

Retraction

Retracted: Simple Preparation of the CuO•Fe₃O₄/Silica Composite from Rice Husk for Enhancing Fenton-Like Catalytic Degradation of Tartrazine in a Wide pH Range

Adsorption Science and Technology

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This article has been retracted by Hindawi following an investigation undertaken by the publisher [1]. This investigation has uncovered evidence of one or more of the following indicators of systematic manipulation of the publication process:

- (1) Discrepancies in scope
- (2) Discrepancies in the description of the research reported
- (3) Discrepancies between the availability of data and the research described
- (4) Inappropriate citations
- (5) Incoherent, meaningless and/or irrelevant content included in the article
- (6) Peer-review manipulation

The presence of these indicators undermines our confidence in the integrity of the article's content and we cannot, therefore, vouch for its reliability. Please note that this notice is intended solely to alert readers that the content of this article is unreliable. We have not investigated whether authors were aware of or involved in the systematic manipulation of the publication process.

Wiley and Hindawi regrets that the usual quality checks did not identify these issues before publication and have since put additional measures in place to safeguard research integrity.

We wish to credit our own Research Integrity and Research Publishing teams and anonymous and named external researchers and research integrity experts for contributing to this investigation.

The corresponding author, as the representative of all authors, has been given the opportunity to register their agreement or disagreement to this retraction. We have kept a record of any response received.

References

- [1] K. H. P. Ngoc and A.-T. Vu, "Simple Preparation of the CuO•Fe₃O₄/Silica Composite from Rice Husk for Enhancing Fenton-Like Catalytic Degradation of Tartrazine in a Wide pH Range," *Adsorption Science & Technology*, vol. 2022, Article ID 6454354, 16 pages, 2022.

Research Article

Simple Preparation of the $\text{CuO}\cdot\text{Fe}_3\text{O}_4/\text{Silica}$ Composite from Rice Husk for Enhancing Fenton-Like Catalytic Degradation of Tartrazine in a Wide pH Range

Khanh Huyen Pham Ngoc and Anh-Tuan Vu 

School of Chemical Engineering, Hanoi University of Science and Technology, Vietnam

Correspondence should be addressed to Anh-Tuan Vu; tuan.vuanh@hust.edu.vn

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SiO_2 was prepared from rice husk (RH) with the assistance of cetrimonium bromide (CTAB), and the $\text{CuO}\cdot\text{Fe}_3\text{O}_4/\text{SiO}_2$ composite was prepared by a simple coprecipitation method to enhance the Fenton-like degradation of dyes in a wide pH range. SiO_2 was a mesoporous material with a relatively large surface area of $496.4\text{ m}^2/\text{g}$ and a highly relative pore volume of $1.154\text{ cm}^3/\text{g}$. The Fe_3O_4 and CuO particles with the size of 20–50 nm were well dispersed in the composite, making the composite tighter and causing the disappearance of large pores in the range of 20–55 nm. The surface area and pore volume of the composite were reduced to $248.6\text{ m}^2/\text{g}$ and $0.420\text{ cm}^3/\text{g}$, respectively. $\text{Fe}_3\text{O}_4/\text{SiO}_2$ and Fe_3O_4 samples only exhibited high catalytic activity in an acidic medium, while the $\text{CuO}\cdot\text{Fe}_3\text{O}_4/\text{SiO}_2$ composite could effectively work in a wide pH range of 3–7. Besides, the effects of reaction conditions such as catalyst dosage, H_2O_2 concentration, and initial dye concentration on the catalytic performance of the composite were studied. The optimal conditions for the degradation of dye were tartrazine (TA) concentration of 50 mg/L, dosage catalyst of 0.5 g/L, H_2O_2 concentration of 120 mM, and pH 5. The $\text{CuO}\cdot\text{Fe}_3\text{O}_4/\text{SiO}_2$ composite reached the highest activity at pH 5, showing a degradation efficiency (DE) of 93.3% and a reaction rate of 0.061 min^{-1} . The reusability of the catalyst was investigated by cyclic experiments. The DE of the 3rd reuse remained at 55.1%, equivalent to 93.5% of the first use. The catalytic mechanism for the Fenton system has also been proposed.

1. Introduction

The rice husk is obtained from the milling of rice. It is a huge source of silica raw material that is discharged into the environment every year. Currently, the annual production of rice in the world is estimated at 700 million tons. RH contains about 20% of the weight of rice; its composition includes cellulose (50%), lignin (25%–30%), silica (15%–20%), and moisture (10%–15%) [1]. Vietnam is one of the leading rice-exporting countries in the world [2]; the annual rice production is 37 million tons, equivalent to 7.4 million tons of RH discarded annually. It could be used as fuel, water filter, rice husk firewood, biogas product, construction materials, and activated carbon product [3, 4]. An alternative, using RH to create highly functional silica, is an attractive research to scientists. Many shapes of silica have been made

from RH such as spheres, rods, and plates for applications in construction, environment, energy storage, and catalyst [3, 5–7], where the mesoporous silica and its composite have been proven as an effective material in the adsorption and degradation of organic substances in wastewater due to its high surface area, good thermal stability, and favorable hydrothermal stability [8].

The rapid development of industry, agriculture, and services in developing countries leads to a large amount of wastewater being discharged into the environment every year [8]. Water sources are seriously polluted from wastewater causing serious impacts on ecosystems and human health. One of the typical toxic organic substances is the dye used in textiles, leather, cosmetics, printing, paper, and paint in industries [9]. The dye is the most widely used for dyeing acrylic fibers, which ionize in an aqueous solution

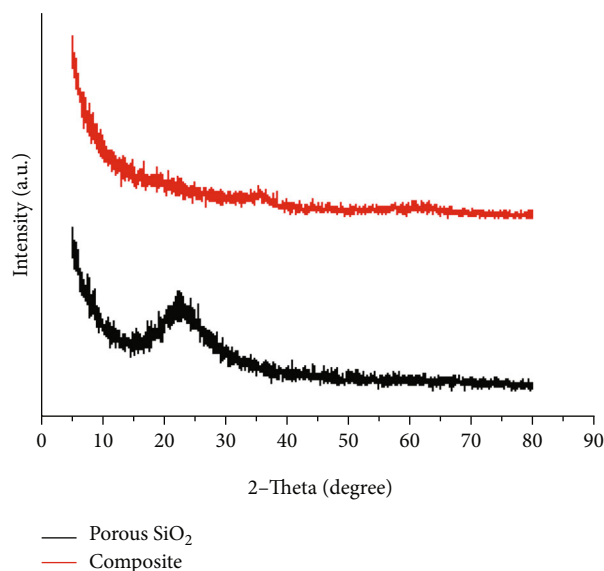


FIGURE 1: XRD patterns of porous SiO_2 and $\text{CuO}\cdot\text{Fe}_3\text{O}_4/\text{SiO}_2$ composite.

and produce colored cations [10]. Dