which contains 1 g of catalyst and 50 mL of 1 M NaCl solution in a 250 mL Erlenmeyer flask was shaken at a speed of 130 rpm for 4 hours. Next, the mixture was filtered. Then, the liquid was titrated by 0.1 M NaOH solution.

The - $\text{SO}_3\text{H}$  content per 1 g of catalyst is calculated by the following formula:

$$N_{-\text{SO}_3\text{H}} = \frac{(0.1 \times V)}{1} \times \frac{50}{20} (\text{mmol}\cdot\text{g}^{-1}), \quad (1)$$

where  $V$  is the volume of used NaOH solution (mL) and  $N_{-\text{SO}_3\text{H}}$  is the - $\text{SO}_3\text{H}$  content per 1 g of catalyst.

**2.5. Catalytic Tests.** The activity of the catalysts was evaluated through the esterification reaction between lactic acid 50% (obtained from 85% lactic acid solution by the dilution) and ethanol (mole ratio 1 : 4) at 82°C [29]. The weight ratios of the sulfonated biochar and GO catalysts to lactic acid are 5% and 1%, respectively. Because of the difficulty in filtering, the weight ratio of GO catalyst cannot be not higher than 1%. To make it easier to compare the catalytic activity between GO and GO/AC, the contents of GO included in the GO/AC catalyst are equal to that of the GO catalyst.

Ethyl lactate product was determined by the internal standardization method on an Agilent 7890A gas

chromatograph equipped with an FID. The yield of ethyl lactate was calculated by the following formula:

$$\text{ethyl lactate yield (\%)} = \frac{n_{\text{ethyl lactate}}}{n_{\text{ethyl lactate}}^0} \times 100, \quad (2)$$

where  $n_{\text{ethyl lactate}}$  is the real mole of ethyl lactate that is determined by the gas chromatography test and  $n_{\text{ethyl lactate}}^0$  is the theory mole of ethyl lactate that is a value with 100% conversion of lactic acid.

**2.6. Recycling Catalyst Tests.** After completion of the reaction, the GO/AC and sulfonated biochar catalysts were filtered and washed three times by using hot distilled water ( $\geq 80^\circ\text{C}$ ). Then, the catalysts were dried at  $105^\circ\text{C}$  for 8 h. The recycled catalysts were reused for lactic acid esterification.

### 3. Results and Discussion

**3.1. Catalyst Characterization.** The structural properties of sulfonated biochar, activated carbon, graphene oxide, and GO/AC determined by the XRD method are shown in Figure 1. There is a broad peak at  $20^\circ$  to  $30^\circ$  of 2-theta-scale; these data mean that the sulfonated biochar catalyst has an amorphous structure [10]. There is a specific peak observed at  $11^\circ$  of 2-theta-scale (corresponding to the crystal of graphene oxide) for both graphene oxide and the GO/AC catalysts [22]. However, in the case of GO/AC catalyst, the peak is much lower in intensity. This result confirmed the successful synthesis of graphene oxide from expanded graphite and indicated that there was interaction between the graphene oxide and activated carbon in the GO/AC catalyst.

Figure 2 shows the SEM images of the sulfonated biochar, activated carbon, graphene oxide, and GO/AC catalysts. The results indicate a porous structure with large capillaries, a solid structure, and a transparently layered structure for the sulfonated biochar (Figure 2(a)), activated carbon (Figure 2(b)), and graphene oxide (Figure 2(c)), respectively. Figure 2(d) shows that the GO/AC catalyst shows a “sandwich” structure in which the activated carbon is surrounded by graphene oxide layers, proving that the GO/AC catalyst was successfully prepared.

The FT-IR spectra of the catalysts are shown in Figure 3. In the infrared spectra of sulfonated biochar, graphene oxide, and GO/AC catalysts, there are characteristic vibration bands of -OH bonding and the C=O group, including the -COOH functional group at  $3416$ ,  $3387$ ,  $3444$   $\text{cm}^{-1}$  and  $1709$ ,  $1698$ ,  $1694$   $\text{cm}^{-1}$ , respectively. There are also valence vibrations of S=O bonding included in the -SO<sub>3</sub>H group at  $1040$ ,  $1059$ , and  $1108$   $\text{cm}^{-1}$  [10, 23]. Meanwhile, valence vibrations of S=O are not observed in the case of the activated carbon catalyst, indicating that there is no presence of -SO<sub>3</sub>H groups in the activated carbon structure.

Specific surface areas of the catalysts are presented in Table 1. The results showed that the areas of the catalysts are quite high (over  $400$   $\text{m}^2$   $\text{g}^{-1}$ ). Because of the filling of GO particles in the micropores of the activated carbon, there is a decrease in the specific surface area of the GO/AC in

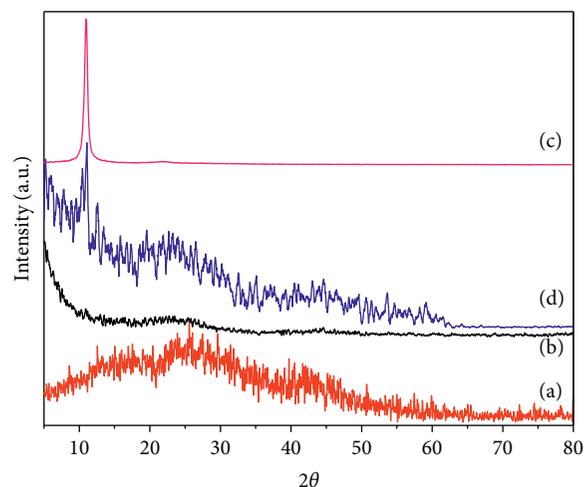


FIGURE 1: XRD patterns of sulfonated biochar (a), activated carbon (b), graphene oxide (c), and GO/AC (d).

comparison with the original activated carbon ( $150.7$   $\text{m}^2$   $\text{g}^{-1}$  lower). However, after 6 cycles, there was a slight increase of  $S_{\text{BET}}$  of GO/AC ( $49$   $\text{m}^2$   $\text{g}^{-1}$  higher) in comparison with initial GO/AC. This can be explained by some reasons. Firstly, during the esterification, small amounts of GO may be removed from the surface of AC to the reaction medium. Moreover, the specific surface area of AC is higher than that of GO.

Table 1 also presents the sulfonic acid group (-SO<sub>3</sub>H) contents of the catalysts. The results showed that the sulfonic acid group contents were  $1.14$   $\text{mmol}\cdot\text{g}^{-1}$ ,  $0.35$   $\text{mmol}\cdot\text{g}^{-1}$ , and  $0.92$   $\text{mmol}\cdot\text{g}^{-1}$  for sulfonated biochar, GO/AC, and GO catalysts, respectively. There was not much difference in sulfonic acid content between GO and sulfonated biochar catalysts.

**3.2. Catalytic Tests.** Figure 4 presents the ethyl lactate yield related to the reaction time for all the catalysts. All the tests were carried out under the same conditions.

According to the results presented in Figure 4, it can be seen that the catalytic activity decreases in the following order: graphene oxide ( $51.0\%$ ) > sulfonated bio-char ( $37.0\%$ )  $\approx$  GO/AC ( $35.4\%$ )  $\gg$  activated carbon ( $20.0\%$ ) after 420 min of reaction time. This order seems to be related to the sulfonic acid content and dispersion properties of each catalyst. Although the sulfonic acid content of sulfonated biochar and graphene oxide is similar ( $1.14$   $\text{mmol}\cdot\text{g}^{-1}$  and  $0.92$   $\text{mmol}\cdot\text{g}^{-1}$ , respectively), graphene oxide catalysts showed much higher activity than the sulfonated biochar catalysts, which may be due to the higher dispersion of graphene oxide in aqueous medium compared to sulfonated biochar. As previously mentioned, the dispersion of graphene oxide was high as a “pseudo-homogeneous” catalyst because there is the presence of numerous hydrophilic functional groups (-COOH, -OH, and -CHO) in its structure. Consequently, it is easy for the “accessible sulfonic groups” of graphene oxide catalyst to be active in the reaction that leads to an increase in ethyl lactate yield. However, its

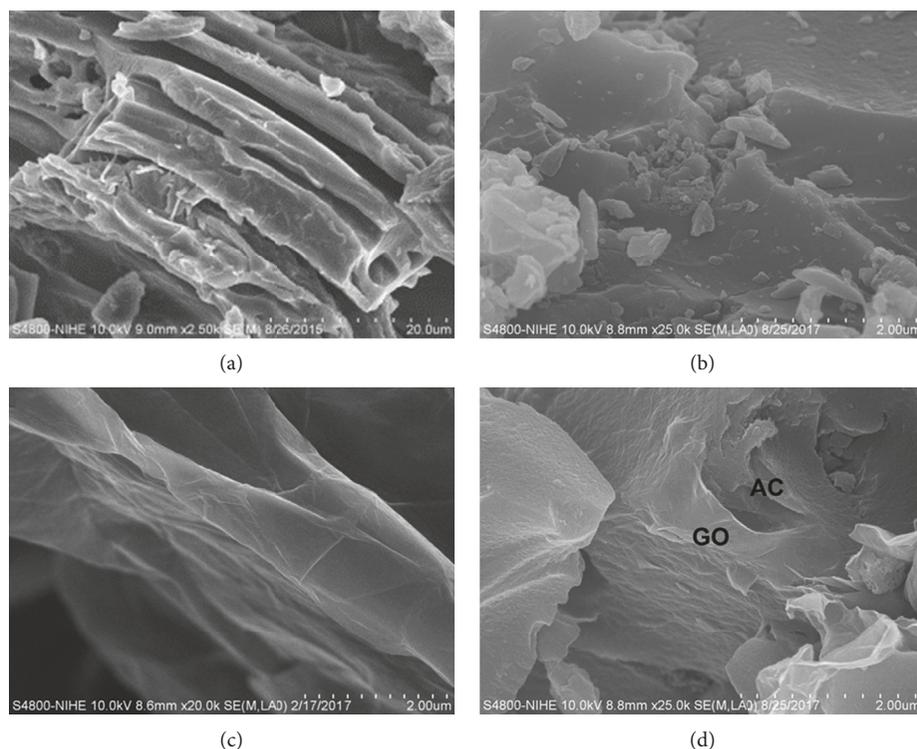


FIGURE 2: SEM images of sulfonated biochar (a), activated carbon (b), graphene oxide (c), and GO/AC (d).

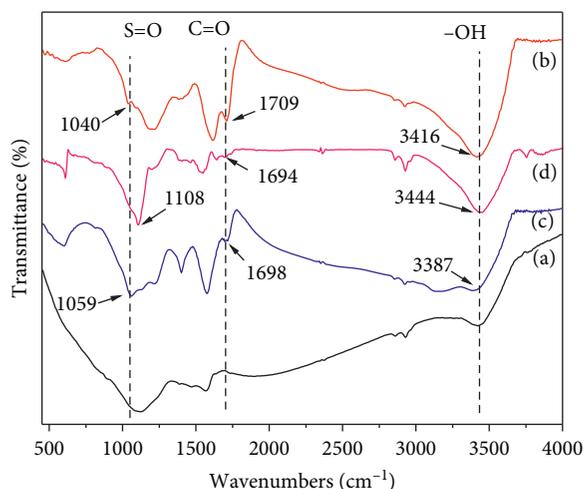


FIGURE 3: FT-IR spectra of activated carbon (a), sulfonated biochar (b), graphene oxide (c), and GO/AC (d).

drawback is a difficulty with filtering or taking the catalyst away from the reactants. Hence, we only used 1% by weight of graphene oxide in order to be able to analyze ethyl lactate by gas chromatography.

In the case of the sulfonated biochar and GO/AC catalysts, their catalytic activities are similar, although the  $-\text{SO}_3\text{H}$  content of the GO/AC catalyst is only  $0.35 \text{ mmol}\cdot\text{g}^{-1}$ , which is three times lower than that of the sulfonated biochar catalyst. This result confirms that a good combination of graphene oxide and activated carbon can serve as a catalyst for the esterification of lactic acid. As shown in

TABLE 1: Specific surface areas and sulfonic acid group ( $-\text{SO}_3\text{H}$ ) content of the catalysts.

Catalysts	$S_{\text{BET}}$ ( $\text{m}^2\cdot\text{g}^{-1}$ )	$-\text{SO}_3\text{H}$ content ( $\text{mmol}\cdot\text{g}^{-1}$ )
Sulfonated biochar	423.4	1.14
Sulfonated biochar after 4 cycles of reaction	—	0.64
Activated carbon	721.1	0
Graphene oxide	215.9	0.92
GO/AC	570.3	0.35
GO/AC after 6 cycles of reaction	618.9	0.29

Table 1, there is no  $-\text{SO}_3\text{H}$  group included in the structure of activated carbon, explaining why this catalyst showed the lowest catalytic activity.

**3.3. Recycling Tests of Catalysts.** The GO/AC and sulfonated biochar catalysts were recycled six and four times, respectively. Ethyl lactate yields of each recycling test are presented in Figure 5. Figure 5(a) noted that the activity of GO/AC catalyst decreased slowly from the 1<sup>st</sup> to the 3<sup>rd</sup> cycle, respectively, from 35.4% to 30.3% after a reaction time of 420 min, that means 14.4% of reduction, and it seem to be unchanged from 3<sup>rd</sup> to 6<sup>th</sup> cycles, the percentage of decrease is only 3.3%. In the same way, with sulfonated biochar catalyst (see Figure 5(b)), the activity was decreased from 37.0% in the 1<sup>st</sup> cycle to 26.1% in the 4<sup>th</sup> cycle, that is equal to 29.5% of reduction. Hence, stability of GO/AC is much higher than sulfonated biochar catalyst.

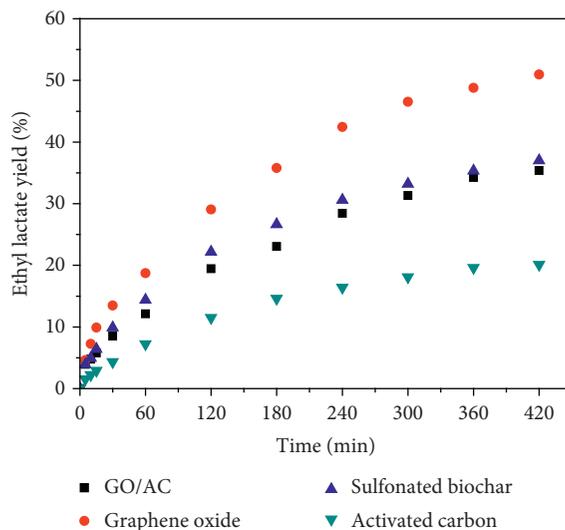


FIGURE 4: Ethyl lactate yield versus reaction time.

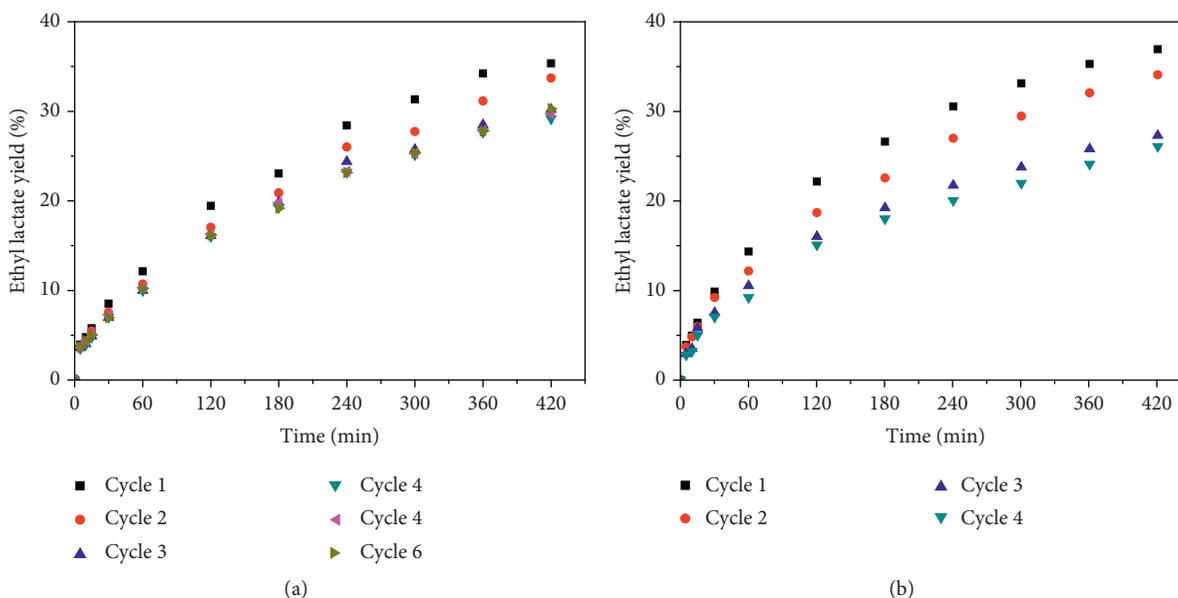


FIGURE 5: Test of recycled GO/AC (a) and sulfonated biochar (b) catalysts.

The  $-\text{SO}_3\text{H}$  contents presented in Table 1 confirm that the durability of GO/AC is higher than sulfonated biochar catalyst. In details, the functional group in GO/AC reduced from  $0.35 \text{ mmol}\cdot\text{g}^{-1}$  to  $0.29 \text{ mmol}\cdot\text{g}^{-1}$  that means 17.1% of decrease after 6 cycles. However, the value of sulfonated biochar is near 2.6 times higher, 43.9%, after 4 cycles. The result also confirms that in the active phase, GO was well dispersed and attached onto the support, activated carbon.

In addition to the strong attachment of graphene oxide onto activated carbon, it seems that the sulfonic group  $-\text{SO}_3\text{H}$  of the GO/AC catalyst was more stable than that of the sulfonated bio-char. To explain this phenomenon, FT-IR spectra of 6-times recycled graphene oxide catalyst are presented in Figure 6. The FT-IR spectra of the GO/AC after

6 cycles of reaction also showed vibrations at  $3423 \text{ cm}^{-1}$ ,  $1705 \text{ cm}^{-1}$ , and  $1080 \text{ cm}^{-1}$  corresponding to the presence of the  $-\text{OH}$ ,  $-\text{COOH}$ , and  $-\text{SO}_3\text{H}$  groups, respectively.

In our knowledge, there are some qualitative causes of the bond between GO and AC support. Firstly, the connection as esterification of the similar functional groups like carboxyl ( $-\text{COOH}$ ) and hydroxyl ( $-\text{OH}$ ) (see Figure 7), which present in both GO and AC surface [30], can contribute to the combination to become stronger. Moreover, Ai and Jiang [31] reported another explanation that both GO and AC include aromatic rings in their structure. It means that  $\pi$ - $\pi$  interactions may present when GO is coated on AC surface. As a result, the combination becomes better.

Because of some above results, GO/AC catalyst shows not only better catalytic activity but also higher stability than

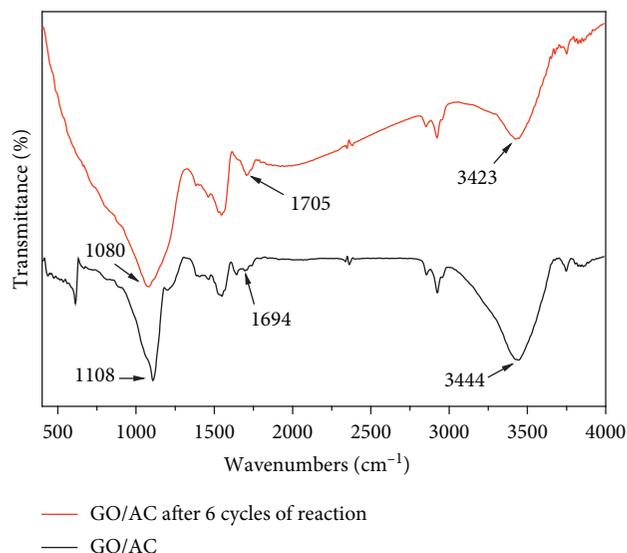


FIGURE 6: FT-IR spectra of GO/AC and GO/AC after 6 reaction cycles.

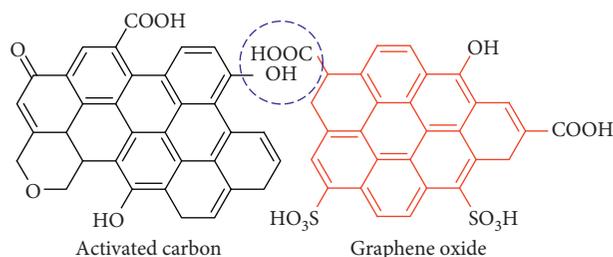


FIGURE 7: Self-esterification of activated carbon and graphene oxide.

sulfonated biochar in lactic acid esterification to form ethyl lactate. This catalyst demonstrates a combination of “solubility” of the active-phase graphene oxide and a high surface area as well as ease of separation of the activated carbon.

#### 4. Conclusions

Graphene oxide, graphene oxide supported on activated carbon (GO/AC), and sulfonated biochar catalysts were synthesized and investigated as acidic heterogeneous catalysts for lactic acid esterification to form ethyl lactate. The catalytic activity of the catalysts is in the following order: graphene oxide > sulfonated bio-char  $\approx$  GO/AC > activated carbon. It seems that catalytic activities are related to the  $-SO_3H$  content, especially the accessible  $-SO_3H$  content. Among the catalysts, the GO/AC and sulfonated biochar catalysts showed similar activity with an approximate yield of 35% ethyl lactate after 420 min of reaction time. This catalytic activity of GO/AC is remarkable because of the presence of only 1% by weight GO as the active phase. In addition, the results of the recycled catalyst tests showed that the GO/AC catalytic activity was stable after the 3<sup>rd</sup> cycle and reached a yield of 30.3% ethyl lactate after 420 min of reaction time. Under the same reaction conditions, the

catalytic activities of sulfonated biochar decreased sharply with a decrease in ethyl lactate yield from 37.0% to 26.1% after four recycling times. The remarkable catalytic activity and stability of the GO/AC catalyst are explained by good dispersion, stability of partial esterification, and the  $\pi$ - $\pi$  interactions between active-phase graphene oxide and activated carbon. From the point of view of application, it is concluded that the GO/AC catalyst shows high potential as a catalyst for the esterification of lactic acid.

#### Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

#### Conflicts of Interest

The authors declare that they have no conflicts of interest.

#### Acknowledgments

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## Research Article

# Effect of Silver Nanoparticles on Tropical Freshwater and Marine Microalgae

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The increase in synthesis and application of silver nanoparticles (AgNPs) in the last decade has resulted in contamination of AgNPs in the aquatic environment. The presence of AgNPs in aquatic environments has posed toxic effects to aquatic organisms and ecological damage. In this study, two tropical microalgae species including the freshwater *Scenedesmus* sp. and the marine diatom *Thalassiosira* sp. were employed to examine the toxic effects of AgNPs. The toxic effects were determined by analyzing different end points, such as half maximal effective concentration (EC<sub>50</sub>), algae growth inhibition, algae cell size, chlorophyll-*a* content, and total lipid accumulation. The results suggested that AgNPs presented different toxicity mechanisms for microalgae and showed to be more toxic in freshwater than in marine environment. The EC<sub>50</sub> values of AgNPs after 72 h for the growth inhibition of *Scenedesmus* sp. and *Thalassiosira* sp. were  $89.92 \pm 9.68$  and  $107.21 \pm 7.43$   $\mu\text{g/L}$ , respectively. AgNPs at a certain concentration have resulted in change in cell diameter, reduction in chlorophyll-*a* content, and enhancement of the total lipid production in the tested microalgae. Thus, local species should be involved in the toxic assessment. This research contributes on understanding the toxicity of AgNPs on freshwater and marine environments.

## 1. Introduction

The rapid development and application of nanomaterials in different industrial sectors have resulted in contamination of nanomaterials in the aquatic environment [1, 2]. In particular, nanomaterials containing silver have been widely used in various industries and applications [3], because of its antibacterial activity. More than 1300 products associated with NP technology are now available [4], in which 438 products (account for 24%) contain AgNPs [5]. In the USA, over 50% of the registered biocidal silver products by the Environmental Protection Agency (EPA) likely contain AgNPs. And, about 230 tons production with AgNPs is produced each year from European countries [6]. Although the concentration from nondetectable to over 0.1 mg/L of AgNPs has been detected from surface waters, the quantitative monitoring program for AgNPs in water environment is not currently available [7]. Therefore, the contamination of these nanomaterials has recently become environmental concerns due to the potential hazards in aquatic ecosystem [8, 9].

In ecological ecosystems, the microalgae are primary producers and play a vital role in the food chains. Thus, the bad effects of pollutants on microalgae species may break the balance of whole ecosystems [10]. The toxic effect and behavior of nanomaterial in the ecosystems on microalgae have been recently reviewed [3, 11]. Previous studies have indicated that AgNPs caused inhibition of growth in freshwater green microalgae [12], decrease photosynthesis activity in the unicellular green algae *Chlamydomonas reinhardtii* [13], and stimulate the antioxidant activities in the marine flagellate *Chattonella marina* [14]. AgNPs caused depletion in chlorophyll content and morphological malformations in the freshwater green alga *Pithophora oedogonia* [15]. Decrease in chlorophyll content, viable algal cells, increased reactive oxygen species (ROS) formation, and lipid peroxidation in the freshwater microalga *Chlorella vulgaris* and marine microalga *Dunaliella tertiolecta* were observed after exposure to AgNPs for 24 h [16]. Huang et al. [10] reported that AgNPs at a concentration of 0.5 mg/L caused both significantly induced excess intracellular ROS and

decreased cell viability in the marine diatom *Skeletonema costatum*.

Although the adverse effects of AgNPs on different organisms have been reported, previous studies however focus largely on freshwater environment [6]. There is little understanding about toxic effects of AgNPs on marine species, particularly the ones from tropical region. Therefore, the aims of this study was to investigate the toxicity of AgNPs to different species including the freshwater microalgae, *Scenedesmus* sp. (Chlorophyceae), and the marine diatom, *Thalassiosira* sp. (Bacillariophyceae). The toxic effects were determined by analyzing different end points, such as half maximal effective concentration ( $EC_{50}$ ), algae growth inhibition, algae cell size, chlorophyll-*a* content, and total lipid production.

## 2. Materials and Methods

**2.1. Silver Nanoparticles.** Silver nanoparticles were prepared as previously reported by Becaro et al. [17]. Briefly, stock solution of AgNPs was prepared by dissolving 10 g/L of  $AgNO_3$  (Aldrich Chemical Co., MO, USA) in MQ-water and heating at 80°C for 5 min. To this solution, 5 g/L of polyvinyl alcohol (PVA) as a stabilizing agent was added with constant stirring. Ultraviolet-visible (UV-Vis) absorption was monitored from 300 to 600 nm by using a BioThermo spectrophotometer. Diameter of particle size and morphology were characterized by a transmission electron microscope (TEM). Samples were kept in dark at  $4.0 \pm 1^\circ C$  and used within 6 months. The physicochemical properties of AgNP were stable under this condition [18].

**2.2. Test Species.** In this study, the freshwater microalgae *Scenedesmus* sp. isolated from the Saigon River, Ho Chi Minh City, Vietnam, and the marine diatom *Thalassiosira* sp. isolated from coastal waters of the Can Gio Sea, Ho Chi Minh City, Vietnam, were used. The green algae *Scenedesmus* sp. was maintained in COMBO medium (pH:  $7.5 \pm 0.3$ ) [19], and the diatom *Thalassiosira* sp. was maintained in F/2 medium (pH:  $8.0 \pm 0.3$ ) enriched with 0.2  $\mu m$  filtered seawater. Both cultures were grown on a 12 h light:dark cycle at a temperature of  $28 \pm 1^\circ C$  under light intensity of 50  $\mu mol$  photons/ $m^2$ s provided by cool white fluorescent tubes.

**2.3. Algae Growth Inhibition Test.** The inhibition of AgNP on growth of *Scenedesmus* sp. and *Thalassiosira* sp. was examined following the OECD 201 guideline methods [20]. Briefly, AgNP at the concentration of 0, 5, 20, 50, 100, and 200  $\mu g/L$  was spiked in Erlenmeyer flasks (500 mL) containing 300 mL culture medium, and living stocks of *Scenedesmus* sp. and *Thalassiosira* sp. were added to the initial concentration of  $5 \times 10^4$  cell/mL. Samples were prepared in triplicate and incubated at 27°C for 72 h under a 12 h:12 h light-dark cycle. The pH of all test solutions was measured at the beginning and end of the test. After 72 h, subsamples of culture medium

(about 10 mL) were fixed with Lugol's solution and cell density was determined by using a Sedgewick Rafter counting chamber. About 200 mL of culture medium was collected at the end of the test, filtered onto glass fiber filters (GF/C, Whatman, England), dried at 45°C for 48 h, and stored at  $-20^\circ C$  prior to total lipid extraction and analysis. The cell size of microalgae was measured directly by using an ocular micrometer. The graduation in arbitrary units is calibrated by using a microscope calibration slide.

The AgNPs concentration that resulted in 50% inhibition growth of algae over 72 h ( $EC_{50}$ , 72 h) was calculated by using the specific growth rate (SGR). The SGR for each species was evaluated by the difference cell density after 72 h as follows:

$$\delta_{x-y} = \frac{\ln C_y - \ln C_x}{t_y - t_x}, \quad (1)$$

where  $\delta_{x-y}$  is the SGR from time  $x$  to time  $y$ ,  $t_y - t_x$  is the duration of exposure periods in  $h$ , and  $C_y$  and  $C_x$  are the cell density at times  $x$  and  $y$ , respectively.

The inhibition growth rate (IGR) of algae was determined as follows:

$$IGR = \frac{\delta_C - \delta_T}{\delta_C} \times 100, \quad (2)$$

where IGR (%) is the inhibition growth rate of each microalgae species,  $\delta_C$  is the average growth rate of the control, and  $\delta_T$  is the average growth rate of the exposures.

**2.4. Chlorophyll-*a* Determination.** To determine the chlorophyll-*a* fraction, a known volume of culture samples (10 mL) was filtered using filter paper (GF/C, Whatman, England), and then the chlorophyll-*a* was extracted using 80% acetone for overnight in dark (4°C). After centrifugation, the supernatant was used to measure chlorophyll-*a* at 630–750 nm by using a spectrophotometer (UV-VIS, Harch, 500), and the concentration of chlorophyll-*a* (% of control) was calculated according to Metzner et al. [21].

**2.5. Total Lipid Extraction and Measurement.** The dried biomass was ground into powder; the total lipid in the homogenized cells was extracted according to the method of Bligh and Dyer [22] and analyzed using gravimetric quantification methods according to the procedure of Han et al. [23]. Briefly, about 50 mg dry weight (DW) of algae biomass (M1) was homogenized and digested with 3 mL of 1 mol/L HCl in 50 mL centrifuge tube at 80°C for 30 min. Then, the cell debris was collected after centrifugation. Lipid was then extracted with 3 mL methanol:chloroform (2:1 v/v) for 3 h and mixed well. Lipids settle in the upper phase was collected to a new dish that had been preweighed (M2). The dish was then dried completely and reweighed (M3). Lipid concentration (LC) was determined gravimetrically as follows:

$$LC (\%) = \frac{(M3 - M2)}{M1} \times 100. \quad (3)$$

**2.6. Statistical Analysis.** The growth inhibition (%) of each species was determined according to the method of OECD [20]. The effective concentration ( $EC_{50}$ ) values after 72 h for each species were evaluated by using the IGR at 50% by nonlinear regression. The data in tested treatments were presented as the mean  $\pm$  SD. One-way analysis of variance (ANOVA) and post hoc Tukey's honestly significant difference (HSD) were applied to identify the significant difference between exposure and control treatments. All data were log-transformed to normalize the distribution before analysis. Significant difference was considered at  $P$  values  $< 0.05$ .

### 3. Results

**3.1. Characterization of AgNPs.** The morphology, absorbance wavelength, and size distribution of AgNPs are shown in Figure 1. The TEM image of AgNPs is shown in Figure 1(a). The UV-Vis absorbance wavelength showed that the samples of AgNPs generated a single peak with maximum absorbance at 410 nm (Figure 1(b)). The particle size of AgNPs stock solution under TEM measurements indicated the dominant of particles with diameter from 6 to 10 nm (Figure 1(c)).

**3.2. Growth Inhibition.** The inhibition of AgNPs at the concentration from 5 to 200  $\mu\text{g/L}$  on the *Scenedesmus* sp. and *Thalassiosira* sp. after a 72 h exposure is shown in Figures 2(a) and 2(b). A 72 h exposure of *Scenedesmus* sp. and *Thalassiosira* sp. to sublethal concentrations of AgNPs caused a concentration-dependent inhibition of growth. The 72 h  $EC_{50}$  values of AgNPs for the growth inhibition of *Scenedesmus* sp. and *Thalassiosira* sp. were  $89.92 \pm 9.68$  and  $107.21 \pm 7.43 \mu\text{g/L}$ , respectively. AgNPs from the concentration of 20  $\mu\text{g/L}$  or higher resulted in significant inhibition on the growth of both algae. The freshwater green algal *Scenedesmus* sp. showed greater sensitivity than the marine diatom *Thalassiosira* sp. to AgNPs. Exposure to AgNPs at 200  $\mu\text{g/L}$  inhibited completely the growth of *Scenedesmus* sp., whereas this concentration of AgNPs inhibited almost 100% growth of *Thalassiosira* sp. (Figure 2). The pH value rises slightly from  $7.5 \pm 0.3$  at the beginning of the experiment to  $7.8 \pm 0.3$  at the end in the test with *Scenedesmus* sp. (in COMBO medium), while with *Thalassiosira* sp. (in F/2 medium), the pH value remains at approximately  $8.0 \pm 0.4$  throughout the period of incubation.

**3.3. Algal Cell Diameter.** Cell diameter of the green algal *Scenedesmus* sp. was  $4.31 \pm 0.15 \mu\text{m}$ . There was no difference in cell diameter of the *Scenedesmus* sp. between the control and treatments after 72 h exposure to AgNPs (Figure 3(a)). In the case of the marine diatom *Thalassiosira* sp., the cell diameter was not different from the control after 72 h exposure to AgNPs with concentration of 5, 20, and 50  $\mu\text{g/L}$ , but AgNPs with concentration of 100 and 200  $\mu\text{g/L}$  caused significant increase in cell diameter with respect to the control. The control treatment had an average cell diameter of  $8.98 \pm 0.17 \mu\text{m}$ , while the cell diameter increased up to

$9.12 \pm 0.31\%$  and  $8.05 \pm 0.39\%$  in the exposures with 100 and 200  $\mu\text{g/L}$  of AgNPs, respectively (Figure 3(b)).

**3.4. Chlorophyll-*a* Content.** Results of chlorophyll-*a* contents in *Scenedesmus* sp. and *Thalassiosira* sp. were changed significantly upon exposure to AgNPs. In the freshwater green algal *Scenedesmus* sp., exposure to AgNPs at the concentration of 5 and 20  $\mu\text{g/L}$  was not different with the control, but exposure to AgNPs at the concentration of 50, 100, and 200  $\mu\text{g/L}$  resulted in significant decrease in chlorophyll-*a* content (the highest decrease of 21.5% in the treatment with 200  $\mu\text{g/L}$  of AgNPs, with respect to the control) (Figure 4(a)). Chlorophyll-*a* content varied almost the same trend in the marine diatom *Thalassiosira* sp. The chlorophyll-*a* content in the lowest treatment of AgNPs (5  $\mu\text{g/L}$ ) was not different from the control but the treatments with AgNPs from 20 to 200  $\mu\text{g/L}$  resulted in significant decrease in chlorophyll-*a* contents. The lowest level of chlorophyll-*a* (14.5%) was found in the treatment with 200  $\mu\text{g/L}$  (Figure 4(b)).

**3.5. Lipid Accumulation.** Silver nanoparticles had great influence on the lipid production of *Scenedesmus* sp. and *Thalassiosira* sp. AgNPs at the concentration of 5 and 20  $\mu\text{g/L}$  led to a significant increase in total lipid production in *Scenedesmus* sp., with the maximum total lipid increase of 8.1% and 7.6%, compared with the control, respectively. In contrast, AgNPs at higher concentration (100 and 200  $\mu\text{g/L}$ ) resulted in significant decrease in total lipid production. The highest concentration of AgNPs (200  $\mu\text{g/L}$ ) resulted in the lowest total lipid production (Figure 5(a)). In the marine diatom exposed to AgNPs, total lipid production was significantly increased (from 11.6 to 17.4%, compared with the control) in all treatment with AgNPs. The highest increase of total lipid production (17.4%) was found in the treatment with 100  $\mu\text{g/L}$  (Figure 5(b)).

### 4. Discussion

In aquatic environment, green algae and diatom are not only the primary producers for higher tropic levels but also play an important role for the normal functioning of aquatic ecosystems [10]. Numerous studies have demonstrated that NPs generated adverse effects on freshwater and marine microalgae species [3, 24–26]. NPs are well known for their involvement of ROS in both animal and plant cells, causing oxidative stress and cellular damage [27, 28]. Zhang et al. [29] demonstrated the mechanism of the photosynthetic toxicity against the green alga *Scenedesmus obliquus* by using silver nanoclusters (AgNCs). The authors found that the photosynthetic toxicity of AgNCs was largely attributed to the “joint-toxicity” effect of particulate form of AgNCs and their released  $\text{Ag}^+$  which resulted in the disruption of the electron transport chain of light reaction and affected the content of main enzymes of the Calvin cycle of algae cells. Other toxicity mechanisms of NPs in algae cells are the interaction with the algae cell wall or binding to the cell surface that resulted in the formation of large aggregates

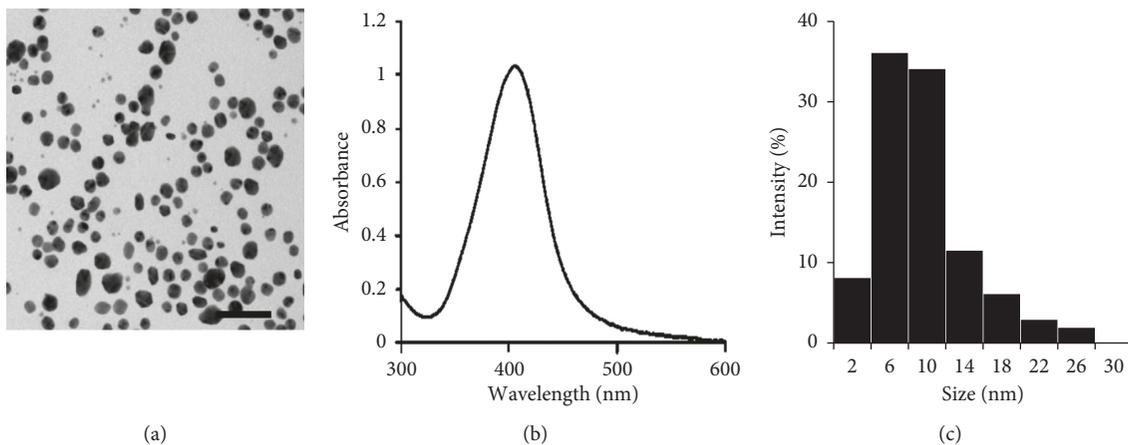


FIGURE 1: Morphology (a), absorbance wavelength (b), and size intensity (c) of silver nanoparticles (AgNPs) (scale bar: 50 nm).

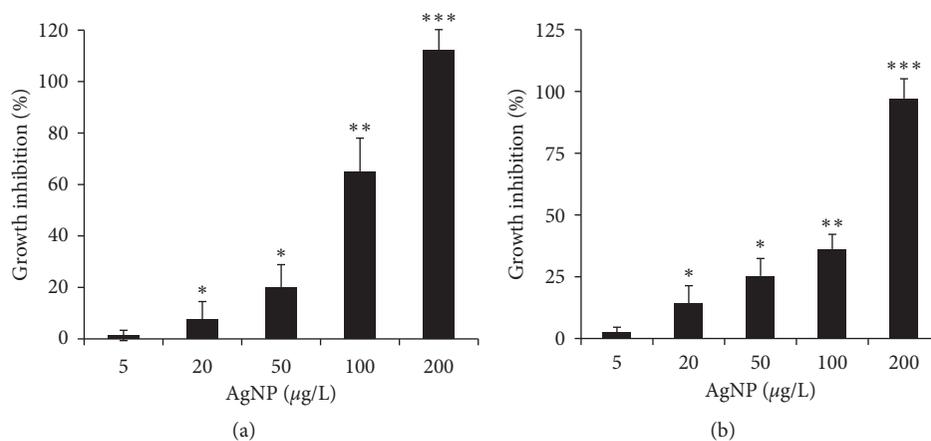


FIGURE 2: Effect of silver nanoparticles on growth of (a) *Scenedesmus sp.* and (b) *Thalassiosira sp.* Asterisks show significant differences compared with the control (\* $P < 0.05$ ; \*\* $P < 0.01$ ; \*\*\* $P < 0.001$ ).

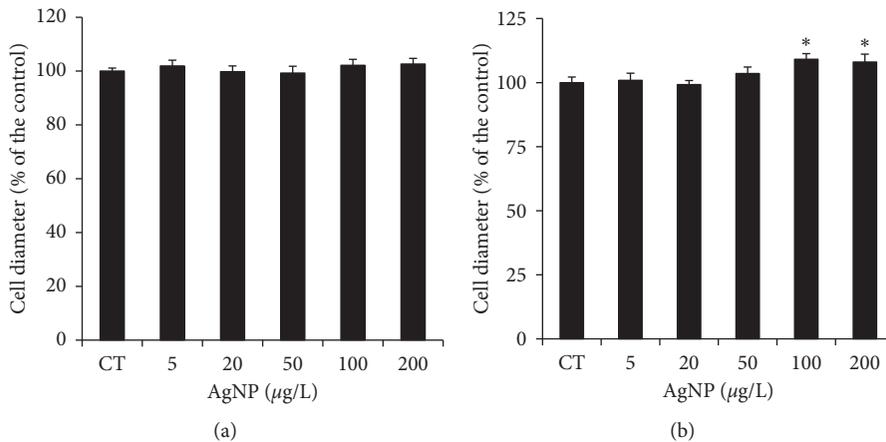


FIGURE 3: Algal cell diameter ( $\mu\text{m}$ ) of (a) *Scenedesmus sp.* and (b) *Thalassiosira sp.* upon exposure to silver nanoparticles. Asterisks indicate significant differences compared with the control (\* $P < 0.05$ ).

[16, 30]. The formation of aggregates could entrap algal cells and block cell division with consequent inhibition of cell division [31, 32].

The toxicity of NPs on algae may vary from algae species, exposure duration and dose, coating, and size [11, 24, 26, 33]. Sendra et al. [25] indicated that AgNPs have

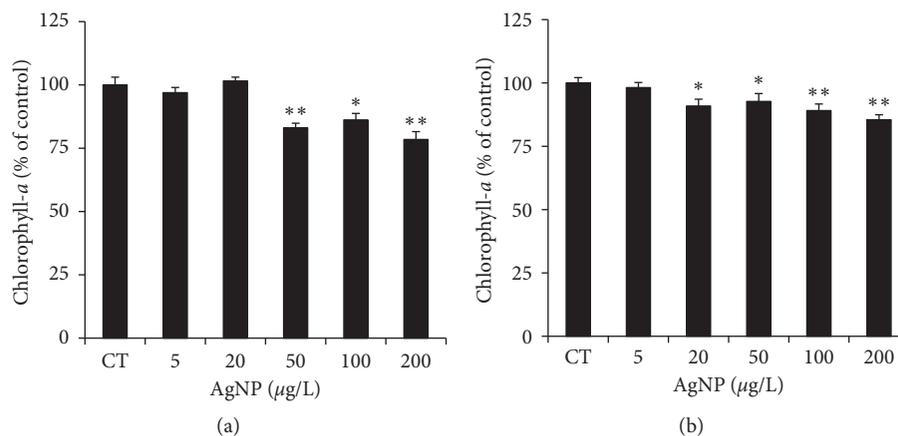


FIGURE 4: Chlorophyll-*a* content of (a) *Scenedesmus sp.* and (b) *Thalassiosira sp.* upon exposure to silver nanoparticles. Asterisks indicate significant differences compared with the control (\* $P < 0.05$ ; \*\* $P < 0.01$ ).

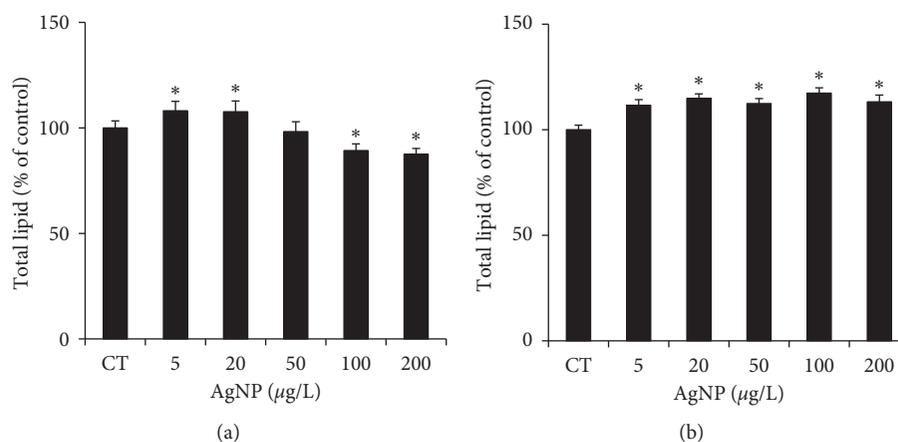


FIGURE 5: Total lipid content of (a) *Scenedesmus sp.* and (b) *Thalassiosira sp.* upon exposure to silver nanoparticles. Asterisks indicate significant differences compared with the control (\* $P < 0.05$ ).

generated direct and indirect deleterious impacts on algae in different exposure environment. Generally, AgNPs tend to dissolve to  $\text{Ag}^+$  under the presence of oxygen in aqueous environment [34]. Thus, both AgNPs and  $\text{Ag}^+$  are present in the environment and hazardous effects of AgNPs to algae cells were contributed from the effect of AgNPs and their released  $\text{Ag}^+$ . In freshwater algae, the toxic effect of  $\text{Ag}^+$  was the main mechanism, while under marine condition with the present of high chloride ions ( $\text{Cl}^-$ ), large amount of AgNPs are oxidatively dissolved and generate Ag/AgCl-NPs and  $\text{AgCl}_x^{(x-1)-}$  compound. The formation of silver/silver chloride nanoparticles decreases the toxic effect of AgNPs to organisms [25, 26, 34, 35]. In addition, the toxic effects of NPs may depend on various factors such as exposure duration, dose of exposure, and environmental conditions [29]. When exposing the marine algae *Dunaliella tertiolecta* to both ZnO NPs and the bulk ZnO, Manzo et al. [33] reported that the toxic effects of ZnO NPs on the tested algae were stronger than of the bulk ZnO, and the toxicity mechanisms of bulk ZnO may not relate to the ion of zinc. In addition, when using different marine and freshwater species for the toxicity test, Aravantinou et al. [24] found

that toxic effects of ZnNPs obviously depended on the microalgae species as well as the exposure duration and dose. Results of the present study agree well with Sendra et al. [25] that AgNPs is more toxic in freshwater than in marine environment. Probably, the high generation of the dissolved ion  $\text{Ag}^+$  in freshwater media resulted in higher toxicity of AgNPs in freshwater microalgae [25, 29].

Previous studies often used physiological alterations as indicators for assessment toxicity of NPs in microalgae [10, 25, 35]. Chlorophyll-*a* content is commonly used to indicate the photosynthesis efficiency or the cell division of algal species [10, 36]. Exposure of microalgae to NPs has resulted in the reduction of chlorophyll-*a* content due to the damage in the pigment of the exposed cells or reduction of the pigment-protein complexes [10, 36]. The decrease in chlorophyll-*a* content in both tested algae upon exposure to AgNPs may be a result of accelerating the activity of the chlorophyllase or stimulating ROS production [10]. Results of the present study are in agreement with the observations of Wei et al. [36] and Huang et al. [10] that AgNPs has induced a physiological response in the freshwater and marine algae through reduction of chlorophyll-*a* content [10]. Under stress condition, living cells have the ability to

generate enzymatic and nonenzymatic antioxidants to regulate ROS adverse effects. Thus, intracellular ROS have been commonly used as biomarkers to quantify the toxic effects of pollutants [10, 25, 35]. In addition, morphological characteristics such as cell size, cell teratology, or deformity have been used as bioindicators for evaluating toxicity of hazardous substances [37]. In this study, exposure to a specific concentration of AgNPs resulted in elevation in cell size of the marine diatom *Thalassiosira* sp. as well as depletion in chlorophyll-*a* content. These results indicated chlorophyll-*a* content and the morphological response in diatom frustule can be used to monitor hazardous substances in water environment.

Green algae and diatoms are known for storing lipid level up to 50% as a reserve food material under stress condition [28, 38]. Higher lipid contents in green algae and diatoms under heavy metals or nanoparticles stress have been reported [28, 38]. Under stress condition, algal cells tend to adjust the cellular metabolism and store more large molecules such as proteins and lipid [10]. Algae can tolerate toxic effects typically at lower doses of toxicants [28]. In this study, the lipid content in the green algae *Scenedesmus* sp. increased significantly at low dose of AgNPs, but decreased as higher dose of AgNPs could be reflected from the above mechanisms. He et al. [28] demonstrated that a specific concentration of NPs could promote neutral lipids accumulation in the green algae *S. obliquus*, but further increase of NPs has resulted in the inhibition of cell growth and reduction of lipid production. Results of this study were also in agreement with observations of Huang et al. [10] that there is a reduction in the chlorophyll-*a* content but an elevation in lipid contents in a dose-dependent manner upon exposure the marine diatom *S. costatum* to AgNPs. Further studies are needed to determine the optimum growth rates as well as for lipid production in the tested species, which could be used to make biodiesel in tropical regions.

## 5. Conclusions

By using two tropical microalgae species including the freshwater *Scenedesmus* sp. and the marine diatom *Thalassiosira* sp., the present study demonstrated the different toxic effects of AgNPs in freshwater and marine environments. The present results indicated the toxic effects of AgNPs may vary in different aquatic environments. Results indicated that AgNPs are more toxic in freshwater than in marine environment. AgNPs at a certain concentration have resulted in change in cell diameter, reduction in chlorophyll-*a* content, and stimulation of the total lipid production in the tested microalgae. Thus, morphological characteristic of microalgae can be used as an effective tool for monitoring nanoparticles in water.

## Data Availability

The data used to support the findings of this study are included within the article.

## Conflicts of Interest

The author declares that there are no conflicts of interest regarding the publication of this paper.

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## Research Article

# Synthesis of Magnesium Oxide Nanoplates and Their Application in Nitrogen Dioxide and Sulfur Dioxide Adsorption

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In this research, nanostructured magnesium oxide was synthesized through the sol-gel calcination or hydrothermal calcination method using various surfactants. The X-ray diffraction pattern of the materials confirmed that all the prepared magnesium oxide samples were single phase without any impurity. The scanning electron microscopy images and specific surface area values showed that sodium dodecyl sulfate was the most suitable surfactant for the synthesis of magnesium oxide nanoplates with the diameter of 40–60 nm, the average thickness of 5 nm, and a specific surface area of 126 m<sup>2</sup>/g. This material was utilized for nitrogen dioxide and sulfur dioxide adsorption under ambient condition. The saturated adsorption capacities of magnesium oxide were 174 mg/g for nitrogen dioxide and 160 mg/g for sulfur dioxide, making the magnesium oxide nanoplates a promising candidate for toxic gas treatment.

## 1. Introduction

Nowadays, air pollution caused by the emission of toxic gases from human and industrial activities poses not only tremendous threats to human health but also the destructive effects to the ecosystem. Nitrogen dioxide (NO<sub>2</sub>) and sulfur dioxide (SO<sub>2</sub>) are criteria pollutants that have adverse impacts on the environment. Both of NO<sub>2</sub> and SO<sub>2</sub> are released from natural and anthropological sources including forest fires, volcanic eruptions, transportation systems, and the combustion process. While NO<sub>2</sub> gas could be harmful to human due to cardiovascular damage and respiratory pathway [1, 2], SO<sub>2</sub> gas can affect the human health with breathing problems, cardiovascular complications, bronchitis, and eyes irritation [3, 4]. Some studies show that for every 10 ppb increase in SO<sub>2</sub> concentration, the risk of death increased by 0.2–2% [5]. This increasing risk requires feasible solutions to deal with. Various methods have been developed by scientists and experts

including molecular sieves, membrane separation, adsorption, and catalyst [6–9]. Among them, adsorption is one of the most effective methods for toxic gas treatment owing to simple processing and regeneration at low cost. Several materials such as activated carbon, hydroxide, metal oxide, sepiolite, and metal organic frameworks (MOFs) have been widely used as effective adsorbents [10–13].

During the development of nanoscience and nanotechnology, the application of inorganic nanomaterial as toxic gas adsorbents has attracted much attention because of their large specific surface area and high reactivity. Due to the economical and eco-friendly properties, nano-magnesium oxide (MgO) is a potential adsorbent of toxic gas [14–18]. However, to the best of our knowledge, there have been very few reports using MgO for the adsorption of NO<sub>2</sub> and SO<sub>2</sub>.

Nanostructured MgO has been synthesized by various physicochemical techniques, such as sol-gel calcination,

chemical precipitation, and hydrothermal and microwave fabrication [19–28]. In this research, we successfully synthesized MgO nanoplates by sol-gel calcination and hydrothermal calcination methods. The influence of surfactant on the morphology of nanostructured MgO was investigated. The MgO nanoplates were used for NO<sub>2</sub> and SO<sub>2</sub> adsorption.

## 2. Materials and Methods

All chemicals were of analytical grade and directly used without further purification. Magnesium nitrate hexahydrate (Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 99.9%), sodium hydroxide (NaOH, 99.8%), polyethylene glycol (PEG 6000), cetyltrimethylammonium bromide (CTAB, 98%), sodium dodecyl sulfate (SDS, 98.5%), sulfur dioxide (99.9%), and nitrogen dioxide (99.5%) were purchased from Sigma-Aldrich and used without any further purification.

**2.1. Synthesis of Nanostructured MgO.** Nanostructured MgO was prepared by the sol-gel calcination or hydrothermal calcination method [29, 30] described as follows.

**2.2. Sol-Gel Processing.** Typically, 10 mmol Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (2.56 g) was dissolved in 250 ml distilled water, and 0.5 mmol surfactant (3 g PEG 6000, 0.182 g CTAB or 0.144 g SDS) was added into the magnesium nitrate solution. Then, 100 ml NaOH 0.2 M solution was added dropwise into this mixture and stirred vigorously until a relatively high viscosity gel was formed. The gel was stirred gently overnight and then filtered, washed several times with distilled water, and dried at 80°C for 4 hours before calcinating at 500°C for 4 hours to obtain a white solid powder.

**2.3. Hydrothermal Processing.** The hydrothermal process was performed in a Teflon-lined stainless steel autoclave. 10 mmol Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (2.56 g) was dissolved in 250 ml distilled water, and 0.5 mmol surfactant (3 g PEG 6000, 0.182 g CTAB or 0.144 g SDS) was added into the magnesium nitrate solution. Then, 100 ml NaOH 0.2 M solution was added dropwise into this mixture. Afterward, the resulting mixture was transferred into the autoclave and heated at 100°C for 2 hours. After cooling down to room temperature, the precipitate was collected by vacuum filtration and calcinated at 500°C for 4 hours to obtain a white solid powder.

**2.4. Characterization of Materials.** All the obtained MgO materials were characterized by different physicochemical techniques. The functional groups on the surface of materials were determined by Fourier-transform infrared spectroscopy (FT-IR, Thermo Fisher, USA). Phase identification was performed by the X-ray diffraction (XRD) technique, using Cu K $\alpha$  ( $\lambda = 1.54056 \text{ \AA}$ ) radiation (D/max Ultima III, Rigaku, Japan). The morphology and particle size were given by scanning electron microscope (SEM, Hitachi, S-4800). The specific surface area was measured from the nitrogen adsorption/desorption at 77 K using the Brunauer–

Ennett–Teller (BET) method (TriStar II Plus, Micromeritics Instrument Corp, USA). The chemical composition of MgO material after adsorption was analyzed with energy-dispersive X-ray spectroscopy (SEM-EDX) (HORIBA-EMAX80; Hitachi High-Technology).

**2.5. Adsorption Experiments.** The experiments of evaluating the NO<sub>2</sub> and SO<sub>2</sub> adsorption on MgO nanoplates were carried out under ambient temperature. SO<sub>2</sub> or NO<sub>2</sub> gas was mixed with nitrogen carrier gas (5% SO<sub>2</sub> or NO<sub>2</sub> in N<sub>2</sub> atmosphere). A glass tube reactor was loaded with 100 mg of MgO powder with the pretreatment at 200°C for 1 hour. Then, a stream of NO<sub>2</sub> gas or SO<sub>2</sub> gas was supplied with a flow rate of 50 ml/min. The uptake quantities were recorded as a function of time. The adsorption of NO<sub>2</sub> and SO<sub>2</sub> on MgO nanoplates were monitored by FT-IR and EDX. The MgO nanoplates were collected and regenerated by calcination at 500°C for 4 hours. The schematic diagram for NO<sub>2</sub> and SO<sub>2</sub> adsorption experiment is shown in Figure 1.

## 3. Results and Discussion

**3.1. Characterization of Magnesium Oxide Nanoplates.** In this study, three different surfactants (PEG, CTAB, and SDS) were utilized for the synthesis of MgO nanocrystals by sol-gel and hydrothermal methods. Their crystalline structures are presented in Figure 2. The most intense peaks in XRD patterns of the synthesized MgO samples were observed at  $2\theta$  of 37.16°, 43.12°, and 62.40° which were well-matched with those of JCPDS data file of standard MgO no. 78-0430 [31]. The XRD patterns of MgO synthesized by using different surfactants and synthesis methods were basically similar to the surfactant-free MgO, indicating that the crystal structure of MgO was not affected by surfactants or synthesis methods. Furthermore, both sol-gel and hydrothermal methods produced MgO crystal with single phase.

The morphology of MgO samples is illustrated in Figures 3 and 4. BET specific surface area values of nano-MgO are shown in Table 1. Evidently, surfactant-free MgO samples exhibited undefined morphology and high aggregation.

Among the three surfactants, PEG showed less influence in controlling the size and morphology of MgO nanoplates. In addition, MgO materials synthesized using this surfactant have relatively low surface areas (98 m<sup>2</sup>/g for the sol-gel method and 110 m<sup>2</sup>/g for the hydrothermal method). In contrast, SDS was a suitable surfactant for the formation of MgO nanoplates with well-defined morphology and high surface area (115 m<sup>2</sup>/g for sol-gel method and 126 m<sup>2</sup>/g for hydrothermal method) (Figure 5). This phenomenon might be explained by the electrostatic interaction between surfactants and MgO surface. The nonionic nature of PEG does not allow effective interaction with positively charged MgO surface while the negatively charged SDS interacts effectively with the surface of MgO. Interestingly, MgO samples synthesized by the hydrothermal method had smaller average size and higher surface area compared with the samples prepared by the sol-gel method. There are two possible

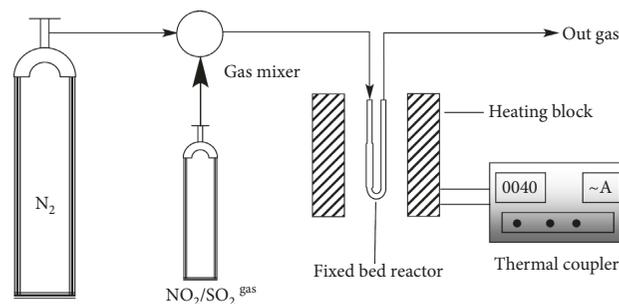


FIGURE 1: Schematic diagram of the experimental setup for  $\text{NO}_2$  and  $\text{SO}_2$  adsorptions.

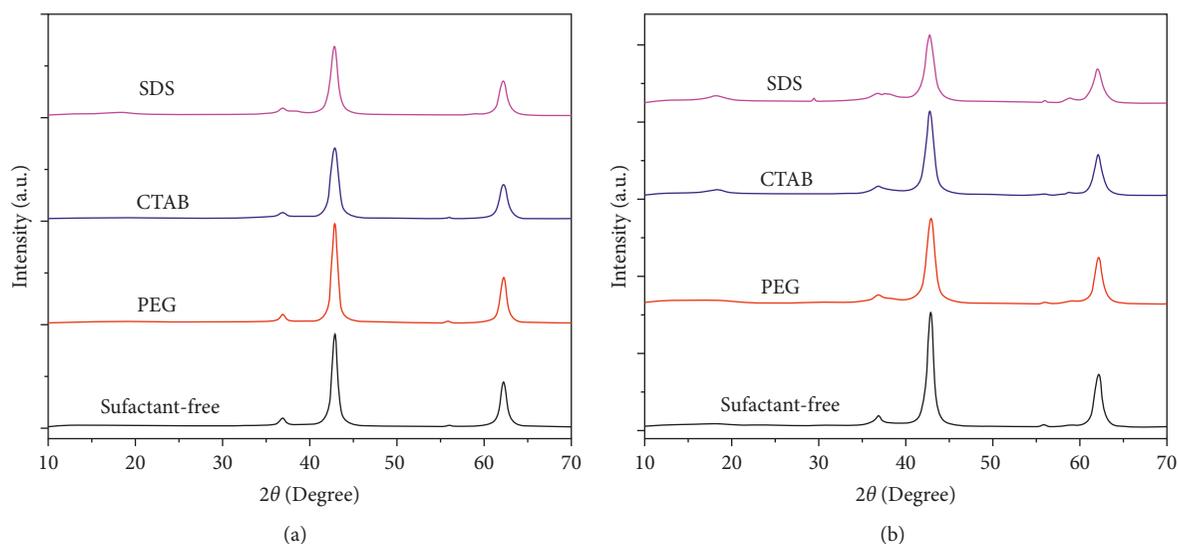


FIGURE 2: XRD patterns of nano-MgO synthesized by (a) the sol-gel method and (b) the hydrothermal method.

reasons for these higher surface areas. Firstly, during the hydrothermal process, the generating and loss of water molecules between adjacent layers of hydroxyl ions create defects, intercrystallite channels, and cracks inside the structure of MgO, which increase the surface area and porosity of the material [30]. Secondly, when increasing temperature suddenly, the formation of nucleations is facilitated which results in the decline of precursor concentration and hence, crystals are formed with smaller size. Due to the highest surface area and good morphology, the MgO nanoplate material synthesized by hydrothermal method using SDS was chosen for the adsorption of  $\text{NO}_2$  and  $\text{SO}_2$  gases.

**3.2. Investigation of Adsorption Ability of the Material.** Fourier-transform infrared spectroscopy was employed to determine the presence of  $\text{NO}_2$  on the surface of MgO (Figure 6(a)). It was shown that after 10 min of adsorption, a new peak appeared at  $1384\text{ cm}^{-1}$  which is assigned for  $\text{NO}_3^-$  vibration [32]. The appearance of  $\text{NO}_3^-$  is explained by the interaction between  $\text{NO}_2$  and the metal sites of MgO which facilitates the dissociation of  $\text{NO}_2$  into  $\text{NO}_3^-$  and  $\text{NO}$  [32, 33]:



The intensity of this peak increased with the increase of the adsorption time, indicating higher loading of  $\text{NO}_2$  on MgO nanoplates. Figure 6(b) presents the results of the adsorption experiment for  $\text{NO}_2$ . The uptake rate increased rapidly during the first 20 min with the adsorbed amount of  $111\text{ mg}_{\text{NO}_2}/\text{g}_{\text{MgO}}$ . After 60 min of adsorption, the adsorbed  $\text{NO}_2$  reached 89% of the maximum capacity (the adsorption equilibrium was achieved after 180 min of adsorption with the uptake value of  $174\text{ mg}_{\text{NO}_2}/\text{g}_{\text{MgO}}$ ). The EDX results (Figure 6(c)) verified the existence of N elements on MgO nanoplates with 4.55 wt.%, corresponding to the  $\text{NO}_2$  adsorption of  $176\text{ mg}/\text{g}_{\text{MgO}}$ , which was in agreement with the adsorption result. The SEM image (inset in Figure 6(c)) illustrated the surface of MgO sample after the adsorption process without any change in comparison with the original sample. In addition, XRD patterns of MgO sample after 180 min of exposure to  $\text{NO}_2$  showed no difference with the initial sample (Figure 6(d)).

The results of the  $\text{SO}_2$  adsorption on MgO nanoplates are presented in Figure 7. Because of the number of basic sites over MgO, a  $\text{SO}_{2,\text{gas}} + \text{MgO} \longrightarrow \text{MgSO}_3$  reaction could be expected [33, 34]. The presence of  $\text{SO}_2$  on the MgO surface was affirmed by the broadband at  $984\text{ cm}^{-1}$  [35] in the IR spectrum (Figure 7(a)). This band enlarged along the

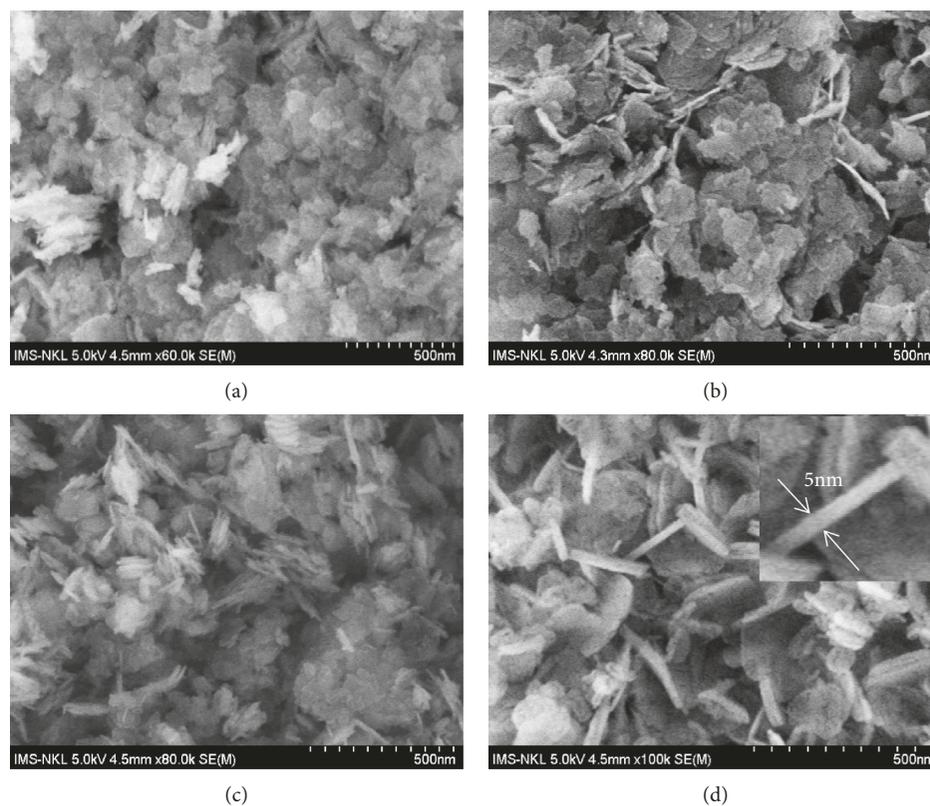


FIGURE 3: SEM images of nano-MgO prepared by the sol-gel method using different surfactants: (a) surfactant-free, (b) PEG, (c) CTAB, and (d) SDS.

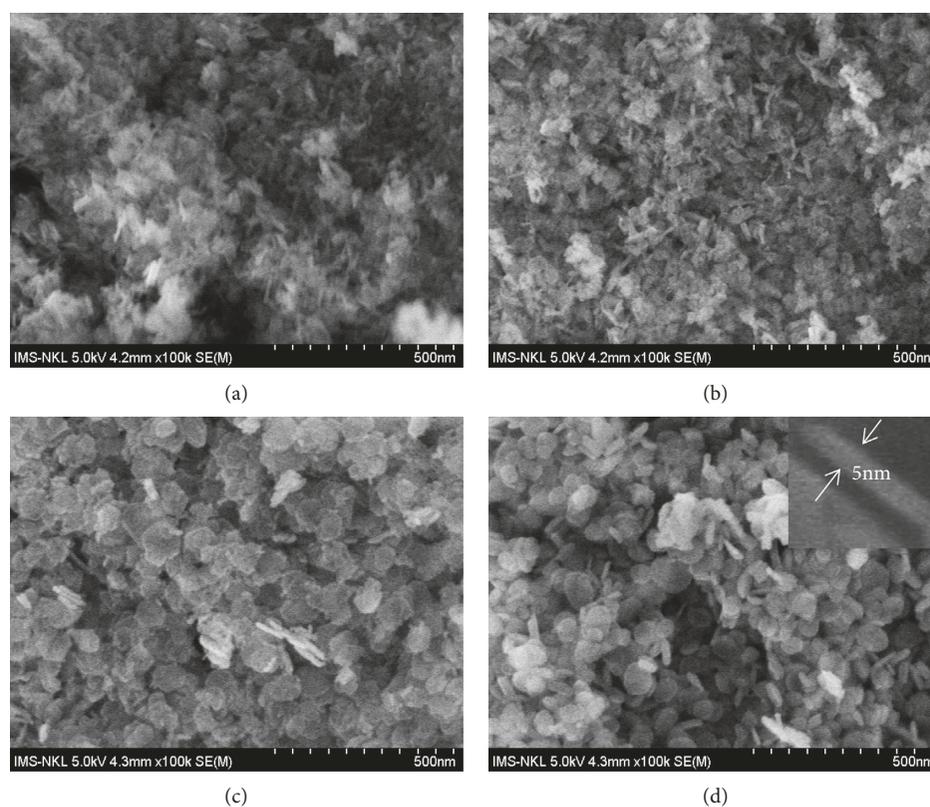


FIGURE 4: SEM images of nano-MgO prepared by the hydrothermal method using different surfactants: (a) surfactant-free, (b) PEG, (c) CTAB, and (d) SDS.

TABLE 1: BET specific surface area values of nano-MgO synthesized by using different surfactants.

	Method	Surfactant-free	PEG	CTAB	SDS
$S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ )	Sol-gel	66	98	100	115
	Hydrothermal	88	110	119	126

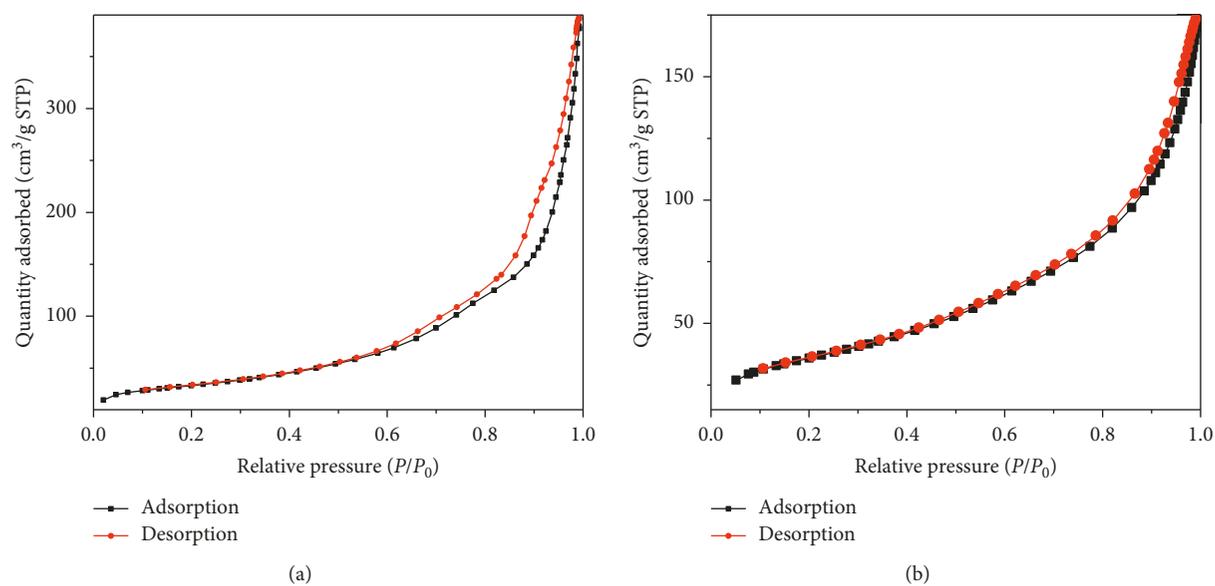
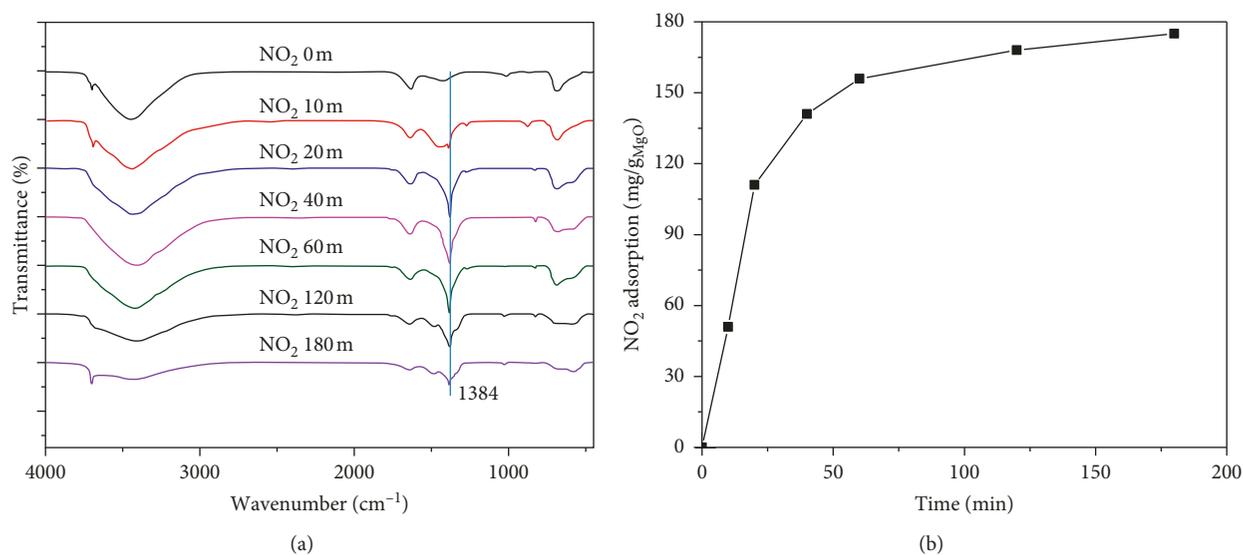
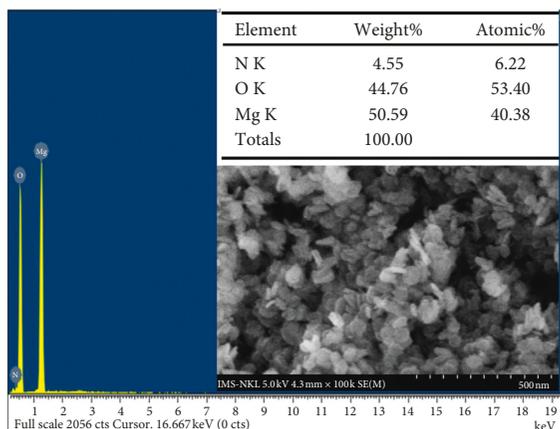
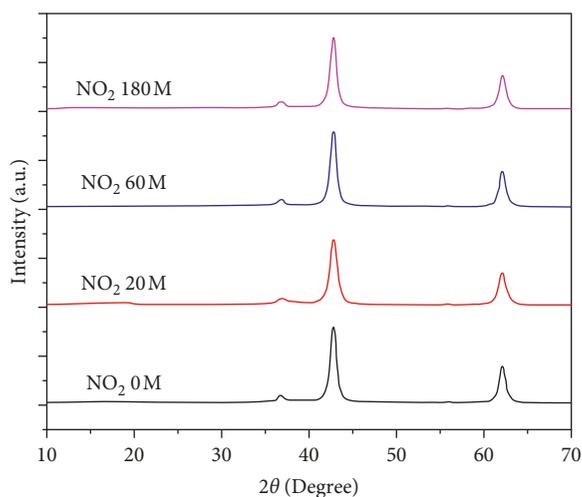
FIGURE 5:  $\text{N}_2$  adsorption/desorption isotherms of MgO nanoplates synthesized using SDS by (a) the sol-gel calcination method and (b) the hydrothermal calcination method.

FIGURE 6: Continued.

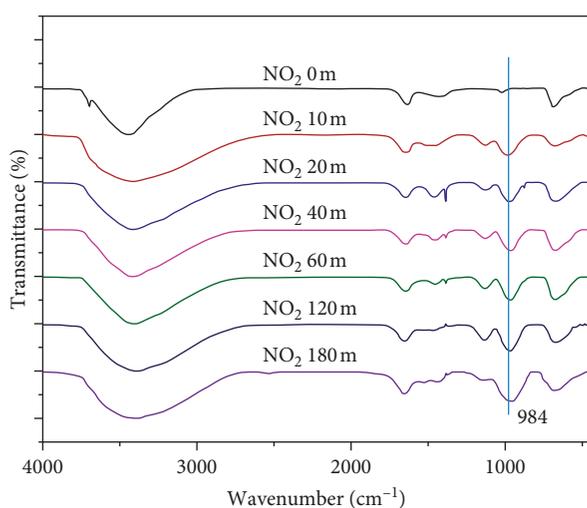


(c)

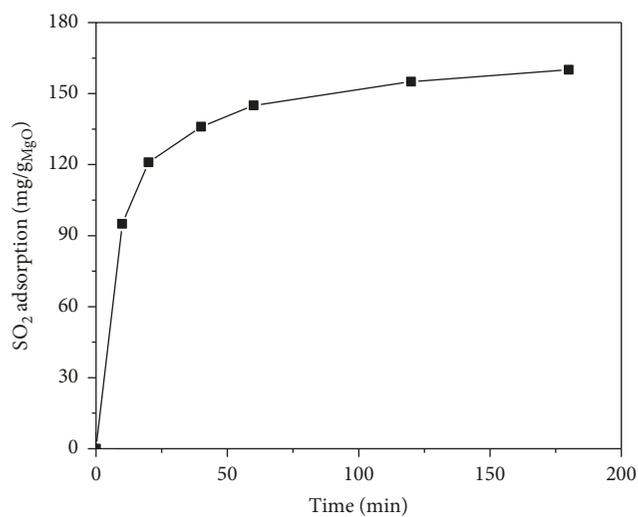


(d)

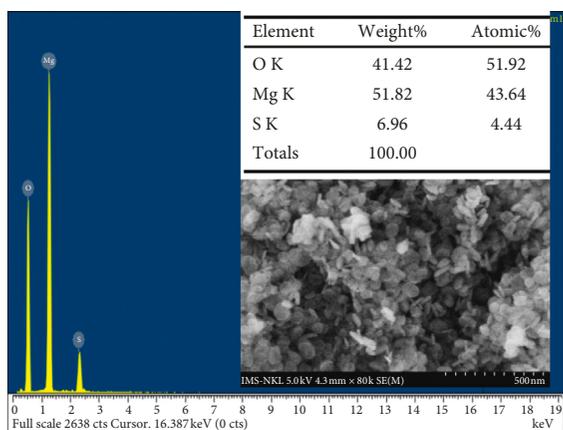
FIGURE 6: (a) FT-IR spectra of MgO samples after different adsorption times; (b) quantity of NO<sub>2</sub> adsorbed on MgO; (c) EDX spectrum and SEM image of MgO after 180 min of adsorption; (d) XRD patterns of MgO samples after different adsorption times.



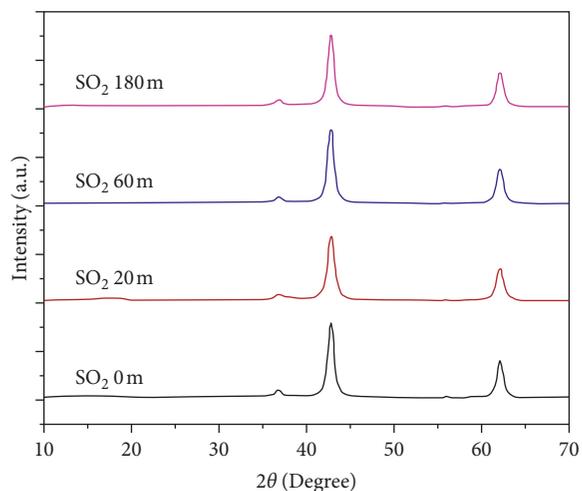
(a)



(b)

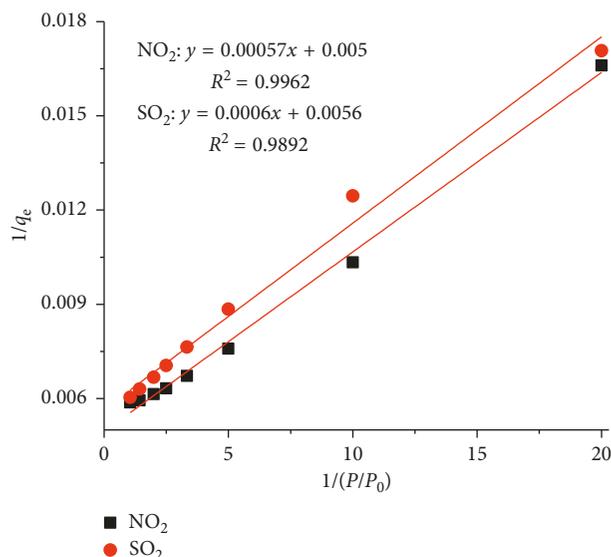


(c)



(d)

FIGURE 7: (a) FT-IR spectra of MgO samples after different adsorption times; (b) quantity of SO<sub>2</sub> adsorbed on MgO; (c) EDX spectrum and SEM image of MgO after 180 min of adsorption; (d) XRD patterns of MgO samples after different adsorption times.

FIGURE 8: Langmuir adsorption isotherm of NO<sub>2</sub> and SO<sub>2</sub> over MgO nanoplates.TABLE 2: NO<sub>2</sub> and SO<sub>2</sub> adsorption capacity of MgO nanoplates compares with well-known adsorbents.

Adsorbent	Experimental condition	Adsorption time (min)	Saturated adsorption capacity (mg/g)		Reference
			NO <sub>2</sub>	SO <sub>2</sub>	
Porous media prepared from sewage sludge ( $S_{\text{BET}} = 21.2 \text{ m}^2/\text{g}$ )	(i) Concentration: NO <sub>2</sub> : 70 ppm (0.007%) in nitrogen SO <sub>2</sub> : 100 ppm (0.01%) in nitrogen	70 (NO <sub>2</sub> ); 100 (SO <sub>2</sub> )	1.12	0.98	[36]
	(ii) Moisture: 0%		(0.0244 mmol/g)	(0.0214 mmol/g)	
Zeolite-coated porous media ( $S_{\text{BET}} = 13.1 \text{ m}^2/\text{g}$ )	(iii) Adsorbent weight: 0.55 g	40 (NO <sub>2</sub> ); 65 (SO <sub>2</sub> )	2.08	1.72	[36]
	(iv) Gas flow rate: 17000 ml/min (v) Temperature: 25°C		(0.0451 mmol/g)	(0.0374 mmol/g)	
Activated carbon ( $S_{\text{BET}} = 1077 \text{ m}^2/\text{g}$ )	(i) Concentration: NO <sub>2</sub> : 4856 ppm (0.4856%) in nitrogen SO <sub>2</sub> : 1170 ppm (0.1170%) in nitrogen (relative pressure: 2.47)	60	135.70	42.10 (2.73 wt.%)	[37]
	(ii) Moisture: 0%		(2.95 mmol/g)		
MgO nanoplates ( $S_{\text{BET}} = 126 \text{ m}^2/\text{g}$ )	(iii) Adsorbent weight: 1.5 g	180	174.00	160.00	This research
	(iv) Gas flow rate: 583 ml/min (v) Temperature: 30°C				
MgO nanoplates ( $S_{\text{BET}} = 126 \text{ m}^2/\text{g}$ )	(i) Concentration: 5% in nitrogen	180	174.00	160.00	This research
	(ii) Moisture: 0%				
MgO nanoplates ( $S_{\text{BET}} = 126 \text{ m}^2/\text{g}$ )	(iii) Adsorbent weight: 0.1 g	180	174.00	160.00	This research
	(iv) Gas flow rate: 50 ml/min (v) Temperature: 25°C				

adsorption time. As shown in Figure 7(b), the amount of SO<sub>2</sub> measured after 10 min reached 95 mg/g<sub>MgO</sub>. After 60 min, the adsorbed SO<sub>2</sub> reached 93% of the maximum capacity (the adsorption equilibrium was achieved after 180 min of adsorption with the uptake value of 160 mg/g<sub>MgO</sub>). The EDX spectrum (Figure 7(c)) confirmed the presence of S on the MgO surface. The content of S element was 6.96 wt.%, corresponding to 13.92 wt.% SO<sub>2</sub> in the sample after 180 min of exposure. The calculated amount of SO<sub>2</sub> was about 162 mg/g<sub>MgO</sub>, similar to the obtained SO<sub>2</sub> adsorption of MgO shown in Figure 7(b). The SEM image (inset in Figure 7(c)) and the XRD patterns (Figure 7(d)) show no

change in morphology as well as the crystalline structure after 180 min of SO<sub>2</sub> exposure compared with the original MgO sample, indicating the high stability of MgO nanoplates under the experimental condition.

The Langmuir model was used to evaluate the adsorption of NO<sub>2</sub> and SO<sub>2</sub> over MgO nanoplates. The Langmuir adsorption isotherm plots of NO<sub>2</sub> and SO<sub>2</sub> adsorption over MgO nanoplates are shown in Figure 8. The  $R^2$  values of 0.9892 (in the case of SO<sub>2</sub>) and 0.9962 (in the case of NO<sub>2</sub>) illustrate the fitness of the Langmuir model for the adsorption. The equilibrium adsorption capacity value ( $q_e$ ) was calculated with the relative pressure ( $p/p_0$ ) value of 1. The  $q_e$

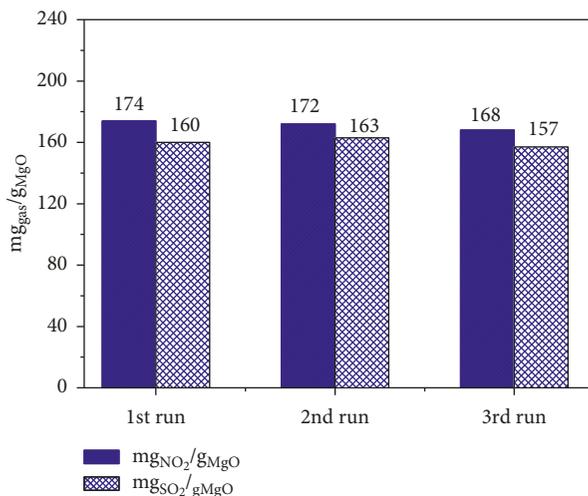


FIGURE 9: Diagram of adsorption capacity of NO<sub>2</sub> and SO<sub>2</sub> over MgO nanoplates after three cycles.

calculated values for the adsorption of NO<sub>2</sub> and SO<sub>2</sub> are 178.52 mg/g and 161.29 mg/g, respectively. These values were similar to the obtained experimental values of 174 mg/g (in the case of NO<sub>2</sub>) and 160 mg/g (in the case of SO<sub>2</sub>). This result shows the compatibility between experimental and theoretical calculations.

Furthermore, the adsorption capacity of NO<sub>2</sub> and SO<sub>2</sub> over MgO nanoplates was compared with that of reported porous adsorbents. The adsorption capacity and experimental conditions of these materials are summarized in Table 2. Interestingly, the MgO nanoplates exhibited relatively higher adsorption capacity than microporous activated carbon and zeolite [36, 37].

In order to evaluate the recycle of MgO nanoplates, this adsorber was regenerated and reused for NO<sub>2</sub> and SO<sub>2</sub> adsorption. The NO<sub>2</sub> and SO<sub>2</sub> adsorption capacity at the third cycle only decreased 3.45 and 1.87%, respectively (Figure 9). The result further confirmed the potential applicability of MgO nanoplates for the adsorption of NO<sub>2</sub> and SO<sub>2</sub>.

#### 4. Conclusions

To summarize, MgO nanoplates were well synthesized by sol-gel and hydrothermal methods using PEG, CTAB, and SDS as the morphology-controlling agents. The MgO nanoplates prepared by the hydrothermal method using SDS surfactant exhibited high specific surface area (126 m<sup>2</sup>/g) and well-defined morphology of nanoplates with the diameter of 40–60 nm and the average thickness of 5 nm. The adsorption experiments showed high NO<sub>2</sub> and SO<sub>2</sub> uptake values on MgO nanoplates (174 mg/g and 160 mg/g, respectively). Moreover, the MgO samples were highly stable under the exposure of NO<sub>2</sub> and SO<sub>2</sub>. These results indicate that MgO is a potential candidate for the adsorption of toxic gases. Further work is ongoing to investigate the adsorption behavior of the material in severe condition. In addition, the kinetic and mechanism of adsorption will be studied for the

future application of MgO nanoplates in toxic gas removal and enhancement of the performance of gas treatment on MgO.

#### Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

#### Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

#### Acknowledgments

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## Research Article

# Preparation of Graphene Nanoplatelets by Thermal Shock Combined with Ball Milling Methods for Fabricating Flame-Retardant Polymers

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Graphene nanoplatelets were successfully prepared from graphite powder by simple and scalable thermal shock combined with ball milling methods. The formation of the graphene nanoplatelets were observed by field-emission scanning electron microscopes and Brunauer–Emmett–Teller methods with the much smaller number of layers and the considerable increase of specific surface area in comparison to the initial expanded graphite material. The other characterizations such as Fourier transform infrared spectroscopy and X-ray powder diffraction methods of graphene nanoplatelets showed unchanged structure. These graphene nanoplatelets were combined with aluminum trihydroxide and zinc borate to prepare flame-retardant polycarbonate plastic and chlorine-sulfonated polyethylene rubber. The prepared composites showed the improvement of flame resistance properties with V0 level according to the UL-94 test method, and the limiting oxygen index value was higher than 27.

## 1. Introduction

Graphene nanoplatelets (Gnps) and their derivatives are potential flame-retardant additives applied for preparation of flame-retardant polymers [1]. It can be combined with polymer matrix as a nanofiller for the case of plastic [1–4], rubber [5, 6], or coating agent for the case of fabric [7–9]. The flame resistance effect of Gnps depends mainly on their dispersity in polymer matrix. Beside the factor of compatibility between Gnps and polymers, the size and layer number of Gnps also play an important role. Gnps can be prepared by two main methods, the bottom-up and top-down methods [10, 11]. The bottom-up methods, such as chemical vapor deposition and epitaxial growth, are expensive and cannot meet the requirement of big quantitative production of Gnps. On the contrary, the top-down methods are expected to meet large-scale production of graphene with low cost. Graphite material can be cracked and exfoliated using a very useful mechanical method reported by Babak Alinejad et al. [10]. This method simply

used NaCl as an exfoliation agent because this salt is harder than graphite. The mixture of graphite powder and NaCl salt particles were grinded by using a planetary ball mill for 2–5 hours to crack graphite flakes to nanosized pieces. In this paper, we apply another simple method to produce Gnps material by using thermal shock combined with ball milling methods. An expanded graphite (EG) is firstly prepared from graphite powder. Next, a planetary ball milling machine is used for EG exfoliation to form Gnps. The ball milling of the EG instead of graphite powder is expected to improve the exfoliation effectiveness. Properties of the obtained Gnps are characterized by fourier transform infrared the spectroscopy (FTIR), X-ray powder diffraction (XRD), field-emission scanning electron microscope (FE-SEM), and Brunauer–Emmett–Teller (BET) methods. The prepared Gnps are used to fabricate the plastic and rubber flame-retardant materials. The obtained flame-retardant materials are measured the fire resistance property by UL-94 and limiting oxygen index (LOI) methods.

## 2. Materials and Methods

**2.1. Chemicals.** Graphite powder (<20  $\mu\text{m}$ , synthetic, Sigma-Aldrich), hydrogen peroxide ( $\text{H}_2\text{O}_2$ , AR, 30–32%, Xilong Scientific), sulfuric acid ( $\text{H}_2\text{SO}_4$ , 98%, AR, Xilong Scientific), sodium chloride (NaCl, AR, 99.5%, Xilong Scientific), aluminum trihydroxide (AR, Xilong Scientific), zinc borate (99%, Kayseri, Turkey), polycarbonate plastic (Lotte Chemicals, Korea), and chlorine-sulfonated polyethylene rubber (CSM-3304, KunLun Co. Ltd, China) were used.

**2.2. Gnps Preparation.** Gnps were prepared from graphite powder via two steps. In the first step, graphite powder was undergone a thermal treatment. Typically, graphite powder was pretreated by being added to the mixture of  $\text{H}_2\text{O}_2$  (30%): $\text{H}_2\text{SO}_4$  (98%) = 1 : 1.5 (v/v) at 20°C for 2 h. The solid was filtered and washed by DI water to have the pH = 7. The obtained solid was dried at 80°C for 24 h. This solid was thermal shocked by using a microwave at 800 W for 60 s. The solid was subjected to the pretreatment and the thermal shock once again by the same procedure described above to obtain EG sample. In the second step, the EG was grinded by using NaCl salt as discussed in [10]. 5 g EG sample was mixed with NaCl salt (EG : NaCl = 3 : 1 in molar ratio). A planetary ball milling machine (Pulverisette 5) with ball to powder weight ratio of 20 : 1 was used to grind the obtained mixture with a rotational speed of 350 rpm for 2 h in argon inert gas medium. NaCl salt was removed from the obtained powder by DI water using an ultrasonic bath. The final sample was centrifuged and dried at 80°C under vacuum to get the final sample.

**2.3. Flame-Retardant Polymers Preparation.** Gnps were used as nanofiller additive for flame-retardant polycarbonate (PC) plastic and chlorine-sulfonated polyethylene (CSPE) rubber preparation. Typically, a mixture of Gnps, conventional flame-retardant aluminum trihydroxide (ATH), and/or zinc borate (ZB) was melt-compounded with PC plastic or CSPE rubber in a Brabender closed mixing machine. PC plastic or CSPE rubber was melted in the first 4 min with a rotor speed of 50 rpm at 200°C (PC) and 85°C (CSPE). The above mixture with different percentage of Gnps, ATH, and/or ZB was then added to the compound with PC plastic or CSPE rubber for 10 min. The compounded sample was hot-pressed in a Brabender molding machine at 210°C (PC) and 95°C (CSPE) for 7 min to obtain the sample.

**2.4. Materials Characterizations.** The FTIR spectra were recorded using an IMPACT-410 (Nicolet, Germany) infrared spectrophotometer at room temperature in the range 4000–400  $\text{cm}^{-1}$  on thin wafer of KBr in which 1% (w/w) of sample was dispersed. XRD diffraction patterns were recorded on a HUT-PCM-Bruker D8 Advance instrument diffractometer system equipped with Ni-filtered Cu Ka radiation (operating at 40 kV; 40 mA; wavelength  $k = 0.154 \text{ nm}$ ). FE-SEM was carried out using a Jeol JSM-7500F instrument. Sample was dried, mounted on a thin plate, and coated by a thin

gold layer before recording. The BET method was measured by ASAP2010 equipment (Micrometrics-USA). The sample was treated in vacuum of 106 mmHg, at 120°C for 4 h and at 350°C for 9 h.

The fire resistance property of flame-retardant PC plastic and CSPE rubber was tested by the UL-94 method on Atlas Electric HVUL-94 flame test station and LOI analysis on a JF-3 instrument according to GB/T 10707-2008 standard.

## 3. Results and Discussion

### 3.1. Characterization of Gnps

**3.1.1. FTIR and XRD Methods.** The FTIR spectra of the graphite and GNPs samples are shown in Figures 1(a) and 1(b), respectively. Both FTIR spectra show the peaks at about 1635  $\text{cm}^{-1}$  and 1450  $\text{cm}^{-1}$  assigned to C=C skeletal band of aromatic domains [12] and the peak at 3430  $\text{cm}^{-1}$  assigned to OH groups [13]. These OH groups may be corresponded to O–H stretching vibrations of adsorbed water molecules and structural OH groups which do not allow a distinction between C–OH and  $\text{H}_2\text{O}$  peaks. In the FTIR spectrum of Gnps sample, there are more peaks at 2975.09  $\text{cm}^{-1}$  assigned to  $\text{CH}_2$  (the symmetric and antisymmetric vibrations of methylene) [14] and peaks at 1089.48 and 1048.86  $\text{cm}^{-1}$  assigned to OH stretching vibrations [15]. This result shows that by the pretreatment process using  $\text{H}_2\text{O}_2$  and  $\text{H}_2\text{SO}_4$ , more OH groups and  $\text{CH}_2$  were formed. The intercalation of OH groups may help improve the ball milling effectiveness.

In addition, there is no considerable change between the XRD patterns of graphite and Gnps samples by using XRD method (Figure 2). There is a peak with high intensity at 2-theta of 26.4° assigned to the layer-by-layer structure of both graphite and Gnps samples [10, 12]. This result shows that by using thermal shock and ball milling, the Gnps sample was formed without structural transformation in comparison to the graphite sample.

**3.1.2. FE-SEM and BET Methods.** The FE-SEM images (Figure 3) show clearly that the structure of Gnps is layer-by-layer assembly. This structure is similar to the initial graphite structure. However, in comparison to the FE-SEM image of the EG sample (Figure 3(a)), the FE-SEM of the Gnps sample (Figures 3(b)–3(d)) shows clearly the exfoliation of EG to obtain Gnps with a monolayer or a few layers in its morphology.

The exfoliation of EG to Gnps is further demonstrated with the increase of specific surface area by BET result that is shown in Figure 4 and Table 1. The similarity of nitrogen adsorption/desorption curves shows the unchanged structure between EG and Gnps samples (Figure 4). The data in Table 1 show that the EG sample obtained by thermal shock has a BET specific surface area of 5.33  $\text{m}^2/\text{g}$ . After the ball milling process of EG mixed with NaCl salt, BET specific surface area of the obtained GNPs is increased to 638.11  $\text{m}^2/\text{g}$  (Table 1). It is 130 times higher in comparison to BET specific surface area of the EG sample and also higher than the reported result (524.4  $\text{m}^2/\text{g}$ ) that used virgin graphite powder for the ball milling [10]. In addition, the pore volume of Gnps sample is decreased to 0.02  $\text{cm}^3/\text{g}$  from 0.04  $\text{cm}^3/\text{g}$  (the pore

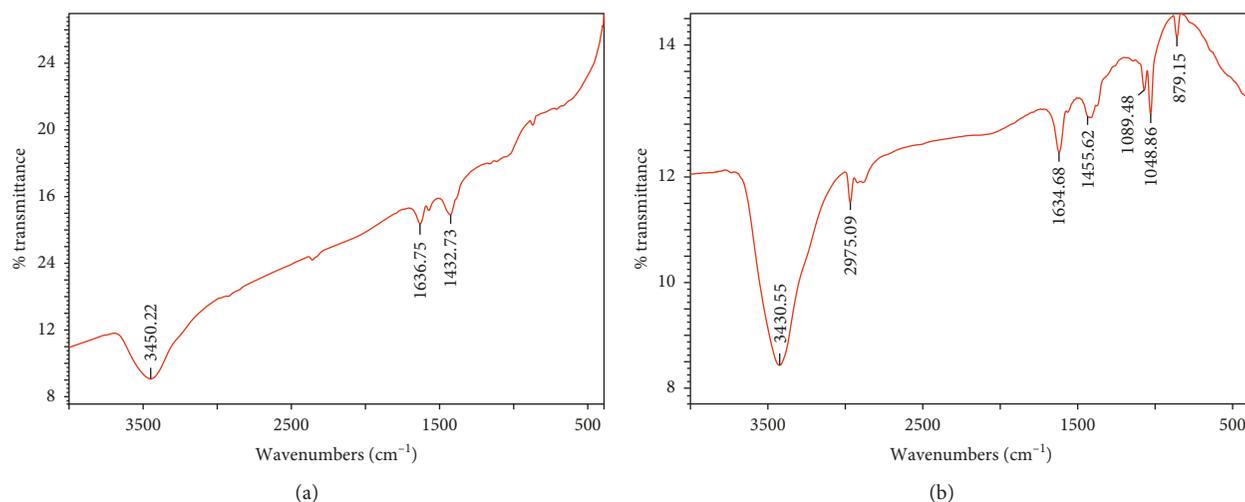


FIGURE 1: FTIR spectra. (a) Graphite sample; (b) Gnps sample.

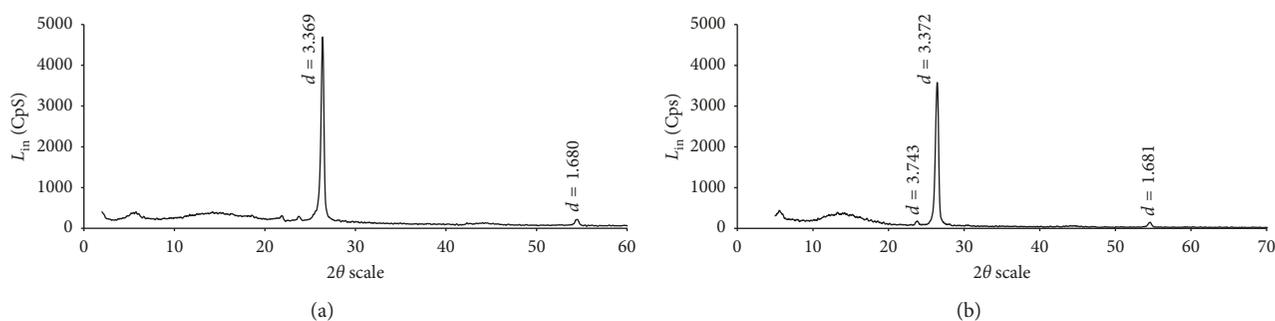


FIGURE 2: XRD patterns. (a) Graphite sample; (b) Gnps sample.

volume of EG sample before the ball milling). This result is in agreement with the FE-SEM result that showed the exfoliation of EG to obtain Gnps material with a few layers.

Gnps have been well known as an effective nanofiller flame-retardant additive with only small amount compounded with polymers (<5 wt.%) [1]. However, to improve the self-extinguishing property of polymers, it is better to use Gnps combined with conventional flame retardants. In this study, the ATH and ZB conventional flame retardants were applied. The compositions of the composite samples are shown in Table 2.

The results in Table 2 show that by using the same content (5 wt.%) of graphite and Gnps as nanofillers to PC material, their flame resistance abilities are UL-94 V2 and V1 levels, respectively. This result shows that the Gnps material is better flame retardant than the graphite material. However, at high content of Gnps, it may result in the agglomeration of Gnps and the decrease of the flame resistance ability. The experiments of decreasing Gnps content have been performed. The observed results show that by decreasing Gnps content to 1.5 and 1.0 wt.%, the UL-94 V0 level is attained. The lower content (0.5 wt.%) of Gnps did not show the good result (UL-94 V2 level).

The self-extinguishing property was improved by combining the Gnps material with the ATH and ZB

conventional flame retardants. The ATH and ZB conventional flame retardants were measured to get the UL-94 V1 level of the PC-ATH and PC-ZB composites. The idea is that by adding more Gnps combined with the PC-ATH and/or PC-ZB composites, the Gnps can help improving PC flame resistance ability to the UL-94 V0 level. The obtained results reach the expectation. By adding Gnps 1.5 wt.% combined with ATH (25 wt.%) or ZB (15 wt.%) to PC, the obtained composites attain the UL-94 V0 level. However, the LOIs of these composite samples are lower than 27% (PC-Gnps-ATH: 22.9%; PC-Gnps-ZB: 24.0%). The LOI of 27% is needed for a flame-retardant composite to become a self-extinguishing material [16]. Thus, the LOI of the composite sample was improved by adding Gnps, ATH, and ZB with the measured optimal contents (1.5 wt.% Gnps, 25 wt.% ATH, and 15 wt.% ZB) to the PC plastic. The result shows that the obtained composite sample (PC-Gnps-ATH-ZB) reaches the UL-94 V0 level and LOI of 29.7%. This shows the role of Gnps to increase the LOI of this sample. Besides the fire resistance measurement, the mechanical property of the samples was also evaluated. The result indicates that the flame-retardant PC (PC-Gnps-ATH-ZB sample) has higher tensile strength (39.5 MPa) in comparison to the virgin PC plastic sample (34 MPa). This shows that adding Gnps can enhance the mechanical property of PC plastic [1].

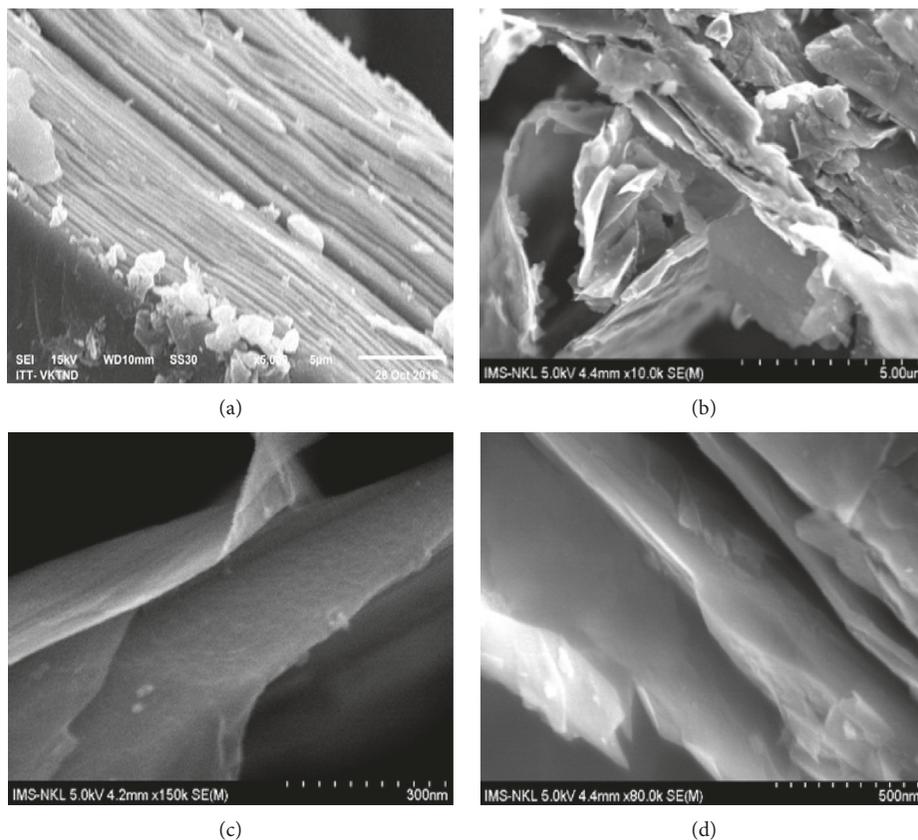


FIGURE 3: FE-SEM images. (a) EG sample; (b–d) Gnps sample.

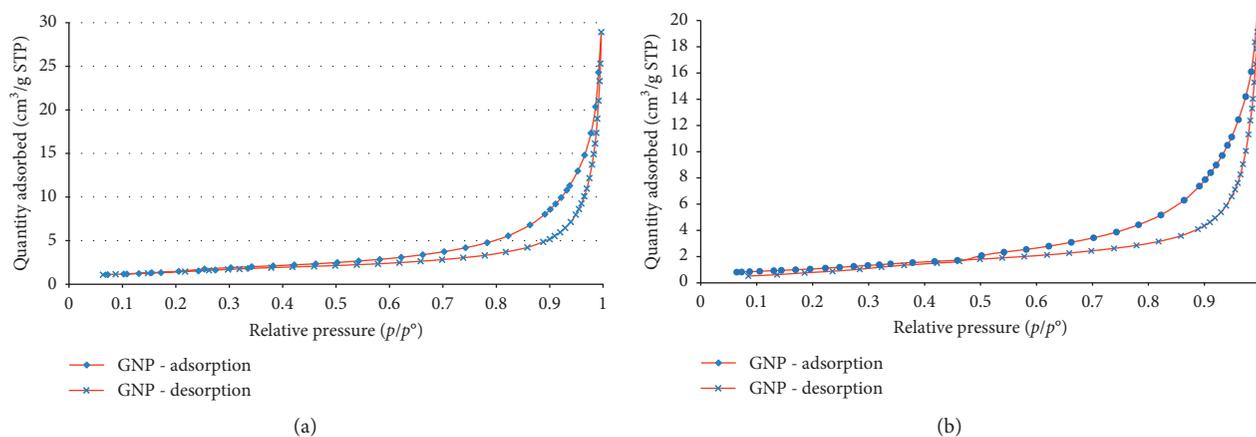


FIGURE 4: Nitrogen adsorption/desorption curves. (a) EG sample; (b) Gnps sample.

TABLE 1: BET data.

Sample	Specific surface area ( $\text{m}^2/\text{g}$ )	Pore volume ( $\text{cm}^3/\text{g}$ )	Pore size (nm)
EG	5.16	0.04	26.58
Gnps	638.11	0.02	27.36

Fire resistance test result of prepared flame-retardant polymers.

Another CSPE rubber polymer was used to illustrate the flame resistance effectiveness of Gnps. ZB has been well known as flame-retardant filler for rubber [17, 18]. The contents

of Gnps (1.0 wt.%) and ZB (15 wt.%) were measured to add to CSPE rubber. The result in Table 2 shows that both the CSPE-Gnps and CSPE-ZB composites attain the UL-94 V1 level. In addition, by combining Gnps and ZB with the contents mentioned above, the CSPE-Gnps-ZB composite (84.0-1.0-15.0 wt.%) sample attains the UL-94 V0 level. However, the LOI of this composite sample attains only 23.1%. This LOI has been improved by increasing Gnps content up to 1.5 wt.%, and the LOI of the CSPE-Gnps-ZB composite (83.5-1.5-15.0 wt.%) reaches the value of 28.6%. This result once again shows that Gnps can be used very effectively as flame-

TABLE 2: Effectiveness of Gnps in combination with the ATH and ZB conventional flame retardants.

Polymer	Filler	Content (wt.%)	UL-94 test	LOI (%)	Tensile strength (MPa)
PC	—	0.0	V2	21.1	34.0
	Graphite	5.0	V2	—	—
		5.0	V1	—	—
		2.0	V1	—	—
	Gnps	1.5	V0	—	—
		1.0	V0	—	—
		0.5	V2	—	—
		25.0	V1	—	—
	ATH	20.0	V2	—	—
		15.0	V2	—	—
		15.0	V1	—	—
	ZB	15.0	V1	—	—
		10.0	V2	—	—
	Gnps-ATH	1.5–25.0	V0	22.9	—
	Gnps-ZB	1.5–15.0	V0	24.0	—
Gnps-ATH-ZB	1.5–25.0–15.0	V0	29.7	39.5	
CSPE	—	0.0	V2	22.1	—
	Gnps	1.0	V1	—	—
	ZB	15.0	V1	—	—
	Gnps-ZB	1.0–15.0	V0	23.1	—
1.5–15.0		V0	28.6	—	

retardant additive, especially for increasing the self-extinguishing property of polymer composite by combining with conventional flame retardants.

#### 4. Conclusions

The Gnps material was successfully prepared with the simple and scalable method of thermal shock combined with ball milling. The characterization methods (FTIR, XRD, FE-SEM, and BET) showed that the initial graphite material was exfoliated to obtain the Gnps material with few layer numbers and unchanged structure. The obtained Gnps material was applied as flame retardant for PC plastic and CSPE rubber. The results obtained by UL-94 and LOI measurement methods showed that by combining the Gnps material with ATH and ZB with suitable content, the PC-Gnps-ATH-ZB and CSPE-Gnps-ZB composite materials can be prepared with highest fire resistance properties (UL-94 V0 level and LOI is higher than 27%). The results also showed that Gnps have important role in improving the LOI of composite material with small added amount (1.5 wt.%).

#### Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

#### Conflicts of Interest

The authors declare that they have no conflicts of interest.

#### Acknowledgments

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## Research Article

# A Facile Synthesis, Characterization, and Photocatalytic Activity of Magnesium Ferrite Nanoparticles via the Solution Combustion Method

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In this study, we adopted the solution combustion method to synthesize magnesium ferrite ( $\text{MgFe}_2\text{O}_4$ ) using urea as the fuel. Various techniques including TGA, XRD, SEM, TEM, FTIR, UV-Vis DRS, and EDS were employed to characterize the synthesized  $\text{MgFe}_2\text{O}_4$  nanoparticles. The XRD analysis revealed that single-phase  $\text{MgFe}_2\text{O}_4$  was formed at a calcination temperature of at 500–600°C for 3 hours in the absence of an intermediate phase. TEM analysis also revealed the formation of monodisperse magnesium ferrite nanoparticles, averaged at 30 nm in size. The photocatalytic activity of the synthesized  $\text{MgFe}_2\text{O}_4$  nanoparticles against methylene blue dye under visible light was investigated, showing the efficiency of 89.73% after 240 minutes of light irradiation with the presence of  $\text{H}_2\text{O}_2$ .

## 1. Introduction

Ferrite nanoparticles,  $\text{MFe}_2\text{O}_4$  where M is any divalent metal ions such as Mg, Mn, Ni, Co, Fe, Cu, etc, find wide applications in several fields [1]. Depending on the area of application, ferrite nanoparticles need to exhibit distinct characteristics. For example, in order to be suitable as an absorbent for decontamination of wastewater, ferrites should have exceptional chemical reactivity, adsorption capacity, and most importantly, reasonable  $M_s$  value, which is critical for magnetic recovery of the adsorbent from the aqueous solution [2]. The choice of synthesis method should also be considered when it comes to exploring the mechanism of formation of ferrite properties. To be specific, the distribution of metallic ions among

crystallographic lattice sites, which defines the characteristics of the materials, largely depends on the synthesis method. This effectively makes the method selection crucial when it comes to adapting the materials to the needs of application [1, 3, 4].

Usually, the maximum band gap energy of ferrites is approximately 2 eV, allowing the materials to effectively absorb visible light [5]. Furthermore, advantageous magnetic properties also offer ferrites useful applications [6]. Both forms of ferrites, in individual photocatalysts or in combination with others, are accentuated in literature for being separable and reusable from the reaction mixture [5, 7]. One of the typical uses of ferrites is as visible light photocatalysts for the degradation of pollutants in water and wastewater [7–10]. This capability of ferrite catalysts is

possible due to effective utilization of light energy, which in turn allows formation of  $e^-/h^+$  pairs on the photocatalytic surface. The  $e^-/h^+$  pairs, owing to their susceptibility to oxidation and reduction, play an important role in formation of reactive oxygen species, such as  $\cdot\text{OH}$  and  $\text{O}_2^{\cdot-}$ , consequently promoting the decomposition of pollutants. Previous studies also suggested the addition of oxidants such as  $\text{H}_2\text{O}_2$  into the reaction to create a Fenton-type system [6, 8, 11, 12] aiding the degradation through formation of hydroxyl radicals.

Among magnetic ferrites, magnesium ferrite ( $\text{MgFe}_2\text{O}_4$ ) is a typical inverse spinel, where  $\text{Fe}^{3+}$  ions are located in the tetrahedral (A) and octahedral (B) sites and  $\text{Mg}^{2+}$  ions are located in octahedral sites only [13]. The application of magnesium ferrite is diverse ranging from that in high-density recording media [14] to that in the fields of heterogeneous catalysis [7, 15–17], adsorption [18–20], anode material [21], cancer cure [22], and sensors [23]. In addition, the material is also a soft magnetic n-type semiconducting materials with a narrow band gap (1.9 eV) [24].

Methods devised for preparation of magnesium ferrite nanocrystallites included the coprecipitation method [19, 25–28], sol-gel method [20, 29], combustion method [30, 31], hydrothermal method [32], thermal decomposition method [33], and solvothermal method [34]. Among the methods used to synthesize ferrite nanoparticles, the solution combustion synthesis is favored for its simplicity, short reaction time, and low annealing temperature [35]. These advantages have made resulting ferrites to have fine particle size, reduced impurities, and improved physical properties [36]. In the combustion reaction, the fuels play the role of forming complexes with metal cations [35]. Frequently used fuels in previous studies included glycine, urea, citric acid, and EDTA (ethylene diammin tetraacetic acid). In this work,  $\text{MgFe}_2\text{O}_4$  nanoparticles are prepared by the solution combustion method with urea as fuel. The structural, chemical composition, thermal, morphology, and photocatalytic activity of  $\text{MgFe}_2\text{O}_4$  nanoparticles are investigated.

## 2. Materials and Method

**2.1. Materials.** All chemicals including magnesium nitrate hexahydrate ( $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ), iron nitrate nonahydrate ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ), urea ( $\text{CH}_4\text{N}_2\text{O}$ ), and methylene blue ( $\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}$ ) were obtained from Merck and used as received.

**2.2. Preparation of  $\text{MgFe}_2\text{O}_4$  Nanoparticles.** The combustion preparation of  $\text{MgFe}_2\text{O}_4$  with urea fuel in this study is described as follows. First, urea was dissolved in water, followed by an appropriate amount of magnesium nitrate hexahydrate and iron nitrate nonahydrate following the mole ratio for  $\text{Mg}(\text{II})/\text{Fe}(\text{III})$  of 1 : 2 under vigorous stirring to form a mixed solution. Afterwards, the mixed solution was further stirred for 4 hours until gel was formed. The gel was then dried in an oven at  $80^\circ\text{C}$  for 10 hours. Finally, the precipitate was calcined at  $500\text{--}800^\circ\text{C}$  for 3 hours with a heating rate of  $5^\circ\text{C}\cdot\text{min}^{-1}$  [37].

**2.3. Characterizations.** The gel precursor was studied for its thermal decomposition behavior through thermogravimetry (TG) and differential thermal analysis (DTA) on a Labsys Evo S60/58988 instrument (Setaram, France) in the temperature range of  $30\text{--}800^\circ\text{C}$  with the heating rate of  $10^\circ\text{C}\cdot\text{min}^{-1}$ . The phase of the obtained powder was characterized by X-ray diffraction (XRD) using a D8 Advance diffractometer (Bruker, Madison, WI, USA) with  $\text{CuK}_\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) in a  $2\theta$  angle ranging from  $20^\circ$  to  $70^\circ$  with a step of  $0.03^\circ$ . The crystallite size of spinel (D) was determined by Scherrer formula:

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (1)$$

where  $\lambda$ ,  $k$ ,  $\beta$ , and  $\theta$  are the X-ray wavelength (0.1504 nm), Scherrer constant (0.89), the full width at half maximum measured in radians, and the angle of diffraction of the (311) peak with the highest intensity, respectively. The morphological properties were analyzed by two techniques including scanning electron microscopy (SEM, Hitachi S-4800, Japan) and transmission electron microscopy (TEM, JEOL-JEM-1010, Japan). For sample composition, energy dispersive X-ray spectroscopy (EDX, JEOL JED 2300 Analysis Station, Japan) was employed. The spinel structure is confirmed for formation by Fourier transform infrared spectroscopy (FTIR Affinity-1S, Shimadzu, Japan). The optical absorption spectra were recorded by UV-Vis absorption spectrometer (U-4100, Hitachi, Japan).

**2.4. Photocatalytic Degradation of Methylene Blue.** The conditions in which experiments are conducted include room temperature, pH of approximately 7 for methylene blue (MB), and continuous circulation mode. Prior to the photocatalytic reaction, the adsorption/desorption equilibrium of the aqueous solution containing the suspension was achieved by stirring in dark environment for 30 mins. 50 mg of  $\text{MgFe}_2\text{O}_4$  was dispersed into 100 mL of MB aqueous solution ( $10 \text{ mg}\cdot\text{L}^{-1}$ ). Subsequently,  $\text{H}_2\text{O}_2$  was introduced and irradiation on the suspension followed immediately using 40 W Compact lamps, Philips. The photocatalytic efficiency of MB ( $H$ ) was calculated using the following equation:

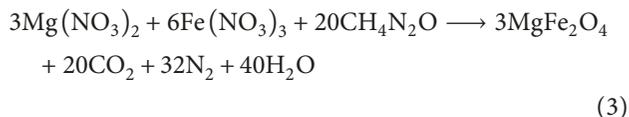
$$H = \frac{C_0 - C_t}{C_0} \times 100\%, \quad (2)$$

where  $C_0$  is the concentration of MB ( $\text{mg}\cdot\text{L}^{-1}$ ). The subscripts 0 and  $t$  denote time points where concentration was measured, at initial equilibrium (0) and after  $t$  irradiation time, respectively. Concentration was measured by an ultraviolet-visible spectrophotometer (UV-1700 Shimadzu, Japan) with a wavelength of 664 nm.

## 3. Results and Discussion

**3.1. Structural Characterization.** In the precursor, urea is not only to provide sufficient heat for the system but also to ensure the formation of stable complexes with the metal ions to increase their solubility and prevent selective precipitation of

metal ions during water removal. The reaction for metal nitrate mixture using urea as the fuel assuming complete combustion can be represented by the following equation [38]:



The TG/DTA of the ferrite precursor are shown in Figure 1(a). It can be observed that there are two exothermal peaks at 137.86°C and 437.04°C. The exothermal peak at 137.86°C has suggested self-combustion, like a process in which the nitrate ions act as an oxidizing agent and urea as fuel. The maximum exothermal peak at 437.04°C could be observed to closely follow a substantial mass loss in the temperature range of 200–450°C, evidencing the occurrence of the decomposition reaction of the ferrite precursor and nitrate. Approximately, the total mass loss that precedes the sharp exothermal reaction is 81.04%, which is consistent with the theoretical result (80.31%). This could be attributable to the relief of gases  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , and  $\text{N}_2$  from the precursor. At temperature higher than 450°C, the weight of the sample remained almost constant. Therefore, the calcining temperature of the samples was selected in the range from 500 to 800°C.

Figure 1(b) displays the FTIR spectra of the  $\text{MgFe}_2\text{O}_4$  precursor and two calcined samples at 500 and 600°C relative to the range of 4000–400  $\text{cm}^{-1}$ . For the precursor sample, three broad absorption bands were observed at approximately 3446, 1656, and 1384  $\text{cm}^{-1}$ , respectively, corresponding to the presence of hydroxyl groups (-OH), the stretching vibration of the carboxyl group, and the presence of  $\text{NO}_3^-$  ions [29]. In the two spectra of the  $\text{MgFe}_2\text{O}_4$  calcined at 500–600°C, two bands at 582 and 586  $\text{cm}^{-1}$  and two bands at 443 and 445  $\text{cm}^{-1}$  could be pairwise indexed to the stretching vibrations of metal-oxygen bonds in tetrahedron sites and in octahedron sites, respectively, suggesting the formation of magnesium ferrite [15, 20]. In addition, the absorption broad bands at 3450 and 3425  $\text{cm}^{-1}$  are, respectively, indicative of the stretching mode of  $\text{H}_2\text{O}$  molecules and hydroxyl groups, and in turn, the presence of  $\text{H}_2\text{O}$  molecules on the surface of  $\text{MgFe}_2\text{O}_4$  nanoparticles [24].

Figure 2 displays different X-ray diffraction patterns of  $\text{MgFe}_2\text{O}_4$  nanoparticles with temperature varying from 500 to 800°C. The two ferrite samples calcined at 500–600°C were obtained as single spinel phase with peaks at 220, 311, 400, 511, and 440, corresponding to the cubic spinel structure (JCPDS card. no. 01-071-1232) [26]. It is showed that the increase in temperature is associated with the improvement of  $\text{MgFe}_2\text{O}_4$  powders. However, from 700 to 800°C, new phases of  $\alpha\text{-Fe}_2\text{O}_3$  were observed. The spinel phase of  $\text{MgFe}_2\text{O}_4$  was confirmed by five XRD peaks at 220, 311, 400, 511, and 440 crystal planes. Results reported in Table 1 also indicate that the crystallite size of  $\text{MgFe}_2\text{O}_4$  was positively associated with the calcination temperature. As temperature moved from 500 to 800°C with 100°C interval, the average crystallite size was expanded from 18 to 61 nm. For the “a” lattice parameter, XRD spectra showed that for  $\text{MgFe}_2\text{O}_4$  nanoparticles, the value fell in the range of 8.344–8.378 Å.

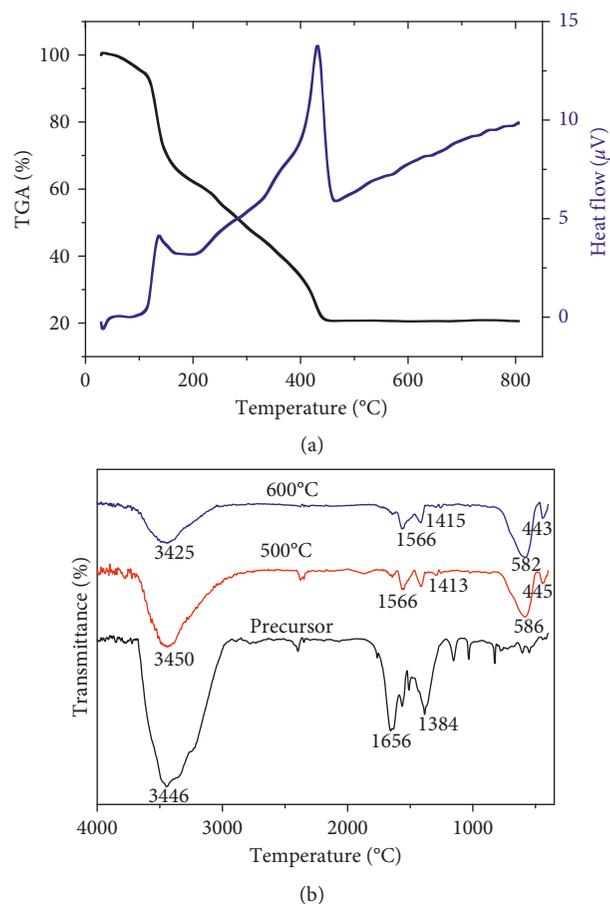


FIGURE 1: TGA/DTA curve of the precursor (a) and FT-IR spectra of the precursor and  $\text{MgFe}_2\text{O}_4$  calcined samples at 500–600°C (b).

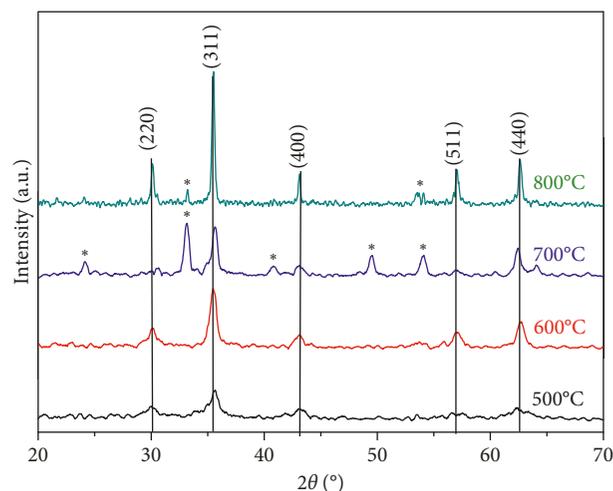
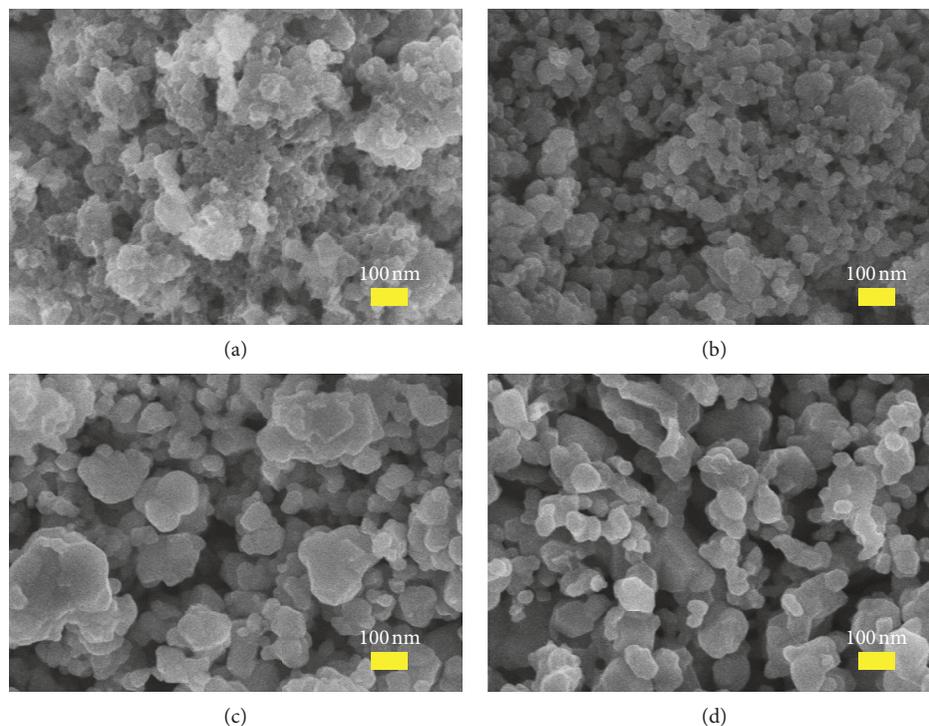


FIGURE 2: X-ray diffraction of  $\text{MgFe}_2\text{O}_4$  calcined samples from 500°C to 800°C.

The SEM images of different samples of  $\text{MgFe}_2\text{O}_4$  nanoparticles corresponding to four calcination temperature points of 500°C, 600°C, 700°C, and 800°C are shown in Figures 3(a)–3(d). Visually, the images showed consistent implication with the XRD results. To be specific,

TABLE 1: Average crystallite size, lattice parameter, and unit cell volume of the samples at different calcination temperatures.

$t_c$ (°C)	Average crystallite size (nm)	Lattice constant $a$ (Å)	Cell volume $V$ (Å <sup>3</sup> )
500	18	8.348	581.76
600	24	8.378	588.06
700	28	8.344	581.06
800	61	8.367	585.75

FIGURE 3: SEM of  $\text{MgFe}_2\text{O}_4$  calcined samples at 500°C (a), 600°C (b), 700°C (c), and 800°C (d).

particle size of the prepared samples were found to be proportionally increasing with temperature. This could possibly be due to the aggregation and coalescence during desiccation.

The TEM image of  $\text{MgFe}_2\text{O}_4$  synthesized at 500°C is presented in Figure 4(a). Evidently, the magnesium ferrite nanoparticles resulted from the solution combustion method were uniform in terms of morphology and crystallite size and reached the particle size of approximately 30 nm.

Figure 4(b) shows chemical purities and elemental composition of the  $\text{MgFe}_2\text{O}_4$  materials produced by energy dispersive X-ray analysis (EDX). The existence of Mg, O, and Fe was determined by their corresponding peaks and the absence of other characteristic peaks. On the contrary, the synthesized sample was pure and did not contain any other elements.

The UV-Visible absorption spectrum was obtained to investigate the optical properties of magnesium ferrite calcined at 500–600°C as shown in Figure 5. By using the Kubelka–Munk equation, the band gap of  $\text{MgFe}_2\text{O}_4$  samples was determined from reflectance spectra via conversion to absorbance [39]. The band gap energy  $E_g$

(eV) of the synthesized photocatalyst is calculated by the following equation:

$$E_g = \frac{h \cdot c}{\lambda_{\max}} = \frac{1240}{\lambda_{\max}}, \quad (4)$$

where  $h$ ,  $c$ , and  $\lambda_{\max}$  are the Planck constant ( $6.62 \cdot 10^{-34} \text{ J} \cdot \text{s} \cdot \text{photon}^{-1}$ ), the speed of light ( $3 \cdot 10^8 \text{ m} \cdot \text{s}^{-1}$ ), and the wavelength at the absorption edge (nm), respectively [40]. At wavelengths 500 and 600°C,  $\lambda_{\max}$  of the samples was calculated to be 679 nm and 687 nm, respectively. Therefore, the calculated band gap energy values are 1.83 eV and 1.81 eV for the  $\text{MgFe}_2\text{O}_4$  samples calcined at 500°C and 600°C, respectively.

**3.2. Photocatalytic Activity of Magnesium Ferrite Nanoparticles.** Nanoparticles of the  $\text{MgFe}_2\text{O}_4$  were tested for catalytic activities by performing photo-Fenton-like degradation of MB. Figures 6(a)–6(e) show different UV-Visible spectra of MB with  $\text{MgFe}_2\text{O}_4$  photocatalyst corresponding to varying conditions including the calcination temperature of the absorbent, availability of  $\text{H}_2\text{O}_2$ , and presence of light irradiation.

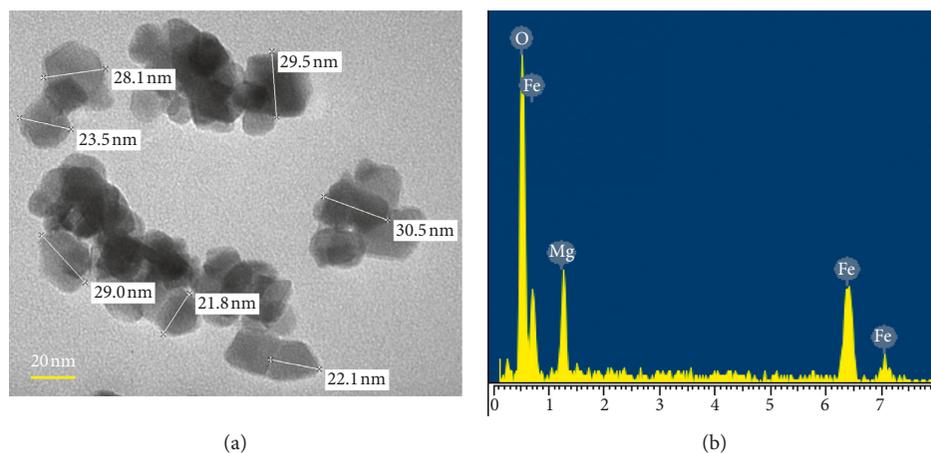


FIGURE 4: TEM and EDS of  $\text{MgFe}_2\text{O}_4$  calcined sample at  $500^\circ\text{C}$ .

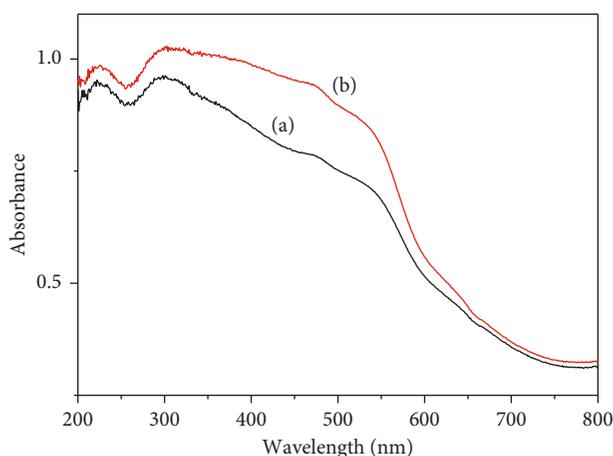


FIGURE 5: The UV-Vis diffuse reflectance spectra of  $\text{MgFe}_2\text{O}_4$  calcined at  $500\text{--}600^\circ\text{C}$ .

The presence of methylene blue is indicated by the two absorption peaks at 609 nm and 664 nm [7]. It is visibly observed that the color of the MB solution gradually changed from blue to light blue and finally to colorless, which is presumably due to the estrangement of the chromophoric group. In the first two spectra where  $\text{H}_2\text{O}_2$  was absent, MB degradation efficiency reached 6.51% (in the dark) and 31.73% (under light irradiation) after 240 minutes, suggesting the positive influence of light on the degradation efficiency. In comparison with the first spectrum, the third spectrum involved the introduction of  $\text{H}_2\text{O}_2$ , showing a significantly higher efficiency at 35.48%. The last two spectra demonstrated the effect of calcination temperature with the presence of  $\text{H}_2\text{O}_2$  and light irradiation. The measured efficiencies were 89.73% and 69.17% corresponding to  $\text{MgFe}_2\text{O}_4$  calcined at  $500^\circ\text{C}$  and  $600^\circ\text{C}$ , respectively, significant and proportional decline of peak intensity with respect to irradiation time was also recognized in these two spectra. These results suggested that light irradiation, ferrite catalyst, and  $\text{H}_2\text{O}_2$  were all required for efficient photo-Fenton degradation of MB dye. Similar results have been

reported for  $\text{NiFe}_2\text{O}_4$  nanoparticles and  $\text{CuFe}_2\text{O}_4$  spheres by various studies [11, 41].

Thus, it is possible to affirm that the main factors for the photodegradation of methylene blue are the crystallite size and the surface area of the  $\text{MgFe}_2\text{O}_4$  nanoparticles. The particle size of the calcined sample at  $500^\circ\text{C}$  is smaller than that of the calcined sample at  $600^\circ\text{C}$ . Therefore, the photocatalytic activity of the sample at  $500^\circ\text{C}$  is higher than that of the calcined sample at  $600^\circ\text{C}$ . This effect was also observed in the case of the methylene blue degradation in the presence of the copper ferrite nanopowders [42] and in the presence of coating titania-silica on cobalt ferrite nanoparticles [43].

A pseudo-first-order kinetic model was adopted to describe the degradation process in the heterogeneous Fenton/photo-Fenton catalysis system [11, 44, 45]. Figure 6(f) plots  $\ln(C_0/C_t)$  versus irradiation time ( $t$ ) for the  $\text{MgFe}_2\text{O}_4$  sample, showing an approximated linear relationship between the two variables. This indicates that the photodegradation of MB follows a pseudo-first-order reaction. Calculation of linear slopes revealed that the rate constant

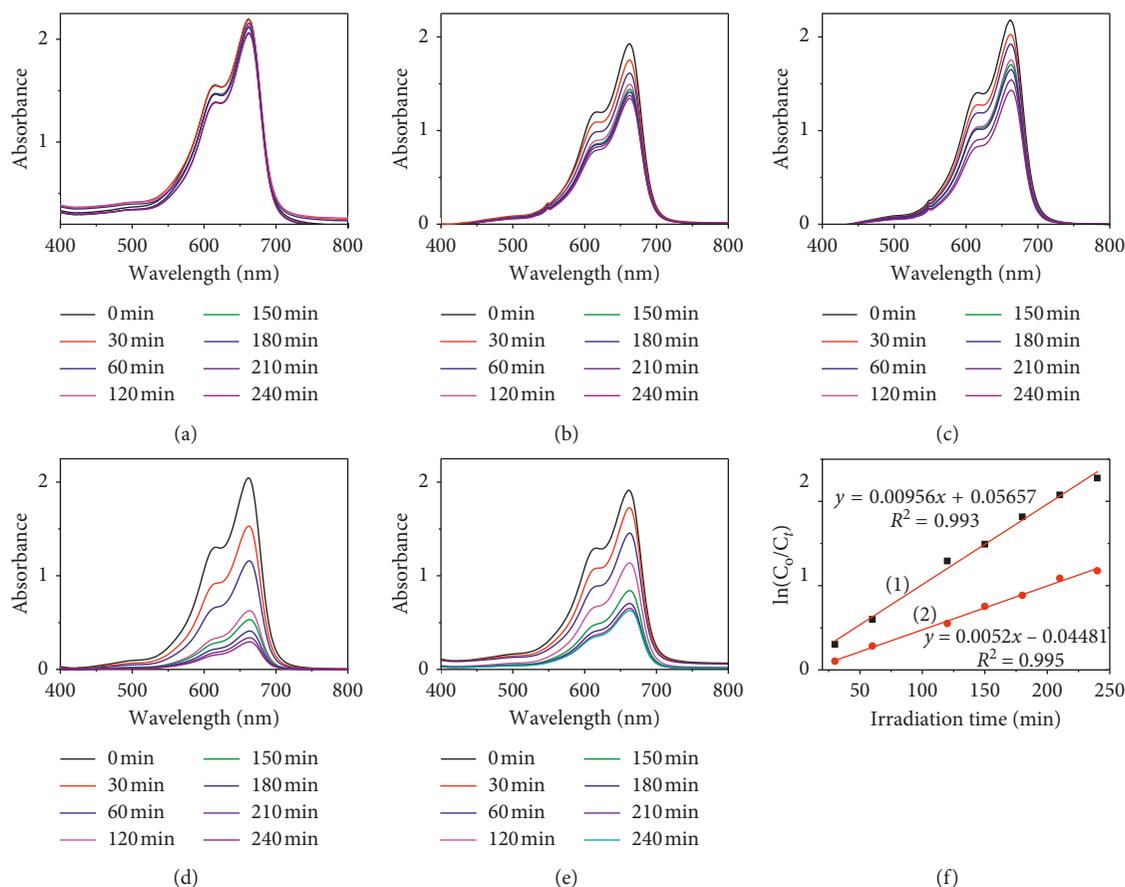


FIGURE 6: UV-Visible spectra of MB in different conditions and calcination temperatures of  $\text{MgFe}_2\text{O}_4$  catalyst: (a)  $500^\circ\text{C}$  + dark, (b)  $500^\circ\text{C}$  + light, (c)  $500^\circ\text{C}$  +  $\text{H}_2\text{O}_2$  + dark, (d)  $500^\circ\text{C}$  +  $\text{H}_2\text{O}_2$  + light, (e)  $600^\circ\text{C}$  +  $\text{H}_2\text{O}_2$  + light, and (f) the plots of  $\ln(C_0/C_t)$  versus irradiation time ( $t$ ) in the presence of  $\text{MgFe}_2\text{O}_4$  calcined samples at  $500^\circ\text{C}$  (1) and  $600^\circ\text{C}$  (2).

( $k$ ) for the  $\text{MgFe}_2\text{O}_4$  samples calcined at  $500^\circ\text{C}$  and  $600^\circ\text{C}$  were  $0.00956 \text{ min}^{-1}$  and  $0.0052 \text{ min}^{-1}$ , respectively.

#### 4. Conclusions

We have successfully synthesized  $\text{MgFe}_2\text{O}_4$  nanoparticles using the solution combustion method with urea as fuel. The particle size of prepared samples was showed to be proportional with rising temperature. Phase-pure  $\text{MgFe}_2\text{O}_4$  nanoparticles were obtained at  $500\text{--}600^\circ\text{C}$  for 3 h with the size about 30 nm. UV-Vis also approximated the band gap which ranged from 1.81 to 1.83 eV. The present study also highlighted the role of  $\text{MgFe}_2\text{O}_4$  in the degradation (89.73% in 240 minutes) of MB dye, suggesting possible applications of the ferrite for photo-Fenton activity in decontamination of wastewater. Kinetics describing the photodegradation process of two samples calcined at  $500^\circ\text{C}$  and  $600^\circ\text{C}$  also revealed that the reaction adhered to pseudo-first order with a rate constant ( $k$ ) of  $0.00956 \text{ min}^{-1}$  and  $0.0052 \text{ min}^{-1}$ , respectively.

#### Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

#### Conflicts of Interest

The authors declare that they have no conflicts of interest.

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## Research Article

# Novel Removal of Diazinon Pesticide by Adsorption and Photocatalytic Degradation of Visible Light-Driven Fe-TiO<sub>2</sub>/Bent-Fe Photocatalyst

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In the study, Fe was used as a dopant to enhance photocatalytic activity of TiO<sub>2</sub>. Then, the Fe-doped TiO<sub>2</sub> was deposited on bentonite, which was pillared by Fe. The synthesized materials were characterized by SEM, XRD, UV-Vis, BET, and point of zero charge (pH<sub>PZC</sub>). Then, the synthesized materials were used for diazinon removal under both dark and visible light conditions to investigate adsorption and photocatalytic degradation abilities of the synthesized materials. The maximum diazinon adsorption capacity of the synthesized Fe-TiO<sub>2</sub>/Bent-Fe was 27.03 mg/g. The obtained results indicated that the Fe-TiO<sub>2</sub>/Bent-Fe exhibited high photocatalytic degradation activity for removal of diazinon even under visible light. The diazinon removal experiments were also conducted using different photocatalyst dosages, under different pH and light sources to figure the optimal conditions for removal processes. The obtained results indicated that optimal photocatalyst dosage and pH were 0.5 g/L and 4.5, respectively. Finally, the natural light generated from solar could be suitable used for diazinon removal by the synthesized Fe-TiO<sub>2</sub>/Bent-Fe.

## 1. Introduction

Many kinds of pesticides releasing into the environment as a result of runoff from agricultural and urban areas cause pollution of soil, air, surface water, and groundwater and are harmful for the human health [1, 2]. Among them, diazinon (*O*, *O*-diethyl *O*-[6-methyl-2-(1-methylethyl)-4-pyrimidinyl] phosphorothioate), an organophosphorus and highly toxic pesticide, is extensively used to control insects and, just in the USA, 6 million pounds of the pesticide are annually used on farming sites [3]. The diazinon has been classified as moderately hazardous class II chemical to humans, aquatics,

mammals, and other species by the World Health Organization (WHO). Shemer and Linden reported that the fatal human doses of diazinon were in the range from 90 to 444 mg·kg<sup>-1</sup> [4]. Kouloumbos et al. reported that toxic effects of the pesticide attributed to its inhibition of the enzyme acetylcholinesterase affecting the nervous system [5]. Therefore, water systems contaminated with diazinon have been treated by various techniques such as adsorption, filtration, membrane separation, biodegradation, oxidation, and chemical coagulation [6]. However, these methods have several certain disadvantages including incomplete removal, high consumption of chemicals, time consuming, and high treatment cost.

Recently, advanced oxidation processes (AOPs), using heterogeneous photocatalysts to produce hydroxyl radicals ( $\cdot\text{OH}$ ), a strong oxidative agent, to totally promote mineralization of organic pollutants into harmless substances such as  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , could be a potential technology for removal of diazinon [7–9]. Titanium oxide ( $\text{TiO}_2$ ) is regarded as the most suitable photocatalyst for the degradation of organic pollutants from wastewaters because of its chemical stability, nontoxicity, low cost, and commercial availability [10–12]. However, because of wide band gap of  $\text{TiO}_2$ , which is approximately 3.2 eV, the photocatalyst could only be activated by UV irradiation, which only accounts for 3–4% of the solar spectrum [13, 14]. The high-energy consumption and safety issues concerning use of UV irradiation are the main disadvantages of  $\text{TiO}_2$  in the practical system. In addition, the fast recombination of the photoexcited electrons and holes is also another disadvantage of the  $\text{TiO}_2$  photocatalyst. Hence, numerous studies have been conducted to effectively enhance the photocatalytic activity of  $\text{TiO}_2$  and to expand its applications in practical systems using visible light or the solar energy as the excitation source [15–21]. Among these, metals have been used as doping agents to implant or incorporate into the  $\text{TiO}_2$  lattice to narrow the band gap of the photocatalyst, thereby enhancing its photocatalytic activity [22–27]. The overlap between d orbital of the substituted metal and d orbital of titanium could narrow band gap or facilitate the visible light absorption of the doped  $\text{TiO}_2$ , leading to its photocatalytic enhancement [28]. Therefore, the first aim of the study is to use Fe as dopant to enhance photocatalytic activity of  $\text{TiO}_2$  to utilize visible light as excitation sources for its photocatalytic removal of diazinon.

In addition, it is difficult to recover powder photocatalysts after being used in practical system for wastewater treatment. Moreover, the photocatalytic activity of a certain photocatalyst strongly depends on its adsorption capacity [29]. Various materials including activated carbon, glass fiber, polyurethane, silica, alumina, and bentonite have been used as supports to fix photocatalysts to overcome such limitations. In the study, bentonite, which is nontoxic, porous, economical, easily available in our country (Vietnam), and also chemically and mechanically stable, was used as support materials for Fe-doped  $\text{TiO}_2$  ( $\text{Fe-TiO}_2$ ). However, the surface area of the natural bentonite is quite small. Many studies reported that the introduction of the inorganic pillars into bentonite could increase its surface area, pore volume, microporosity, and thermal stability [30–32]. Therefore, the study used Fe as a pillar to increase surface area as well as pore volume of the bentonite before being used as support for the  $\text{Fe-TiO}_2$ . Thus, the Fe-doped  $\text{TiO}_2$  supported on bentonite pillared Fe ( $\text{Fe-TiO}_2/\text{Bent-Fe}$ ) would have high photocatalytic activity and adsorption capacity for removal of diazinon.

## 2. Experimental

**2.1. Material Preparation.** First, 10 g bentonite was saturated with  $\text{Fe}^{3+}$  in 100 mL of 1 M solution of  $\text{FeCl}_3$  under constant stirring. The obtained suspension was continuously stirred at

room temperature for 24 h. The resulting product was centrifuged and washed by distilled water until chloride free (tested by  $\text{AgNO}_3$ ). The obtained material was dried at 363 K for 12 h and then milled to get bentonite-pillared Fe ( $\text{Bent-Fe}$ ). Then, the obtained  $\text{Bent-Fe}$  was swelled in pure ethanol solution with weight ratio of 2%. Second, 6 mL tetra isopropyl orthotitanate (TIOT) was slowly dropped into 34 mL ethanol to get a solution “A” while 48.2 mg  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  was diluted in a solution containing 17 mL ethanol, 0.4 mL  $\text{HNO}_3$  (68%), and 1.6 mL distilled water to obtain a solution “B”. Then, the solution “A” was slowly dropped into the solution “B” to get sol  $\text{Fe-TiO}_2$ . Finally, the obtained sol  $\text{Fe-TiO}_2$  was slowly dropped into the swelled  $\text{Bent-Fe}$  with continuously stirring for 4 h and aging for 24 h. The obtained mixture was changed into a Teflon-lined stainless steel autoclave and then heated under 160°C for 6 h. After the autoclave was cooled to room temperature, the precipitate at the bottom of the autoclave was obtained and washed with ethanol and deionized water several times. The product was dried at 80°C for 24 h to get  $\text{Fe-TiO}_2/\text{Bent-Fe}$ . The weight ratio of ( $\text{Fe-TiO}_2$ )/( $\text{Bent-Fe}$ ) was 3 : 1.

**2.2. Photocatalyst Characterization.** The surface morphology of the synthesized materials was analyzed using a JED-2300-Analysis Station Plus, JEOL scanning electron microscope (SEM). X-ray diffraction (XRD) spectra of the synthesized  $\text{TiO}_2$ ,  $\text{Fe-TiO}_2$ ,  $\text{Fe-TiO}_2/\text{Bent}$ ,  $\text{Bent-Fe}$ , and  $\text{Fe-TiO}_2/\text{Bent-Fe}$  materials were obtained using a D8-Advance 5005 model with  $\text{Cu-K}\alpha$  ( $\lambda = 1.5406 \text{ \AA}$ ) radiation over the range  $10^\circ < 2\theta < 70^\circ$ , at a scanning rate of 0.03°/min. The optical absorption abilities of the synthesized photocatalysts were characterized by an UV 3101PC spectrophotometer, Shimadzu. The point of zero charge ( $\text{pH}_{\text{PZC}}$ ) of the synthesized material was determined using the procedure as follows: a 50 mL of 0.01 M NaCl were placed into several closed Erlenmeyer flasks and the pH of each flask was adjusted at 3.0, 4.5, 5.6, and 8.0 by adding HCl (0.01 M) or NaOH (0.01 M). Then, 0.2 g  $\text{Fe-TiO}_2/\text{Bent-Fe}$  was added to each flask. The  $\text{pH}_{\text{PZC}}$  is the point where the line of final pH is crossing the line of initial pH.

**2.3. Removal Experiments.** Experiments were conducted to investigate diazinon removal efficiency by adsorption and photocatalytic degradation of the synthesized materials. In addition, optimal pH, photocatalyst dosage, and light condition were also investigated in the study. In a typical removal experiment, a known dosage of the synthesized photocatalyst (0.25–1 g/L) was transferred to 100 mL of diazinon solution with a distinct concentration (10–50 mg/L) at a certain pH (3–8). The initial pH of solution was adjusted by adding NaOH or HCl (0.1 mol/L) and measured by the pH meter model XT 1200C (Mettler Toledo). After a certain time, the mixture was filtered and the remained diazinon concentrations were measured using a HPLC (Supelco LiChrospher RP-18 column,  $250 \times 4.6 \times 5$ ) coupled to a UV-PDA detector (Shimadzu SPD-M10Avp) at a wavelength of 247 nm. The removal experiment was firstly conducted under dark condition to determine adsorption

capacity of the synthesized material. Then, the visible light was provided to initiate for photocatalytic degradation of diazinon.

### 3. Results and Discussion

#### 3.1. Material Characteristics

**3.1.1. Morphology.** Figure 1 shows the SEM images of the synthesized Bent-Fe and Fe-TiO<sub>2</sub>/Bent-Fe materials. It can be seen that the synthesized Bent-Fe material existed in form of nanolamella with dominant flake-like morphology and curling edges. The SEM image of the synthesized Fe-TiO<sub>2</sub>/Bent-Fe indicated that Fe-TiO<sub>2</sub> particles existed in form of nanospherical particles. The nano-Fe-TiO<sub>2</sub> particles were well-dispersed on the surface of the Bent-Fe layers. This is expected to increase recycling ability of the nano-Fe-TiO<sub>2</sub> photocatalysts after being used for diazinon removal processes. In addition, the deposition of Fe-TiO<sub>2</sub> particles on the surface of the Bent-Fe could increase surface areas of the material, leading to increase in its diazinon removal efficiency. The BET surface area of the synthesized Fe-TiO<sub>2</sub>/Bent-Fe (181.13 m<sup>2</sup>/g) was greatly higher than that of the Bent-Fe (66.22 m<sup>2</sup>/g).

**3.1.2. Crystal Phase Structure.** Figure 1 shows the XRD patterns of undoped TiO<sub>2</sub>, Fe-TiO<sub>2</sub>, and Fe-TiO<sub>2</sub>/Bent-Fe materials. It can be seen that the anatase and rutile phases were observed in the XRD pattern of the undoped TiO<sub>2</sub> material (JCPDS card No. 65-5714 for anatase and JCPDS card no. 21-1276 for rutile). However, there was only anatase phase in the XRD pattern of the synthesized Fe-TiO<sub>2</sub> photocatalyst. This could be due to the incorporation of Fe dopant into TiO<sub>2</sub> lattice prevented the formation of the rutile phase [33, 34]. There was no peak corresponding to Fe component in the synthesized Fe-TiO<sub>2</sub> material which confirmed that Fe incorporated in the TiO<sub>2</sub> lattice. Figure 1 also shows that the phase structure of the Fe-TiO<sub>2</sub> photocatalyst unchanged when the material was deposited on the Bent-Fe. In addition, a peak corresponding to the montmorillonite phase of the bentonite was also observed in the XRD pattern of the Fe-TiO<sub>2</sub>/Bent-Fe material (JCPDS card No. 03-0014) (Figure 2).

**3.1.3. Optical Properties.** Figure 3 shows the UV-Vis light absorption of the synthesized TiO<sub>2</sub>, Bent-Fe, Fe-TiO<sub>2</sub>, and Fe-TiO<sub>2</sub>/Bent-Fe materials. The UV-Vis absorption spectrum of TiO<sub>2</sub> exhibited an absorption edge at 390 nm [35]. However, the materials did not exhibit any noticeable absorption in the visible region. Bent-Fe also shows little visible light absorption. As compared to the UV-Vis absorption spectra of the TiO<sub>2</sub> and Bent-Fe, that of the Fe-TiO<sub>2</sub>, however, not only showed a red shift of the absorption edge but also exhibited higher adsorption ability in the visible region. The band gap structure of the TiO<sub>2</sub> is comprised of a valence band, which is mainly constructed from an O 2p orbital, and a conduction band, which is mainly constructed from an empty Ti 3d orbital. In the Fe-TiO<sub>2</sub>, the 3d orbitals

of Fe dopant not only affected to the top of the valence band and the bottom of the conduction band of the TiO<sub>2</sub> but also inserted into the TiO<sub>2</sub> lattice structure to create a Fe impurity band under the conduction band and upper the valence band of the TiO<sub>2</sub>, formed an optical band gap [33, 36]. Therefore, the photoexcited electrons in the TiO<sub>2</sub> valence band could migrate to the Fe impurity band, and then move from the impurity band to the conduction band via next photon absorption. Thus, the Fe dopant led to decrease in the band-gap energy, recombination rate of photo-excited electrons and holes, as well as increase in visible light absorption of the TiO<sub>2</sub>. The UV-Vis absorption spectrum of Fe-TiO<sub>2</sub>/Bent-Fe shows that the deposition of the Fe-TiO<sub>2</sub> on the surface of the Bent-Fe extended visible light absorption of the Fe-TiO<sub>2</sub>. Krishnan and Mahalingam reported that the increase in visible light absorption was due to the interband transitions i.e., charge transfer transition of interlayer tetrahedral and octahedral atoms in the bentonite material [37].

#### 3.2. Diazinon Removal

**3.2.1. Adsorption of Diazinon.** First, the effect of contact time on the sorption of diazinon was investigated by adding 0.5 g of the synthesized Fe-TiO<sub>2</sub>/Bent-Fe material in 100 mL diazinon solution (16.74 mg/L) at pH 5.6 (natural pH without any adjustment) and room temperature of 25°C. The diazinon adsorption capacities by the synthesized Fe-TiO<sub>2</sub>/Bent-Fe are shown in Figure 4(a). It can be seen that the diazinon adsorption capacities increased with increase in contact time up to 30 min and then tend to stabilize with further increase in contact time. It means that the diazinon adsorption by the synthesized Fe-TiO<sub>2</sub>/Bent-Fe reaches the equilibrium after 30 min. Based on the obtained results, the experiments, which the contact time was fixed (30 min), were conducted to investigate maximum diazinon adsorption capacity of the synthesized Fe-TiO<sub>2</sub>/Bent-Fe. The Langmuir model was applied to calculate the maximum adsorption capacities (Figure 4(b)). It can be seen that the adsorption ability is suitable with the Langmuir model, and the maximum diazinon adsorption capacity ( $q_{max}$ ) by the synthesized Fe-TiO<sub>2</sub>/Bent-Fe was 27.03 (mg/g).

**3.2.2. Photocatalytic Degradation of Diazinon.** In order to investigate photocatalytic degradation of diazinon, 0.5 g Fe-TiO<sub>2</sub>/Bent-Fe material was put in 100 mL diazinon solution (25 mg/L). In the condition, the pH of solution was 5.6 (natural pH without any adjustment). Then, the obtained solution was kept in dark condition for 30 min to get adsorption equilibrium, and then the visible light was provided using a 36 W compact bulb, which could provide visible light in range of 400–700 nm. The diazinon removal results are shown in Figure 5. Under dark condition, an approximately 36.18% diazinon was removed by adsorption of Fe-TiO<sub>2</sub>/Bent-Fe material. When visible light was provided, the diazinon was continuously removed by photocatalytic degradation. The synthesized Fe-TiO<sub>2</sub>/Bent-Fe could absorb significant amount of incident light to generate huge amount

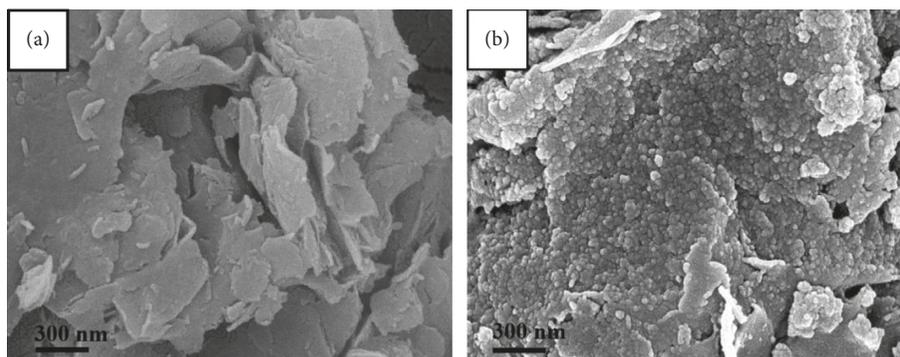


FIGURE 1: SEM images of the synthesized Bent-Fe and Fe-TiO<sub>2</sub>/Bent-Fe materials.

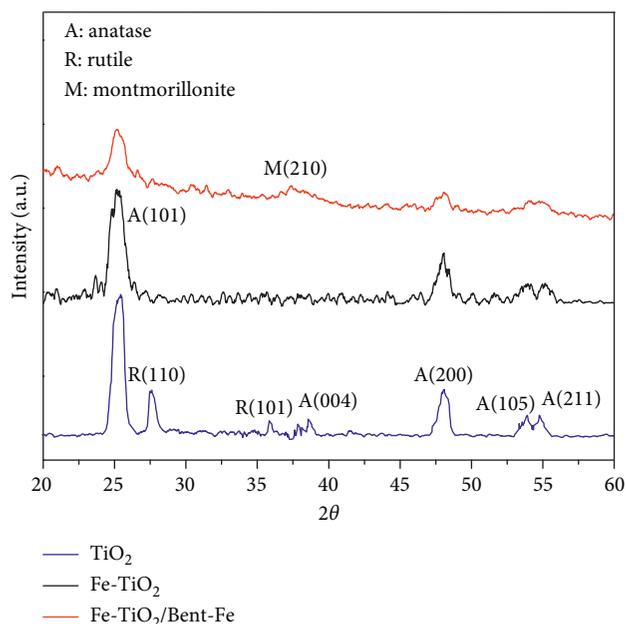


FIGURE 2: XRD patterns of the synthesized TiO<sub>2</sub>, Fe-TiO<sub>2</sub>, and Fe-TiO<sub>2</sub>/Bent-Fe materials.

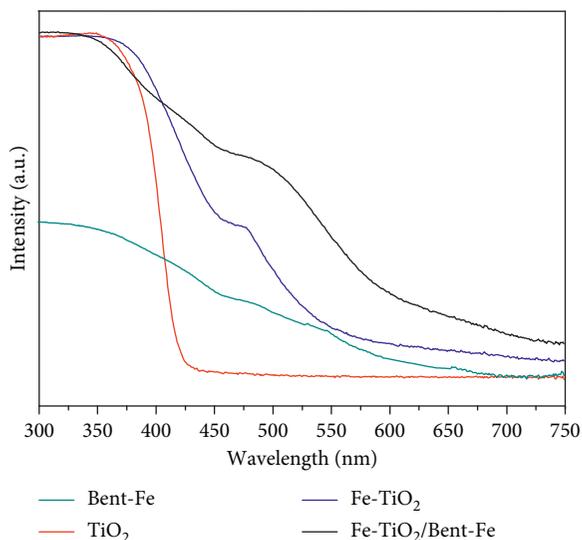


FIGURE 3: UV-Vis absorption spectra of the synthesized TiO<sub>2</sub>, Bent-Fe, Fe-TiO<sub>2</sub>, and Fe-TiO<sub>2</sub>/Bent-Fe materials.

of electrons and holes. Then, the generated electrons and holes could react with H<sub>2</sub>O and O<sub>2</sub>, respectively, to produce strong oxidative radicals, including hydroxyl and superoxide anion radicals, for degradation of diazinon into harmless inorganic materials [38–40]. The total diazinon removal by both adsorption and photocatalytic degradation was approximately 58.3%.

**3.2.3. Optimal Removal Conditions.** The effects of photocatalyst dosages on diazinon removal efficiencies are shown in Figure 6(a). When the photocatalyst dosage was 0.25 g/L, the amount of photocatalyst was not enough for the diazinon removal. The diazinon removal efficiencies increased with increase in photocatalyst dosage up to 1.0 g/L. When the photocatalyst dosages increased, the turbidity of the solution increased. An increased level of suspension turbidity resulted from excessive photocatalyst dosage would block the incident visible light required for the photocatalyst activation [41]. Hence, the photocatalytic degradation efficiency decreased. Thus, the optimal photocatalyst dosage for diazinon removal was 0.5 g/L.

The diazinon removal experiments was conducted under different light conditions including artificial light generated from compact bulb and natural light from solar. The intensity of light from the 36 W compact bulb was 190.985 lux and the intensity of solar light, which was measured in 6 hours of the experiment, varied from 32.500 to 65.200 lux. In the experiments, the photocatalytic dosage, pH, and intimal concentration of diazinon were 0.5 g/L, 5.6, and 25 ppm, respectively. The obtained results are shown in Figure 6(b). The diazinon removal efficiency under natural light generated from solar was 53%, which was slightly lower than that under artificial light generated from compact bulb (58.3%). Thus, the natural light could be suitable used for photocatalytic degradation of diazinon by the synthesized Fe-TiO<sub>2</sub>/Bent-Fe material.

Finally, the diazinon removal experiments were conducted at different pH (3.0, 4.5, 5.6 and 8.0) to investigate optimal pH for the process. In the experiments, the photocatalytic dosage and intimal concentration of diazinon were 0.5 g/L and 25 ppm, respectively. The diazinon removal efficiencies at different pH are shown in Figure 6(c). First, the pK<sub>a</sub> of diazinon is 2.6, thus diazinon is negatively charged at all the selected pH conditions [2]. Point of zero

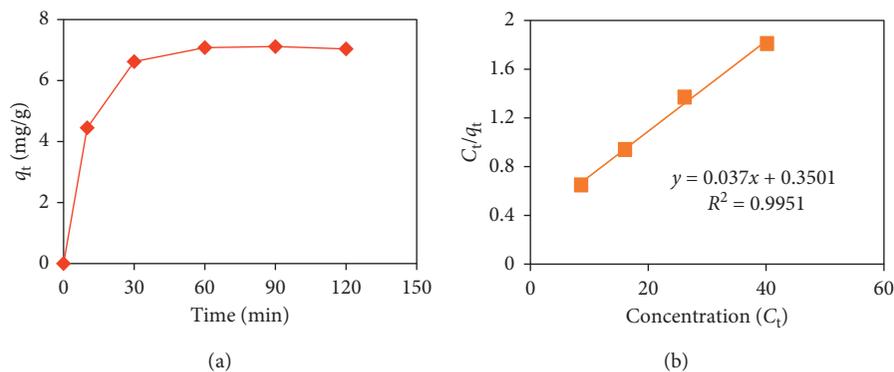


FIGURE 4: Diazinon adsorption capacities by the synthesized Fe-TiO<sub>2</sub>/Bent-Fe (a) and Langmuir model (b).

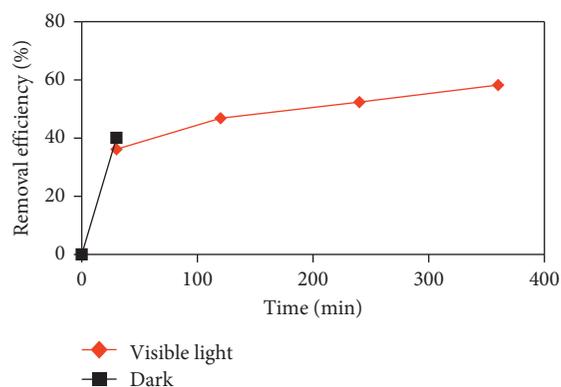


FIGURE 5: Diazinon removal under dark and visible light conditions.

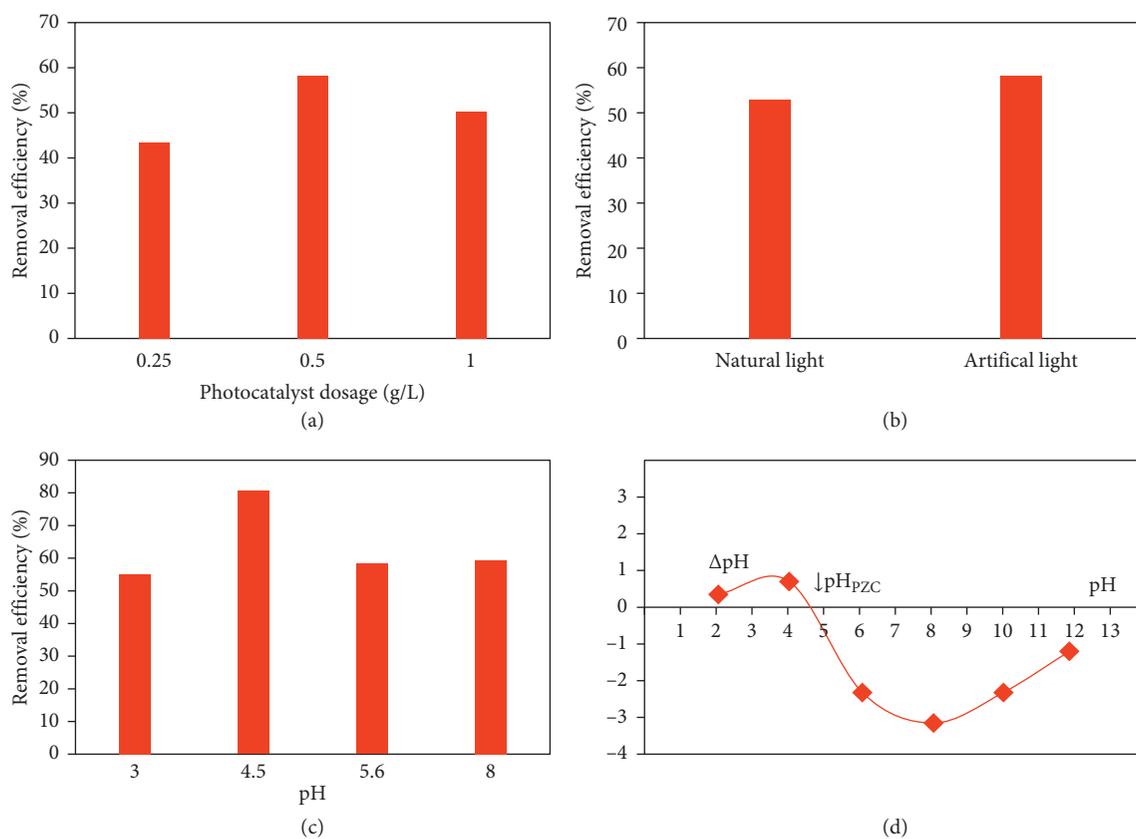


FIGURE 6: Effects of photocatalyst dosage (a), light sources (b), and pH (c) on diazinon removal efficiencies and zeta potential of the synthesized Fe-TiO<sub>2</sub>/Bent-Fe (d).

charge of the synthesized Fe-TiO<sub>2</sub>/Bent-Fe material was approximately 4.6 (Figure 6(d)). As expected, an optimal condition can be developed in the pH range between  $pK_a^{\text{diazinon}}$  and  $pH_{zpc}^{\text{Fe-TiO}_2/\text{Bent-Fe}}$  at which the positively charged Fe-TiO<sub>2</sub>/Bent-Fe material and negatively charged diazinon should readily attract each other. At high pH, both diazinon and Fe-TiO<sub>2</sub>/Bent-Fe have negative charges. Therefore, electrostatic repulsion between diazinon and Fe-TiO<sub>2</sub>/Bent-Fe causes reduced adsorption of diazinon onto material surface, resulting in decreased photocatalytic removal efficiency. Based on the obtained results of this study, pH 4.5 was identified as an optimum condition for the removal of diazinon using Fe-TiO<sub>2</sub>/Bent-Fe material. Under optimal conditions, including dosage (0.5 g/L) and pH (4.5), 80.6% diazinon, which the initial concentration was 25 ppm, has been removed by the synthesized Fe-TiO<sub>2</sub>/Bent-Fe.

Recycling experiments were conducted to analyze the stability of the prepared photocatalyst during the diazinon removal processes. After being used for diazinon removal for 360 min, the photocatalysts were collected and vacuum dried for 4 h under the dark condition and then used for the diazinon removal experiment. The diazinon removal efficiency by Fe-TiO<sub>2</sub>/Bent-Fe in the first and second time of recycle was 76.8 and 69.3%, respectively. The diazinon removal by Fe-TiO<sub>2</sub>/Bent-Fe was not significantly changed after recycling, which demonstrated the stability of the photocatalysts during the removal experiments.

#### 4. Conclusion

We successfully used Fe as a dopant to enhance photocatalytic activity of TiO<sub>2</sub>. Then, the Fe doped TiO<sub>2</sub> was deposited on bentonite, which was pillared by Fe, to enhance its adsorption and recycling ability in the practical system. The synthesized material exhibited high adsorption ability to remove diazinon. The maximum diazinon adsorption capacity of the synthesized Fe-TiO<sub>2</sub>/Bent-Fe was 27.03 mg/g. Even under visible light, the synthesized Fe-TiO<sub>2</sub>/Bent-Fe photocatalyst also exhibited high photocatalytic activity for degradation of diazinon. The optimal photocatalyst dosage for removal of diazinon was 0.5 g/L. The natural light generated from solar could be suitable used for diazinon removal by the synthesized Fe-TiO<sub>2</sub>/Bent-Fe. Finally, the optimal pH for diazinon removal was 4.5, which is preferred for adsorption of diazinon by the synthesized Fe-TiO<sub>2</sub>/Bent-Fe.

#### Data Availability

The data used to support the findings of this study are included within the article.

#### Conflicts of Interest

The authors declare that they have no conflicts of interest.

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## Research Article

# A Novel Approach for Fabricating $\text{LaMnO}_3$ Thin Films Using Combined Microwave Combustion and Pulsed Electron Deposition Techniques

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$\text{LaMnO}_3$  (LMO) nanopowder was synthesized by the microwave combustion method using glycine and nitrate salts of La and Mn as precursors. The as-prepared LMO powder was pressed at high pressure and annealed at  $1000^\circ\text{C}$  for 8 hours to make a target for thin film deposition. The structural and elemental analysis was obtained by X-ray diffraction (XRD) and energy dispersive X-ray spectroscopy (EDS). Thin films of LMO were fabricated using pulsed electron deposition (PED) at room temperature. The effects of discharge voltage and oxygen/argon flux ratio on the produced thin films were studied. The study shows that stoichiometry and structure of the target was preserved well in the thin films prepared with a discharge voltage from 14 to 15 kV, while the oxygen/nitrogen flux ratio did not show a clear effect on the quality of thin films.

## 1. Introduction

Recently, semiconductor magnetic nanomaterials have received much awareness than that of their same bulk materials, due to their size and surface effects, which exhibit unique properties such as photoluminescence, magneto-optical, electrochemical, and photocatalytic activity [1–13]. These unique properties of nanomaterials in turn help to solve a lot of urgent problems related to exhaustion of fossil fuels and environment pollution. In this aspect, production

and application of clean fuels based on nanomaterials become more and more critical for the development of human society [14–17]. In particular, solid oxide fuel cells (SOFCs) have been extensively studied and attracted much attention as a promising way to generate electricity at high efficiency and low cost [18–20]. For such applications, the cathode material must satisfy several criteria such as good electrical conductivity, high porosity to allow gas diffusion, thermal expansion coefficient matching well with that of the solid electrolyte, and chemical stability at a high temperature

[21–23]. Most of the requirements listed above are satisfied by LaMnO<sub>3</sub> perovskites, making it one of the most suitable materials for cathode in SOFCs [24].

Among many effective methods developed to produce nanopowders, microwave-assisted synthesis was first developed in 1985 and has quickly become a major area of study. Since microwave radiations were discovered, these have been widely utilized for synthetic chemistry in order to activate chemical reactions more rapidly and homogeneously [25–29]. Moreover, a self-combustion reaction assisted with microwave is extremely suitable for preparation of perovskite nanomaterials due to notable advantages such as simple and convenient experimental set-up, extremely time, and energy saving, as well as offering homogeneous product [30–32]. These advantages result from a thorough blending among the constituents in an aqueous media under microwave irradiation. Furthermore, an exothermic redox reaction between the fuel and an oxidizer provides a great amount of heat which is necessary for the formation of the perovskite phase [33, 34].

In general, thin films can be manufactured by a variety of methods such as sputtering, thermal evaporation, and molecular-beam epitaxy [35–37]. Pulsed electron deposition (PED) is also a physical thin film deposition technique offering many advantages such as high film homogeneity and low cost. However, this method seems to be not explored for preparation of perovskite thin films even though it is convenient to transfer the target stoichiometry to the deposited films by PED [38].

In this paper, LaMnO<sub>3</sub> (LMO) nanopowder was prepared by microwave combustion where glycine was used as a fuel in a combustion reaction with nitrate salts of lanthanum and manganese. The as-prepared LMO powder was pressed and annealed at 1000°C for 8 hours to make a target for thin film deposition. The fabrication of LMO thin films by PED was investigated in details.

## 2. Experiment

LaMnO<sub>3</sub> nanopowder was prepared by the microwave combustion method. Analytical grade La<sub>2</sub>O<sub>3</sub> (99.99%), Mn(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (99%), and glycine NH<sub>2</sub>CH<sub>2</sub>COOH (99%) were used as the starting materials. Stoichiometric amount of La<sub>2</sub>O<sub>3</sub> was dissolved in HNO<sub>3</sub> to obtain La(NO<sub>3</sub>)<sub>3</sub> solution. Then, La(NO<sub>3</sub>)<sub>3</sub> and Mn(NO<sub>3</sub>)<sub>2</sub> solutions in water at molar ratio of 1 : 1 were mixed well before dropwise addition of glycine.

We first prepared a set of samples with different molar ratios of glycine to the metal ion ( $F = 2.5, 3, 3.5, 4, \text{ and } 4.5$ ) to study the effect of fuel on the nanopowder. After heating on a hot plate at 150°C, the light pink solution evolved into a colorless transparent one and then viscous brown gel. Gel was stored in a glass container covered with an open lid and then quickly transferred to a microwave oven. After a few seconds, the viscous gel bubbled up and autoignited to produce brown fine powder.

The LMO powder was milled, pressed, and annealed at 1000°C for 8 hours to make a target for fabrication of the thin film by pulsed electron deposition system PEBS-20 from

Neocera, Inc. All the LaMnO<sub>3</sub> films were deposited on silicon substrates with the repetition rate of pulses maintained at 5 Hz, pulse width of 100 ns, and 20 000 pulses.

Two sets of thin film samples were prepared to study the effect of discharge voltage (LMO-1) and O<sub>2</sub>/N<sub>2</sub> flux ratio (LMO-2). The deposition of the LMO-1 films was carried out at room temperature and at five discharge voltages: 11, 12, 13, 14, and 15 kV. The N<sub>2</sub> gas and O<sub>2</sub> gas were introduced at a pressure of  $9 \times 10^{-3}$  Torr for enhancing the electron beam and stabilizing the beam propagation to the target with a gas flux of 10 sccm and 15 sccm for oxygen and nitrogen, respectively. LMO-2 films were fabricated at 15 kV with various flux ratios of oxygen and nitrogen: 0 : 25; 5 : 20; 10 : 15; 20 : 5; and 25 : 0 sccm. During the deposition process, the pressure was maintained by balancing between the rate of the turbopump and the flow rate of oxygen and nitrogen gas introduced into the chamber. The as-deposited thin films were annealed at 400, 600, and 800°C for 2 h.

The crystallinity of the thin films was characterized by the X-ray diffraction system (Siemens D5005, Bruker, Germany) with Cu K<sub>α1</sub> ( $\lambda = 0.154056$  nm) radiation. The morphology of the product was investigated by a scanning electron microscope (Nova Nano SEM 450). The composition of the samples was verified by energy dispersive X-ray (EDX) spectrometry (Oxford Isis 300) integrated into the JEOL-JSM 5410 scanning electron microscope.

## 3. Results and Discussion

Figure 1 shows XRD patterns of LaMnO<sub>3</sub> nanoparticles prepared by the microwave irradiation method when using glycine as fuel in the combustion reaction with the glycine-nitrate molar ratio ( $G/N$ ) ( $F = 2.5, 3, 3.5, 4, \text{ and } 4.5$ ).

The sample prepared with  $F = 2.5$  is amorphous because the released energy is not enough for formation of the perovskite phase. With  $F = 3, 3.5, 4, \text{ and } 4.5$ , the LaMnO<sub>3</sub> perovskite phase has formed. Sharp and intense XRD peaks of the samples with  $F = 3$  suggested that crystal quality of those samples is better. The combustion reaction with a higher value of  $F$  liberated more heat. However, gas generated during the reaction can bring out heat from the reaction chamber and reduced the heat used for synthesis of the perovskite material [39]. Heat generated by the reaction might be reduced too much and resulted in an amorphous state of samples with  $F$  greater than 4. XRD patterns indicate that LaMnO<sub>3</sub> nanoparticles, prepared with  $F = 3; 3.5; \text{ and } 4$ , crystallized in a hexagonal structure. Lattice parameters and crystalline size of the samples prepared with different ratios of  $F$  are shown in Table 1.

XRD analysis of the LaMnO<sub>3</sub> nanoparticles prepared by combustion assisted with microwave irradiation also shows the presence of both LaMnO<sub>3</sub> and La<sub>2</sub>CO<sub>5</sub>. La<sub>2</sub>CO<sub>5</sub> is an unwanted phase due to the unavoidable reaction of metal ions with organic precursors.

A pure perovskite is necessary for making cathode of good performance fuel cell. Therefore, such secondary phases need to be removed. As an unsolvable material, La<sub>2</sub>CO<sub>5</sub> cannot be washed away using water, so the nanopowder was annealed at 1000°C to convert the remaining

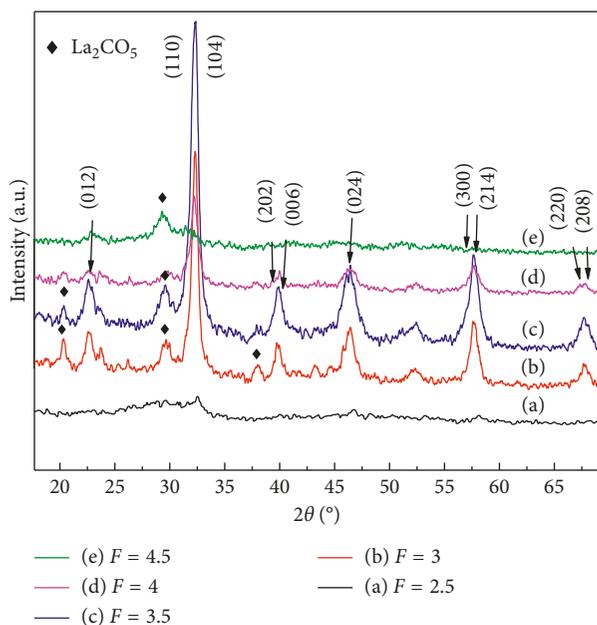


FIGURE 1: XRD patterns of  $\text{LaMnO}_3$  nanoparticles with  $F=2.5, 3, 3.5, 4,$  and  $4.5$ .

TABLE 1: The lattice parameters and crystallite size of the  $\text{LaMnO}_3$  samples with different ratios of glycine/nitrate molar ( $F=3, 3.5,$  and  $4$ ).

Sample	$a$ (Å)	$b$ (Å)	$c$ (Å)	$\bar{d}$ (nm)	Volume of unit cell (Å <sup>3</sup> )
$F=3$	5.54	5.54	13.46	14.1	357.66
$F=3.5$	5.54	5.54	13.47	10.2	357.62
$F=4$	5.55	5.55	13.45	9.9	358.98

$\text{La}_2\text{CO}_5$  into  $\text{LaMnO}_3$ . Figure 2 shows the XRD patterns of  $\text{LaMnO}_3$  samples with a molar ratio of glycine to metal ion of 3 and 3.5 before and after annealing at  $1000^\circ\text{C}$  in 8 h. After annealing, no peak related to  $\text{La}_2\text{CO}_5$  can be seen in the XRD pattern. The result implies the purity of the final nanopowder. Sharper and stronger diffraction peaks show that crystalline sizes of the  $\text{LaMnO}_3$  powder increase clearly after annealing, as expected due to the crystal growth during the annealing process at a high temperature. It should be also noted that, after annealing, a clear peak shift to a higher angle was observed. The reason for lattice expansion in the sample should be taken into account. One possible explanation for lattice expansion in the sample before annealing is small particles size. In other words, in nanomaterials of poor structural order, defect might be introduced at a high concentration, which results in an internal stress in the lattice due to the presence of large  $\text{La}^{3+}$  at interstitial sites in the lattice. The internal stress is responsible for the lattice expansion, as observed for as-prepared nanopowder samples. The corresponding decrease of the lattice parameter is shown in Table 2.

However, the results show that annealing the samples at  $1000^\circ\text{C}$  does not result in transition of the phase structure. Such peak shift to a higher angle, combining with the disappearance of some peaks in the XRD pattern, can be an

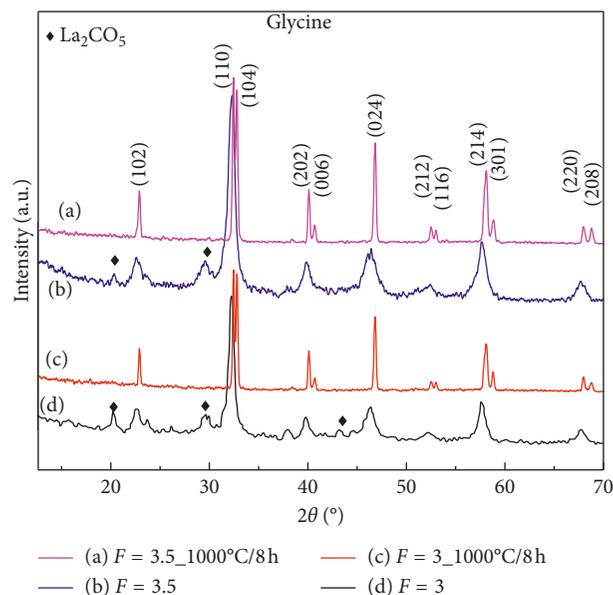


FIGURE 2: XRD patterns of  $\text{LaMnO}_3$  samples with  $F=3$  and  $3.5$  before and after annealing at  $1000^\circ\text{C}$  in 8 h.

indication of a phase transition. The change in the lattice parameter suggests that annealing phase transition from hexagonal to other structures can occur at a higher temperature or in longer time. However, this is not being mentioned in this paper but would be reported in another study.

The energy dispersive X-ray spectra (Figure 3) of the  $\text{LaMnO}_3$  nanopowder with  $F=3$  before and after annealing at  $1000^\circ\text{C}$  in 8 hours only show the peaks of La, O, and Mn. This result indicates that samples are clean and pure.  $\text{LaMnO}_3$  nanopowder prepared with a molar ratio of glycine/nitrate ( $F=3$ ) was used to make a target because the results showed that better crystallinity was achieved for this sample. The as-prepared LMO powder was remilled, pressed at high pressure, and annealed at  $1000^\circ\text{C}$  for 8 hours to make a target. The structure and phase purity of the LMO target was examined by XRD measurements, as shown in Figure 4. The XRD patterns reveal that the structure of the LMO target is still hexagonal. The LMO target showed peaks corresponding to reflection from (102), (110), (104), (202), (204), (212), (214), and (220) planes, where (110) and (104) peaks have the strongest intensity clearly demonstrating the preferred crystal growth during the annealing process.

Even though the LMO target can be fabricated by the normal solid-state reaction method from oxides precursors, using nanopowder of LMO to make the target help in reducing the treating temperature to  $1000^\circ\text{C}$ , the target prepared by the solid-state reaction normally required a much higher annealing temperature ( $1300\text{--}1400^\circ\text{C}$ ) and longer time (12–24 h).

Figure 5 shows XRD patterns of the  $\text{LaMnO}_3$  thin films deposited at 15 kV before and after annealing at different temperatures. It can be seen that the as-deposited films and films annealed at  $400^\circ\text{C}$  and  $600^\circ\text{C}$  were amorphous because no diffraction peak is observed. As annealing temperature is

TABLE 2: The lattice parameter of the  $\text{LaMnO}_3$  samples with different ratios of glycine/nitrate molar ( $F = 3$  and  $3.5$ ) before and after annealing at  $1000^\circ\text{C}$  for 8 h.

Sample	$a$ ( $\text{\AA}$ )	$b$ ( $\text{\AA}$ )	$c$ ( $\text{\AA}$ )	Volume of unit cell ( $\text{\AA}^3$ )
$F = 3$	5.54	5.54	13.46	357.66
$F = 3$ at $1000^\circ\text{C}$	5.51	5.51	13.29	349.43
$F = 3.5$	5.54	5.54	13.47	357.62
$F = 3.5$ at $1000^\circ\text{C}$	5.51	5.51	13.28	351.17

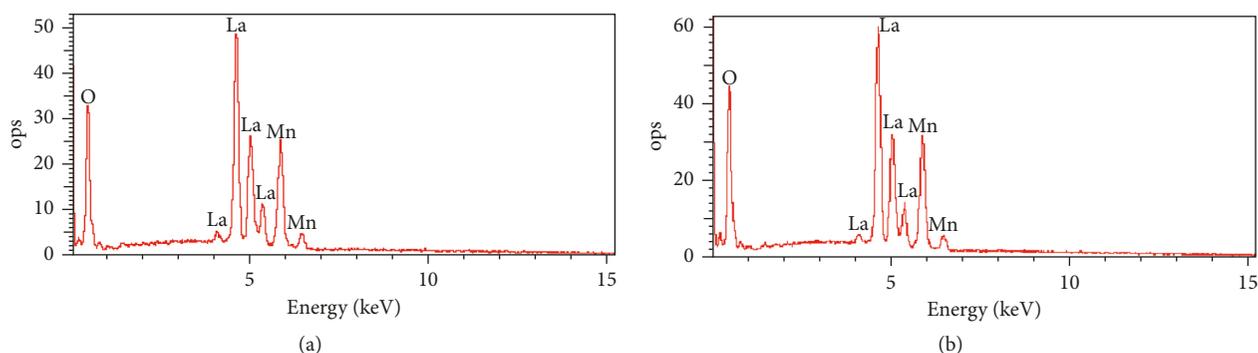


FIGURE 3: EDS spectra of the  $\text{LaMnO}_3$  nanopowder with  $F = 3$  (a) before and (b) after annealing at  $1000^\circ\text{C}$ .

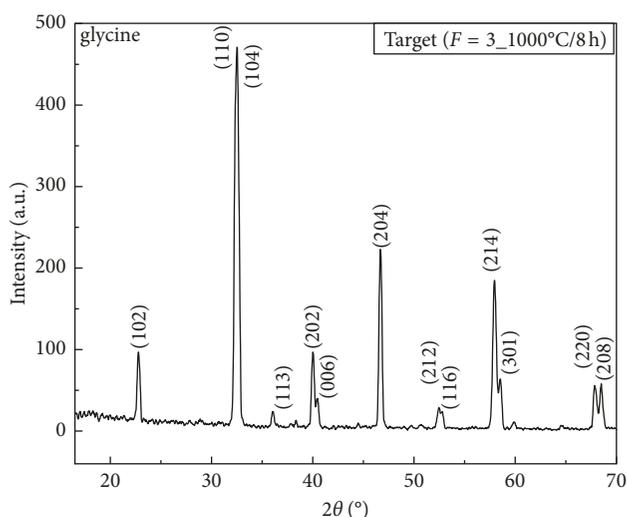


FIGURE 4: XRD pattern of the  $\text{LaMnO}_3$  target made of  $\text{LaMnO}_3$  nanoparticles prepared by self-combustion assisted with microwave irradiation.

raised up to  $800^\circ\text{C}$ , the thin film is crystallized in the hexagonal structure.

Figure 6 shows SEM images of LMO thin films deposited at 15 kV before and after annealing at different temperatures.

SEM images of thin films deposited at 15 kV show that the particle size distribution is quite uniform and post-annealing does not change the morphology of the produced thin films. The film is crack free both before and after being annealed. SEM images also reveal that the films have uniform particulates which are uniformly distributed on the surface.

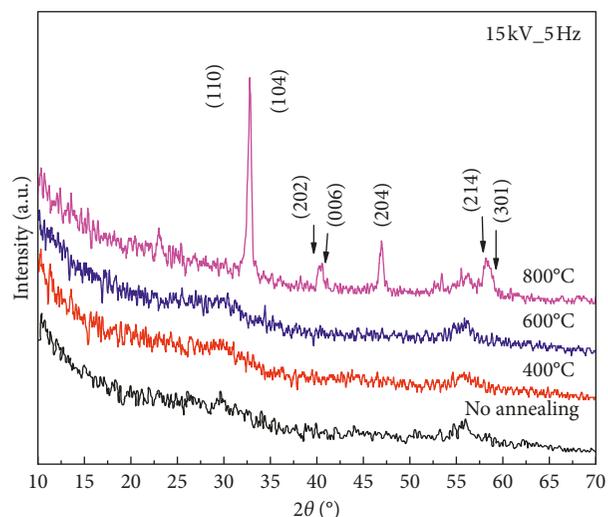


FIGURE 5: XRD patterns of the  $\text{LaMnO}_3$  thin films deposited before and after annealing at  $400^\circ\text{C}$ ,  $600^\circ\text{C}$ , and  $800^\circ\text{C}$  with a discharging voltage of 15 kV.

XRD analysis (Figure 7) shows that all thin films are amorphous for all discharge voltage. Postannealing at a temperature higher than  $800^\circ\text{C}$  is required to obtain crystalline films. However, transition from the amorphous to hexagonal structure occurs only in films deposited at 14 and 15 kV. Other films prepared at voltage lower than 14 kV remains in the amorphous state despite postannealing.

The diffraction peaks were higher at 15 kV which is the maximum voltage available for the used PED system. The above results can be understood that discharge voltage is a critical factor determining the growth of thin films by PED. Voltage higher than 14 kV is required to preserve the

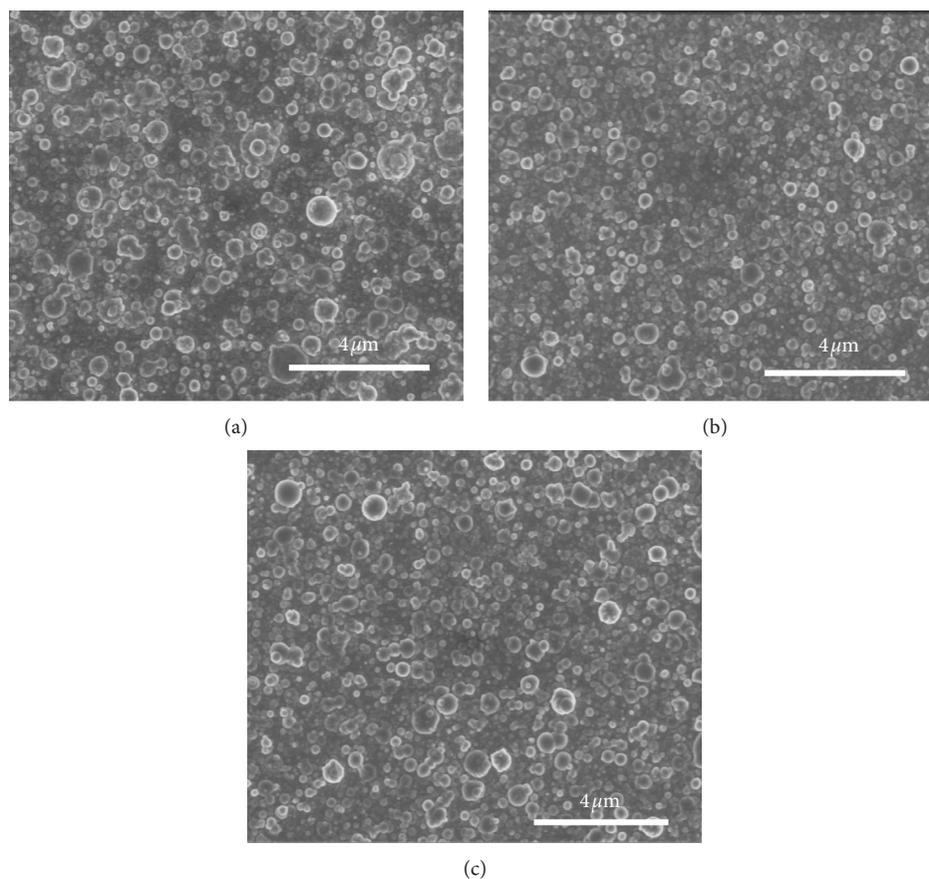


FIGURE 6: SEM images of LMO thin films deposition at 15 kV after annealing at different temperatures (a) as the deposited film; (b) 400°C; (c) 800°C.

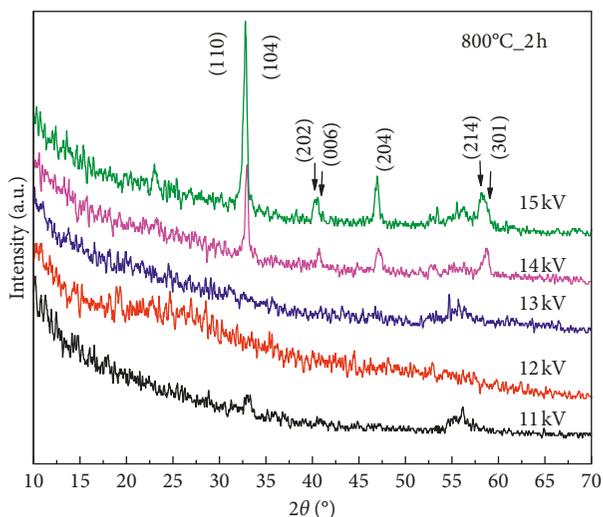


FIGURE 7: XRD patterns of  $\text{LaMnO}_3$  thin films deposited at 11, 12, 13, 14, and 15 kV after annealing at 800°C for 2 h.

stoichiometry composition of the target to the thin films. However, the energy transferred by the electron beam is not enough for the atom to arrange on the substrate in a crystalline structure. Hence, postannealing is necessary to activate the crystallization of the thin films. Lattice

parameters of the films prepared at 14 and 15 kV after annealing are shown in Table 3.

In vacuum deposition techniques, gas ambient may also have a great influence on the structure and morphology of the thin films [40]. We also studied the effect of the  $\text{N}_2/\text{O}_2$  flux ratio on the LMO thin film prepared by pulse electron deposition. Figure 8 shows XRD patterns of the  $\text{LaMnO}_3$  thin films deposited at 15 kV and 5 Hz with different ratios of  $\text{N}_2/\text{O}_2$  flux (25:0, 20:5, 10:15, and 0:25 sccm).

It is clear that the films after postannealing are well crystallized at all different ratios of  $\text{N}_2/\text{O}_2$  flux. The highest intensity was achieved for film grown at  $\text{N}_2/\text{O}_2$  flux (10:15 sccm), indicating that partial pressure of oxygen also has a slight effect on the structure of the thin films.

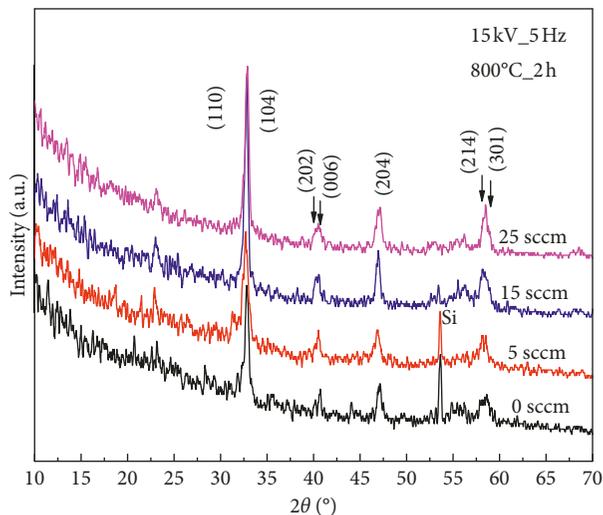
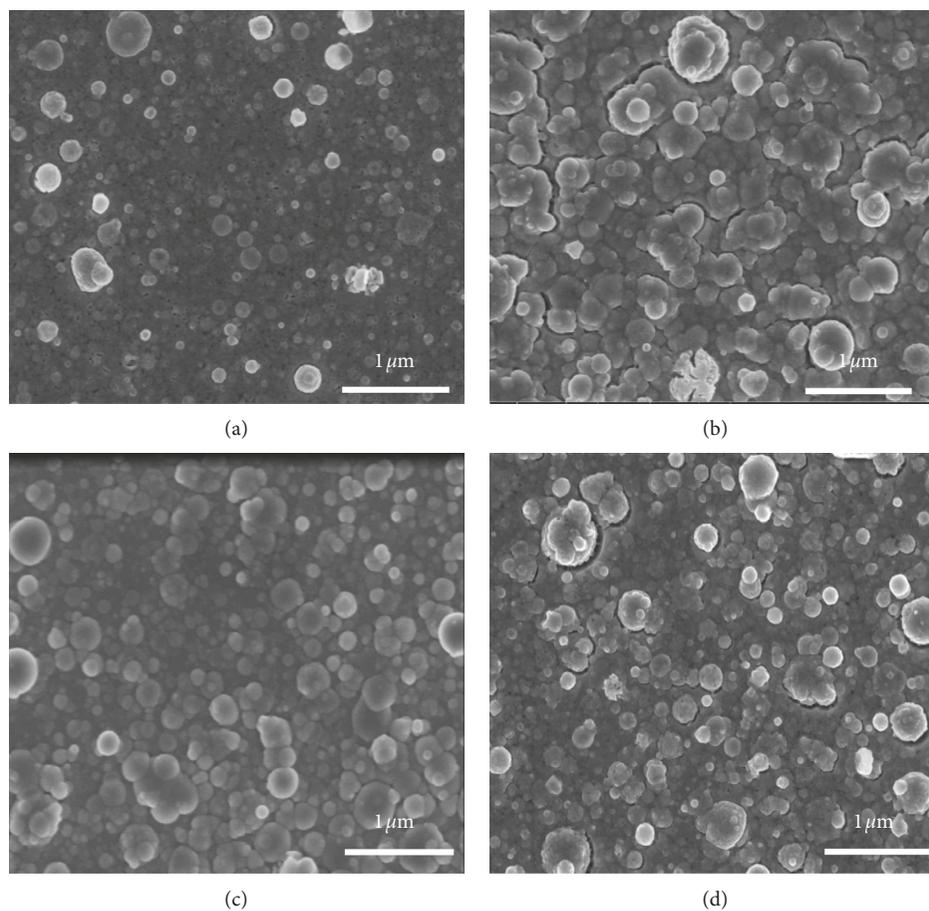
Figure 9 shows SEM images of the LMO-2 films, which were prepared at a different oxygen partial pressure. While the sample prepared in pure nitrogen ambient possesses fine particulates, the samples prepared in oxygen show more particulates. This could be due to the fragmentation of the oxide particulates in the plasma region at higher oxygen partial pressures [41].

#### 4. Conclusion

$\text{LaMnO}_3$  nanopowder was successfully synthesized using combustion assisted with microwave irradiation approach.

TABLE 3: The lattice parameters of the LaMnO<sub>3</sub> thin films deposited at 14 and 15 kV after annealing at 800°C for 2 h.

Sample	Lattice structure	$a$ (Å)	$b$ (Å)	$c$ (Å)	Volume of unit cell (Å <sup>3</sup> )
15 kV at 800°C	Hexagonal	5.46	5.46	13.44	358.03
14 kV at 800°C	Hexagonal	5.49	5.49	13.26	346.24

FIGURE 8: XRD patterns of the LaMnO<sub>3</sub> thin films prepared with different O<sub>2</sub> flux at 0, 5, 15, and 25 sccm after annealing at 800°C for 2 h.FIGURE 9: SEM image of LaMnO<sub>3</sub> thin films with different O<sub>2</sub> flux at (a) 0, (b) 5, (c) 15, and (d) 25 sccm after annealing at 800°C for 2 h.

Using nanopowder helps to lower the temperature of heat treatment of the target. Detailed investigation of LaMnO<sub>3</sub> thin films preparation shows that discharge voltage is a critical parameter for film deposition by PED. The obtained films were amorphous but could be converted into the crystalline phase after annealing at relatively a low temperature of 800°C. Suitable ratio of oxygen/nitrogen flux also contributes to better crystal quality of the thin films. The results demonstrate the potential of using PED as a tool for fabrication of perovskite thin films of high quality for various applications in electronic fields.

## Data Availability

All data used to support the findings of this study are available from the corresponding author upon request.

## Conflicts of Interest

The authors declare that they have no conflicts of interest.

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## Research Article

# Metal-Organic Framework MIL-53(Fe) as an Adsorbent for Ibuprofen Drug Removal from Aqueous Solutions: Response Surface Modeling and Optimization

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Ibuprofen contamination from water sources has been increasingly alarming due to its environmentally accumulative retention; however, the strategies for ibuprofen-containing water treatment are still an enormous challenge. Herein, we described the utilization of metal-organic frameworks MIL-53(Fe) (MIL = Materials of Institute Lavoisier) for the adsorption of ibuprofen in synthetic solution. Firstly, the MIL-53(Fe) was solvothermally synthesized and then characterized using the X-ray diffraction and Fourier-transform infrared spectroscopy techniques. The optimization of ibuprofen adsorption over MIL-53(Fe) was performed with three independent variables including ibuprofen concentration (1.6–18.4 mg/L), adsorbent dosage (0.16–1.84 g/L), and pH (2.6–9.4) according to the experimental design from response surface methodology. Under the optimized conditions, more than 80% of ibuprofen could be eliminated from water, indicating the promising potential of the MIL-53(Fe) material for treatment of this drug. Kinetic and isotherm models also were used to elucidate the chemisorption and monolayer behavior mechanisms of ibuprofen over MIL-53(Fe).

## 1. Introduction

Ibuprofen ((±R, S)-2-(4-(2-methylpropyl)phenyl)propanoic acid, IBU), a nonsteroidal anti-inflammatory drugs (NSAIDs), has widely been used for the treatment of bacterial infection-related diseases in many countries (its chemical structure is shown in Figure 1) [1–4]. However, there is a rapid acceleration in IBU contamination due to

the ineffective treatment of wastewater sources, derived from hospitals and pharmaceutical manufacturers [5–7]. According to recent environmental reports, varying amounts of the IBU residue have been detected in some rivers (i.e., Thames River, UK (0.783 µg/L), and Aura River, Finland (20 µg/L)), significantly exceeding the permissible standards for human health [8]. Besides, the accumulation of the IBU pollutant in water may support

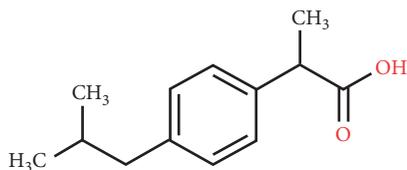


FIGURE 1: 2D structure of the IBU molecule by ChemDraw® ultra 12.0 program.

the antibiotics-resistant bacteria existing in the environment [1, 5, 9]. Therefore, techniques for eliminating this contaminant have received a great attention.

Adsorption is often regarded as a common method for the removal of pollutants in gas and liquid phases [10–15]. Several strong points of this approach include cost-effectiveness and high performance [16, 17]. Thanks to the good reusability of adsorbents, the overall cost can be reduced. Moreover, the adsorption is highly compatible with organic-derived hazardous wastes including IBU contaminant [4]. Therefore, the IBU degradation by the adsorption process has been rapidly developed.

In the adsorption process, solid adsorbents play a decisive role in removing the contaminants [18]. Heterogeneous materials have undergone a long history, especially nanostructured zeolites and mesoporous silica [4, 19–22]. Thanks to the highly porous structure along with open metal sites, these materials have been considered as ideal platforms towards diverse applications in fuel cells, chemical sensing, energy conversion, catalysis, drug delivery, and thin films [23–25]. However, the synthesis strategies for such materials were carried out via many elaborate steps combined with severe condition-controlled reactions, limiting their widespread applications [26]. Several studies reported the use of hazardous and expensive agents (i.e., reversible addition-fragmentation chain transfer (RAFT)) as vital components that control the growing of polymeric organic chains in controlled radical polymerizations, thus imposing the adverse impacts on the environment [26]. It is evident that finding out the greener and sustainable pathways for the fabrication of nanostructured materials is necessary.

Metal-organic frameworks (MOFs) are advanced materials constructed by metal ions or clusters and organic ligands via the coordination bonds [27–30]. Recently, they are considered as remarkable and promising materials because of good crystallinity, complex topologies, high porosity, tunable chemical properties, and large metal cluster density, and thereby, MOFs have attracted much attention in many fields such as drug delivery, catalysis, gas storage, sensor, and adsorption [31]. MIL-53(Fe) or Fe(III)(OH)(1,4-BDC) is a typical class of MOFs generated by a combination between iron(III) cations and 1,4-dicarboxylic acid [32, 33]. This structure consists of  $\text{FeO}_6$  hexagonal chains connecting with dicarboxylate anions to form the three-dimensional networks or SBUs (secondary building units) [34–36]. One of the most emergent features of MIL-53(Fe) compared with other MOFs is the “breathing effect,” which experiences a breathing transition in the presence of guest molecules, thus creating the structural flexibility [37]. Moreover, this

material can be easily synthesized via the conventional strategies, such as microwave or solvothermal method [38, 39]. Unlike the other MOFs such as MIL-88B(Cr) or MIL-101(Cr), which also represents the same “breathing effect,” MIL-53(Fe) is chemically stable and constituted of lower toxic metal centers and thus has gained much attention [40].

In this work, we described the MIL-53(Fe) synthesis by the solvothermal method and its application in IBU adsorption. Some techniques including XRD and FT-IR were used to analyze the as-synthesized products. Moreover, the experiments were optimized based on the response surface methodology.

## 2. Experimental

**2.1. Chemicals and Instruments.** All chemicals in this study were directly used without any purification. 1,4-Benzenedicarboxylic acid ( $\text{H}_2\text{BDC}$ , 98%) was purchased from Merck. Iron(III) chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , 99.0%), and *N,N*-dimethylformamide (DMF, 99.5%) were purchased from Xilong Chemical, China.

The D8 Advance Bruker powder diffractometer was used to record the X-ray powder diffraction (XRD) profiles using  $\text{Cu-K}\alpha$  beams as excitation sources. The FT-IR spectra were recorded on the Nicolet 6700 spectrophotometer to explore the functional groups. The UV-Vis spectrophotometer was used to determine the IBU concentration at wavelength 222 nm. All analytic samples were reactivated at  $105^\circ\text{C}$  under nitrogen atmosphere.

**2.2. Synthesis of MIL-53(Fe).** The MIL-53(Fe) was solvothermally prepared according to a recent study [37]. Firstly, 1.35 g of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and 0.83 g of  $\text{H}_2\text{BDC}$  were dissolved in 25 mL DMF. The mixture was then transferred into a Teflon-lined autoclave and heated up at  $150^\circ\text{C}$  for 6 h. The yellow solid was extracted, refluxed with DMF overnight, washed with  $\text{C}_2\text{H}_5\text{OH}$  for three times ( $3 \times 10$  mL), and then dried at  $80^\circ\text{C}$  for storage in a desiccator. Figure 2 illustrates the synthesis strategy of MIL-53(Fe).

**2.3. Experimental Batches.** The stock solutions (20 mg/L) were prepared by dissolving the IBU substrate in distilled water. Various levels of concentration (1.8–18.4 mg/L) for the adsorption were generated by consecutively diluting the initial stock solutions. A series of HCl and KOH solutions was utilized to adjust the pH indexes. Herein, twenty experimental runs were randomly performed at room temperature following the response surface methodology (RSM) [42]. Firstly, MIL-53(Fe) samples (0.16–1.84 g/L) were mixed with 50 mL of ibuprofen solutions (1.8–18.4 mg/L) at various ranges of pH. The flasks were sealed and placed in the shaking tables (200 rpm). After the adsorption process reached the equilibrium state at 120 min, the adsorbent solids were dispensed and separated using the simple centrifugation. The IBU residual concentrations were identified using UV-Vis spectroscopy at the wavelength of

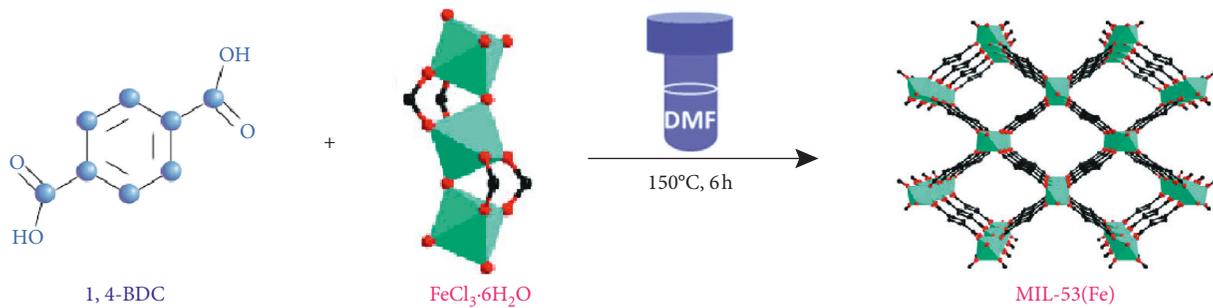


FIGURE 2: Schematic illustration for the synthesis of the MIL-53(Fe). The simulated structure of MIL-53(Fe) and iron(III) clusters was reproduced from [41].

222 nm. The percentage of removal  $y$  (%) and adsorption capacity  $Q$  (mg/g) can be mathematically defined as follows:

$$y(\%) = \frac{C_0 - C_e}{C_0} \cdot 100,$$

$$Q_t = \frac{C_0 - C_t}{m} \cdot V, \quad (1)$$

$$Q_e = \frac{C_0 - C_e}{m} \cdot V,$$

where  $C_0$ ,  $C_t$ , and  $C_e$  are denoted for the initial concentration, concentration at time  $t$  (min), and equilibrium concentrations (mg/L) and  $m$  (g) and  $V$  (mL) are denoted for adsorbent mass and solution volume, respectively.

#### 2.4. Optimization Model with Response Surface Methodology.

Response surface methodology is the empirically statistical method, which allows optimizing the target ( $y$ ) or “response” based on the evaluation of chosen variables ( $x_i$ ) [43]. In this study, three factors as input parameters were selected to investigate including IBU concentration ( $x_1$ ), MIL-53 dosage ( $x_2$ ), and pH ( $x_3$ ). Their random experimental runs were designed according to the guide of the Design-Expert version 10 (DX10) program (Table 1).

The “response” of the model was the removal efficiency ( $y$ ), and thus, the target of this model is to maximize the “response”; the function of three variables is given by the following equation:

$$y = f(x) = \beta_0 + \sum_{i=1}^k \beta_i x_i + \sum_{i=1}^k \sum_{j=1}^k \beta_{ij} x_i x_j + \sum_{i=1}^k \beta_{ii} x_i^2, \quad (2)$$

where  $y$  is the predicted response and  $x_i$  and  $x_j$  are the independent variables ( $i, j = 1, 2, 3, 4, \dots, k$ ). The parameter  $\beta_0$  is the offset coefficient,  $\beta_i$  is the linear coefficient,  $\beta_{ii}$  is the second-order coefficient, and  $\beta_{ij}$  is the interaction coefficient [44].

**2.5. Error Analysis.** In this study, we explored the nonlinear kinetic and isotherm models using error functions, which were fitted by the Origin 9.0 program. Error analysis aims to determine the suitability of any models, and their confidence level could be assessed via commonplace error functions

TABLE 1: List of independent variables and their levels.

Factors	Unit	Code	Levels				
			$-\alpha$	$-1$	$0$	$+1$	$+\alpha$
Initial concentration	mg/L	$x_1$	1.6	5	10	15	18.4
Adsorbent dosage	g/L	$x_2$	0.16	0.5	1	1.5	1.84
pH	—	$x_3$	2.6	4	6	8	9.4

[45]. Thus, coefficient of determination ( $R^2$ ), mean relative error (MRE), and sum square error (SSE) were used, and their mathematical forms were shown in equations (3)–(5). Moreover,  $Q_{i,cal}$  and  $Q_{i,exp}$  are the respective calculated and experimental adsorption capacity values:

$$R^2 = \frac{\sum_{i=1}^n (Q_{i,exp} - \overline{Q_{i,exp}})^2 - \sum_{i=1}^n (Q_{i,exp} - \overline{Q_{i,cal}})^2}{\sum_{i=1}^n (Q_{i,exp} - \overline{Q_{i,exp}})^2}, \quad (3)$$

$$\text{MRE}(\%) = \frac{100}{n} \sum_{i=1}^n \left| \frac{Q_{i,cal} - Q_{i,exp}}{Q_{i,exp}} \right|, \quad (4)$$

$$\text{SSE} = \sum_{i=1}^n (Q_{i,cal} - Q_{i,exp})^2. \quad (5)$$

## 3. Results and Discussion

**3.1. Structural Characterization of MIL-53(Fe).** Figure 3 describes the structural characterization of MIL-53(Fe) using the X-ray diffraction patterns and FT-IR spectra. According to Figure 3(a), several emerging peaks were found at scanning degree of  $9.5^\circ$  (101),  $18.6^\circ$  (002), and  $28.2^\circ$  (302), indicating that the MIL-53(Fe) obtained a crystalline structure. This observation was also commensurate with several previous reports [33, 46, 47], suggesting that the MIL-53(Fe) was solvothermally synthesized.

Moreover, the FT-IR spectrum in Figure 3(b) reveals the collection of functional groups that features the structure of MIL-53(Fe) (Table 2) [48]. In detail, a broad vibration at around  $3420 \text{ cm}^{-1}$  was ascribed to the presence of O-H groups, which adsorbed water existing in the surface of MIL-53(Fe) [49]. The asymmetric ( $\gamma_{as}$  C-O) and symmetric ( $\gamma_s$  C-O) stretching of dicarboxylate linkers could be verified

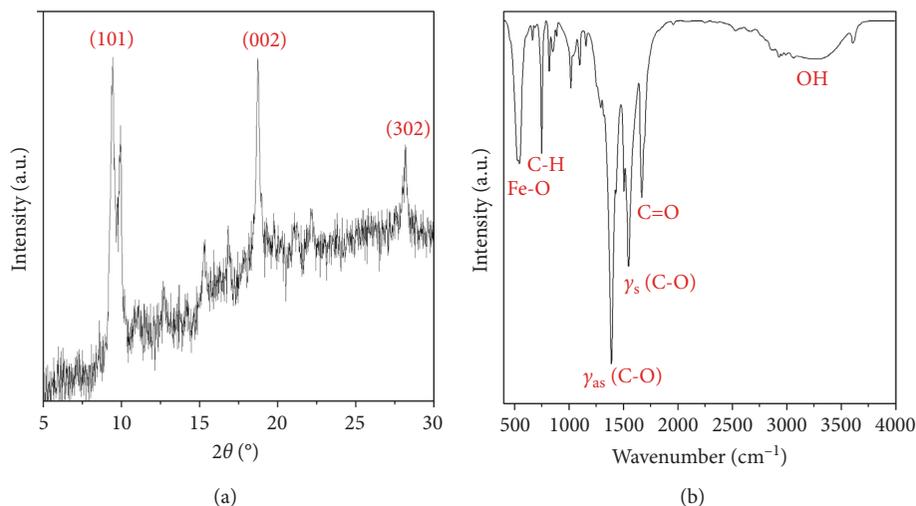


FIGURE 3: X-ray diffraction patterns (a) and FT-IR spectra of MIL-53(Fe) (b).

TABLE 2: The surface functional groups analysis of MIL-53(Fe).

Functional groups	O-H	C=O	$\gamma_{as}$ (C-O)	$\gamma_s$ (C-O)	C-H	Fe-O
Wavenumber ( $\text{cm}^{-1}$ )	3420	1678	1550	1390	745	540

by the appearance of sharp vibrations at  $1550\text{ cm}^{-1}$  and  $1390\text{ cm}^{-1}$ , respectively, [37]. Moreover, the carbonyl groups (C=O) of carboxylate ligand (COO) were visible at  $1678\text{ cm}^{-1}$ , whereas a very sharp peak at  $745\text{ cm}^{-1}$  was consistently corresponding to Csp<sup>2</sup>-H bending vibrations, which belong to the aromatic rings of carboxylates [50]. Especially, the characteristic coordination bonds between Fe<sup>3+</sup> cations and -OOC-C<sub>6</sub>H<sub>4</sub>-COO- carboxylate anions were observed at the low wavenumber ( $540\text{ cm}^{-1}$ ), revealing the existence of a Fe-oxo bond inherent in the structure of MIL-53(Fe) [51]. Therefore, a combination of two characterization results demonstrates that the crystals of MIL-53(Fe) were successfully fabricated.

The morphological properties of MIL-53(Fe) can be analyzed by the SEM technique. Figure 4 showed the MIL-53(Fe) particles at 100 and  $10\text{ }\mu\text{m}$ , which generally well-described the polyhedron-like crystalline structure [32]. However, a clear difference of MIL-53(Fe) samples could be observed between before and after purification. Figure 4(b) demonstrated that a certain part of as-synthesized MIL-53(Fe) morphology was not homogeneous, which may be attributable to the residual 1,4-BDC components. A previous study also implied that this precursor may encapsulate the as-synthesized MIL-53(Fe) crystals [52]. Meanwhile, Figure 4(c) showed a relatively smooth surface of refined MIL-53(Fe) along with the complete disappearance of amorphous solid phases, suggesting that the refinement of as-synthesized MIL-53(Fe) was necessary to eliminate the 1,4-BDC trace [52].

Figure 5(a) diagnosed the textual feature of MIL-53(Fe) using the Raman spectrum. Clearly, a shape peak could be observed at the Raman shift of  $464\text{ cm}^{-1}$ , revealing the existence of gamma bond of Fe-oxo in the structure of MIL-53(Fe). Also, typical peaks of the aromatic C-H bond were found at  $632$  and  $865\text{ cm}^{-1}$ , while the single peak at

$1141\text{ cm}^{-1}$  was ascribed for the bonds between two sp<sup>2</sup>-hybrid carbon atoms of benzene rings and carboxylate groups. Importantly, the asymmetric ( $\gamma_{as}$  C-O) and symmetric ( $\gamma_s$  C-O) footprints of COO- linkers were again confirmed via a couple of consecutive peaks at  $1451$  and  $1501\text{ cm}^{-1}$ , respectively. Finally,  $\nu(\text{C}=\text{C})$  was a kind of typical bond of aromatic cycles, which were emergent at  $1616\text{ cm}^{-1}$ .

To gain the insights into the nature of porosity and pore size in MIL-53(Fe), the pore size distribution was measured and shown in Figure 5(b). It is evident that pore diameters of MIL-53(Fe) exhibited a wide range of sizes, revealing the existence of both micropore and macropore in the structure, but macrosized pore (more than  $50\text{ nm}$ ) was utterly dominant. Notice that there was an infinitesimal amount of micropore, which was less than  $2\text{ nm}$  in length. Moreover, the surface area of MIL-53(Fe) was determined by the N<sub>2</sub> adsorption-desorption isotherm at  $77\text{ K}$ , which was found to be  $5.5\text{ m}^2/\text{g}$ . Tuan et al. also reported the very low surface area, at about  $14\text{ m}^2/\text{g}$ , which may be attributable to the closed pores of MIL-53(Fe) that prevent the arrival of nitrogen molecules [49].

**3.2. Optimization of the Ibuprofen Absorbability of MIL-53(Fe) by RSM Tool.** Herein, we applied the RSM to optimize the removal of IBU in water using the MIL-53(Fe) as an adsorbent. All experiments were designed and analyzed statistically using the DX10 [11]. In detail, three independent variables including initial IBU concentration, MIL-53(Fe) adsorbent dosage, and pH solution at various five levels were investigated. The relationship between IBU removal efficiency and three independent variables can be described by the following equation:

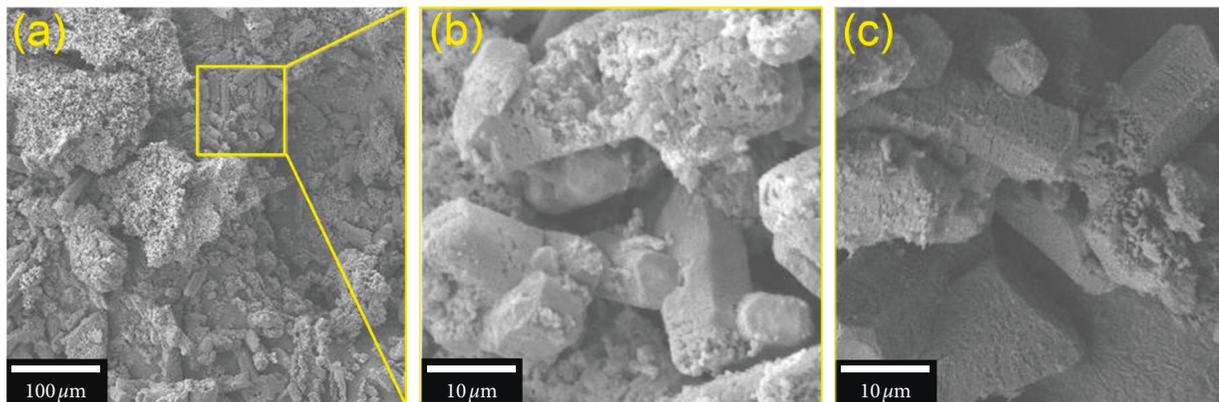


FIGURE 4: SEM images of MIL-53(Fe) before (a), (b) and after refinement (c).

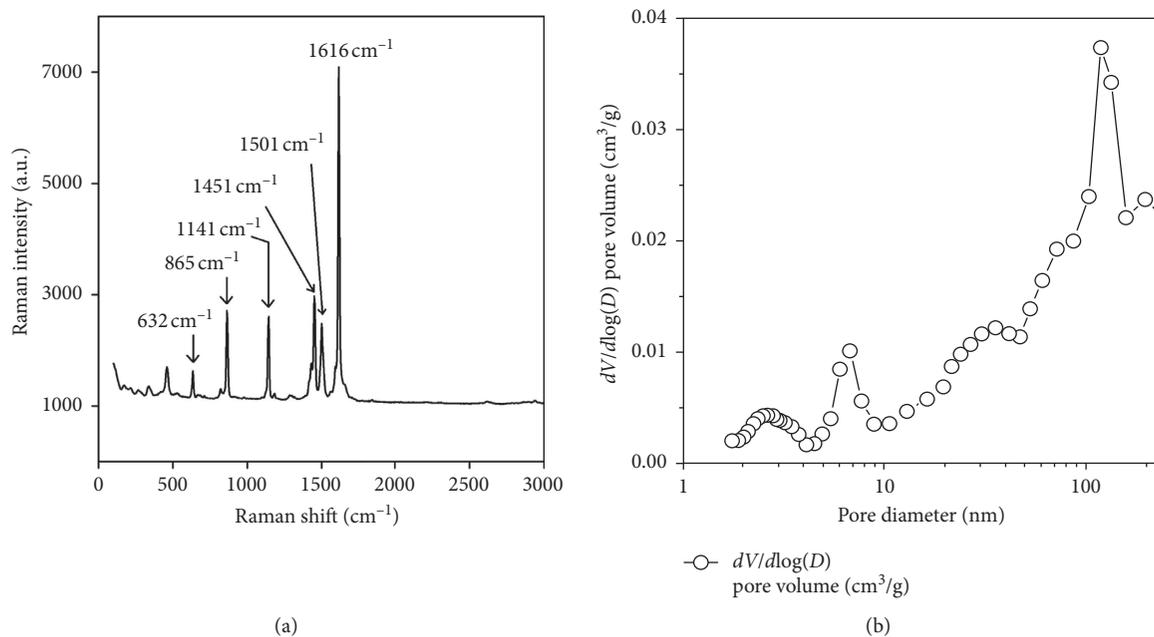


FIGURE 5: Raman spectrum (a) and pore size distribution (b) of MIL-53(Fe).

$$\begin{aligned}
 y(\%) &= 21.56 - 5.21x_1 + 7.15x_2 - 19.58x_3 \\
 &\quad + 6.83x_1x_2 + 0.88x_1x_3 - 4.35x_2x_3 \\
 &\quad + 4.97x_1^2 + 5.69x_2^2 + 11.10x_3^2, \\
 \text{or IBU removal}(\%) &= 21.56 - 5.21(C) + 7.15(\text{dose}) \\
 &\quad - 19.58(\text{pH}) + 6.83(C)(\text{dose}) \\
 &\quad + 0.88(C)(\text{pH}) \\
 &\quad - 4.35(\text{dose})(\text{pH}) + 4.97(C)^2 \\
 &\quad + 5.69(\text{dose})^2 + 11.10(\text{pH})^2.
 \end{aligned}
 \tag{6}$$

The actual and predicted values for the experimental matrix were listed in Table 3. Table 4 illustrates the coefficients of ANOVA data including the sum of squares, degree of freedom, mean square,  $F$  value, and Prob. >  $F$  [43].

Interestingly, determination coefficients ( $R^2$ ) and  $P$  values of the regression model were found to be 0.9621 and <0.0001 with the confidence level of 95%, respectively. Thus, the proposed quadratic model was statistically significant and could be used to assess the effect of factors (initial IBU concentration, MIL-53(Fe) adsorbent dosage and pH) on the IBU absorbability of MIL-53(Fe) [48]. Figure 6(a) also indicates the high compatibility of experimental and predicted values as their data points were closely distributed to the 45-degree line.

Figures 6(b)–6(d) showing the three-dimensional response surfaces reveal the consistent impacts of three factors on the IBU drug removal efficiencies of MIL-53(Fe). Generally, the removal process of IBU was conducive with an increase in the amount of the MIL-53 adsorbent or a decrease in pH values of IBU solutions. Meanwhile, the initial concentration of IBU solution shows a negligible effect on the IBU removal efficiency.

TABLE 3: Experimental design used for investigation of IBU removal over MIL-53(Fe).

N	Variables			IBU removal efficiency (%)	
	$x_1$	$x_2$	$x_3$	Observed	Predicted
1	5	0.5	4	69.8	64.3
2	15	0.5	4	43.8	38.5
3	5	1.5	4	80	73.7
4	15	1.5	4	78.7	75.1
5	5	0.5	8	35.8	32.1
6	15	0.5	8	10.7	9.8
7	5	1.5	8	26	24.1
8	15	1.5	8	30.8	29.0
9	1.6	1	6	37.5	44.4
10	18.4	1	6	23.5	26.9
11	10	0.16	6	20	25.6
12	10	1.84	6	45.1	49.7
13	10	1	2.6	77.1	85.9
14	10	1	10.4	18.6	20.0
15	10	1	6	22.6	21.6
16	10	1	6	17.7	21.6
17	10	1	6	23.8	21.6
18	10	1	6	25	21.6
19	10	1	6	20	21.6
20	10	1	6	22	21.6

Understandably, the improvement of IBU removal percentage may be ascribed to the presence of “adsorption sites” [53]. When an addition of adsorbent was considerable, “adsorption sites” containing the surface functional groups became more dominant, thus increasing the number of IBU molecules captured [54, 55]. By contrast, a decline in the amount of the MIL-53(Fe) adsorbent may result in the rapid saturation of adsorption sites, possibly rendering the treatment of IBU drug ineffective.

Importantly, the decontamination of the IBU pollutant reached the excellent results in the acidic media, while the figures for the basic/neutral solutions were clearly unfavorable. In detail, Figure 6(d) indicates that nearly 100% of IBU could be removed from water at the very low pH values (i.e., pH = 2.6–4.3) and high adsorbent dosage (1.5–1.84 g/L).

By applying the RSM via model confirmation, several optimal conditions were proposed including the factors along with the predicted response value (Table 5). To test the precision and confidence of proposed optimized conditions, a verification experiment was performed using the above proposed conditions. The observed results were in good agreement with the predicted results because there was an ineligious error between predicted and tested results, and “desirability” values were obtained up to 100%, reflecting the excellent closeness of response ( $y$ ) to their ideal values [56]. In other words, the model for the optimization of IBU adsorption over MIL-53(Fe) in this study achieved the high compatibility and thus could be used to design and optimize the experimental conditions.

**3.3. Adsorption Studies.** To gain deeper insights into the adsorption mechanism and behavior of IBU over

MIL-53(Fe), herein, the nonlinear kinetic and isotherm models could be adopted. All experiments were conducted at room temperature, and other experimental conditions were chosen from model optimization (Table 5), at initial concentration (10 mg/L), dosage (1.0 g/L), and pH 2.6. Note that samples were extracted for regular time intervals (0, 10, 20, 40, 60, 80, 100, and 120 min) to investigate the kinetic study, while IBU concentrations were in range from 5 to 20 mg/L. Final IBU content could be measured by using a UV-Vis spectrophotometer at 222 nm.

Any selected model needs to meet the requirements in terms of  $R^2$ , MRE (%), and SSE. A model with a high  $R^2$  value indicates that the predicted data are fitted well with actual data [45]. Meanwhile, lower MRE and SSE values reveal the negligible magnitude of error functions. To assess the models, therefore, terms of  $R^2$ , MRE (%), and SSE were added herein.

For the kinetic models, we optioned four equations including pseudo-first-order, pseudo-second-order, Elovich, and Bangham, which their mathematical forms were illustrated in the equations given in Table 6. Figure 7(a) illustrates the effect of uptake capacity on contact time. It is evident that the adsorption process reached an equilibrium nature after 90 min. According to Table 6, all kinetic models obtained an excellent fitness based on  $R^2$  values (0.981–0.992), indicating the high compatibility between actual and proposed data. Nevertheless, among the models, the pseudo-second-order equation offered the highest degree of suitability because of the highest  $R^2$ , smallest SSE, and very low MRE (%). In fact, Elovich model showed the lowest MRE (3.15%), but its SSE value was so far higher than the pseudo-second-order model, 7.44 compared with 0.39, respectively. Therefore, the pseudo-second-order model could be used to explore the adsorption mechanism of the IBU species onto the adsorbent, which chemisorption plays a crucial role.

For the isotherm models, four equations including Langmuir, Freundlich, Temkin, and Dubinin and Radushkevich (D-R) were applied. Similar to the kinetic models, their mathematical forms were explained in equations given in Table 7. Obviously, the Langmuir demonstrated the most appropriate model via the highest  $R^2$  and lowest MRE and SSE values, suggesting that the monolayer mechanism is more inclining to others. The maximum adsorption capacity ( $Q_m$ ) obtained from the Langmuir equation was calculated at 10.67 mg/g, revealing the favorable adsorption and good capacity of IBU onto MIL-53(Fe).

## 4. Conclusion

The MIL-53(Fe) material was successfully synthesized from the precursors including  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and 1,4-BDC via the solvothermal method and structurally characterized using the X-ray diffraction patterns, FT-IR spectra, SEM, pore size distribution, and Raman. The characterization results implied that the MIL-53(Fe) possessed the crystalline structure, along with a low surface area ( $5.5 \text{ m}^2/\text{g}$ ). Moreover, important functional groups were found (Fe-O, COO, C=O, C-O, C-H, and O-H), proving the presence of these chemical bonds in the structure of MIL-53(Fe). For the optimization

TABLE 4: ANOVA data for the IBU removal models.

Source	Sum of squares	Freedom degree	Mean square	F value	Prob. > F	Note
Model	9093.12	9	1010.35	28.18	<0.0001 <sup>S</sup>	
$x_1$	370.63	1	370.63	10.34	0.0093 <sup>S</sup>	
$x_2$	697.69	1	697.69	19.46	0.0013 <sup>S</sup>	
$x_3$	5235.08	1	5235.08	146.00	<0.0001 <sup>S</sup>	
$(x_1)^2$	372.65	1	372.65	10.39	0.0091 <sup>S</sup>	
$(x_2)^2$	6.13	1	6.13	0.1708	0.6881 <sup>N</sup>	<sup>S</sup> Significant at $p < 0.05$
$(x_3)^2$	151.38	1	151.38	4.22	0.0670 <sup>N</sup>	<sup>N</sup> Nonsignificant at $p > 0.05$
$x_1 \cdot x_2$	356.18	1	356.18	9.93	0.0103 <sup>S</sup>	
$x_1 \cdot x_3$	467.61	1	467.61	13.04	0.0048 <sup>S</sup>	
$x_2 \cdot x_3$	1777.41	1	1777.41	49.57	<0.0001 <sup>S</sup>	

Fit statistics: standard deviations (Std.) = 3.17; mean = 36.43; CV (%) = 16.44;  $R^2 = 0.9621$ .

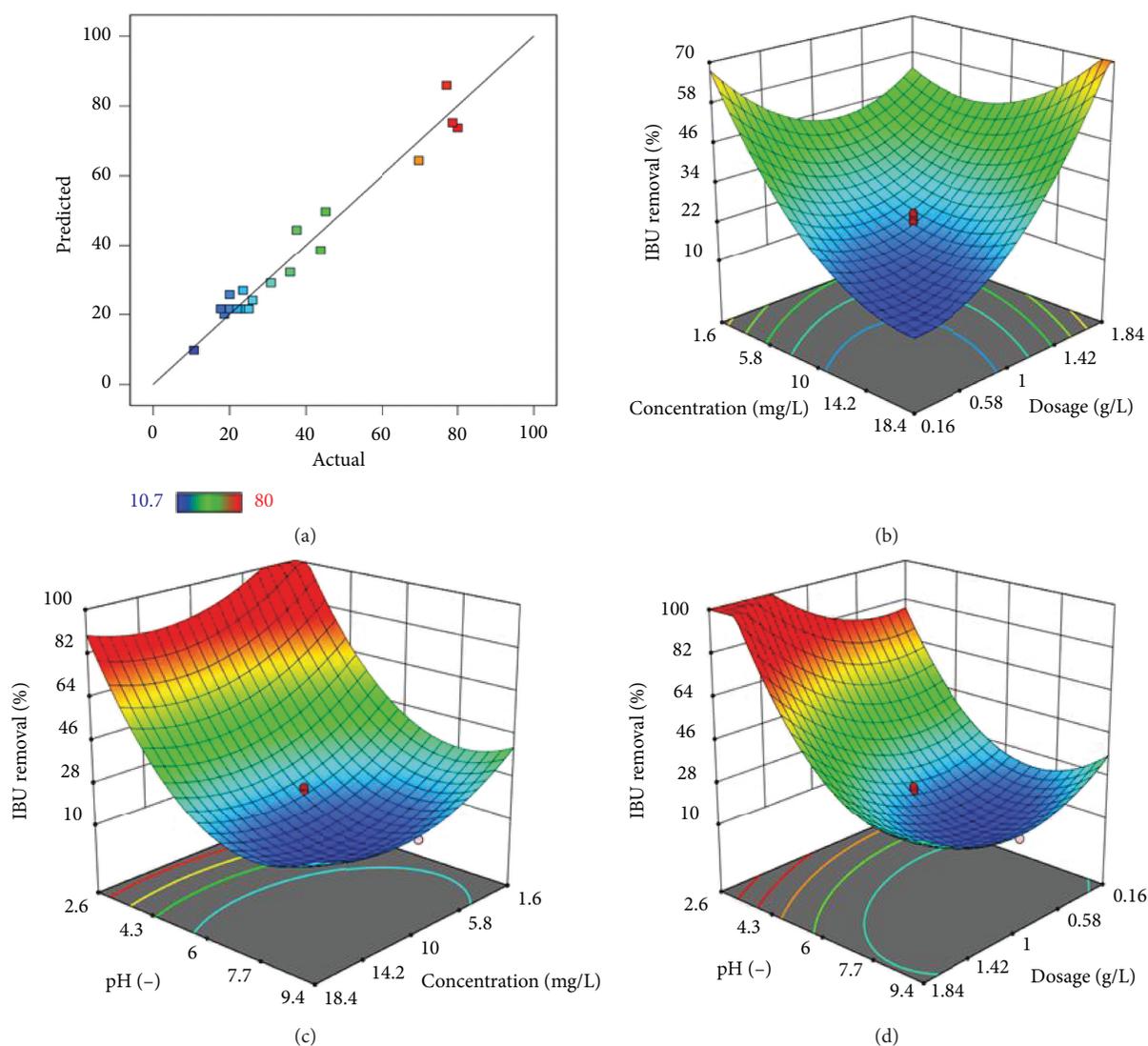


FIGURE 6: Actual versus predicted plots (a) and three-dimensional response surfaces (b)–(d) presenting the effect of factors on the response.

experiment of ibuprofen over MIL-53(Fe), the RSM results indicated that all variables (IBU initial concentration, MIL-53(Fe) dosage, and pH) had a vital impact on the IBU removal efficiency through the very high determination of coefficient ( $R^2 > 0.9$ ) and very low  $P$  value ( $P < 0.0001$ ). Also,

the proposed model was statistically significant and could be used to find out the optimal conditions. The confirmation tests also proved that the model was highly compatible with experimental data because the observed values were consistent with the predicted values and high removal efficiency

TABLE 5: Optimal conditions and confirmation runs.

Concentration (mg/L)	Dosage (g/L)	pH (-)	IBU removal efficiency (%)			"Desirability"
			Predicted (%)	Tested (%)	Error (%)	
5.47	0.67	3.0	82.3	80.2	-2.55	1.0000
10.00	1.00	2.6	85.9	80.8	-5.94	1.0000
8.11	1.51	3.5	83.2	80.0	-3.73	1.0000

TABLE 6: Nonlinear kinetic constants for the adsorption of IBU over MIL-53(Fe).

Kinetic models	Equation	Parameters	Value
Pseudo-first-order	$Q_t = Q_1 \cdot (1 - \exp(-k_1 t))$	$k_1$ (min <sup>-1</sup> )	0.0496
		$Q_1$ (mg/g)	7.87
		MRE (%)	5.29
		SSE	0.83
		$(R_{adj})^2$	0.983
Pseudo-second-order	$Q_t = t / ((1/k_2 Q_2^2) + (t/Q_2))$ $H = k_2 \cdot Q_2^2$	$k_2$ (g/mg·min)	0.0063
		$Q_2$ (mg/g)	9.28
		$H$ (mg/g·min)	0.543
		MRE (%)	3.67
		SSE	0.39
		$(R_{adj})^2$	0.992
Elovich	$Q_t = (1/\beta)(\ln(1 + \alpha\beta t))$	$\alpha$ (mg/g·min)	1.1
		$\beta$ (g/mg)	0.5
		MRE (%)	3.15
		SSE	7.44
		$(R_{adj})^2$	0.989
Bangham	$Q_t = k_B \cdot t^{\alpha_B}$	$k_B$ (mL/(g/L))	1.98
		$\alpha_B$	0.30
		MRE (%)	5.02
		SSE	13.05
		$(R_{adj})^2$	0.981

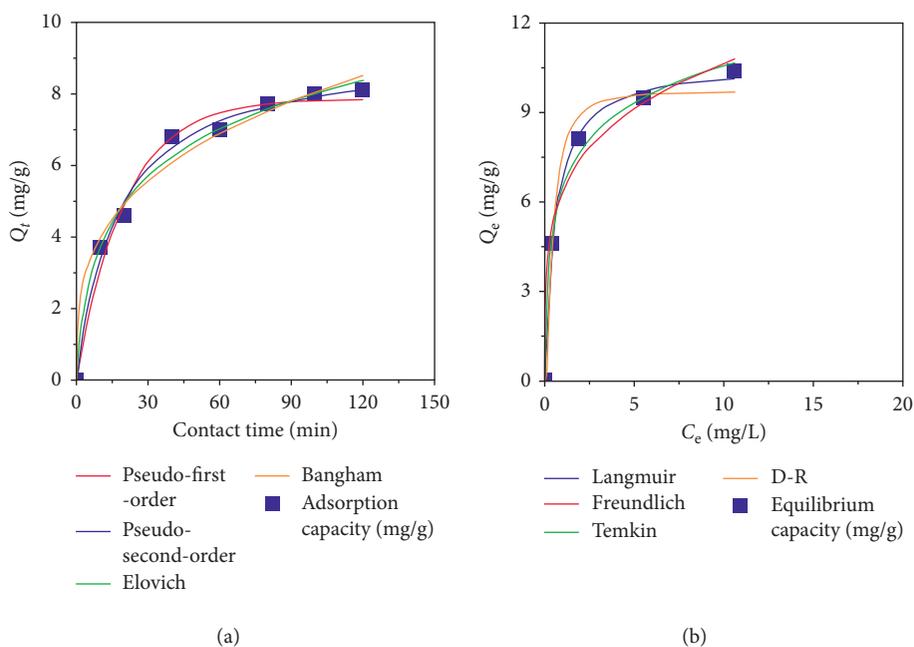


FIGURE 7: Kinetic and isotherm models for adsorption of IBU onto MIL-53(Fe). Experimental conditions consisted of initial concentration (10 mg/L), dosage (1.0 g/L), and pH 2.6 at room temperature.

TABLE 7: Nonlinear isotherm constants for the adsorption of IBU over MIL-53(Fe).

Kinetic models	Equation	Parameters	Value
Langmuir	$Q_e = (Q_m K_L C_e) / (1 + K_L C_e)$ $R_L = 1 / (1 + K_L C_e)$	$k_L$ (L/mg)	1.80
		$Q_m$ (mg/g)	10.67
		$R_L$	0.03
		MRE (%)	2.46
		SSE	0.18
		$(R_{adj})^2$	0.997
Freundlich	$Q_e = K_F C_e^{1/n}$	$k_F$ (mg/g)/(mg/L) <sup>1/n</sup>	6.39
		1/n	0.22
		MRE (%)	6.43
		SSE	0.98
		$(R_{adj})^2$	0.980
		Temkin	$Q_e = B_T \ln(k_T C_e)$ $B_T = (RT)/b$
$B_T$	1.77		
MRE (%)	3.13		
SSE	0.31		
$(R_{adj})^2$	0.993		
D-R	$Q_e = Q_m \exp(-B\epsilon^2)\epsilon = RT \ln(1 + (1/C_e))$ $E = 1/(\sqrt{2B})$		
		$Q_m$ (mg/g)	9.72
		$E$ (kJ/mol)	2.47
		MRE (%)	5.34
		SSE	1.18
		$(R_{adj})^2$	0.978

obtained (80.0–80.8%). Kinetic and isotherm models also suggested that the adsorption process obeyed the chemisorption and monolayer behavior mechanisms.

## Data Availability

No data were used to support this study.

## Conflicts of Interest

The authors declare that there are no conflicts of interest.

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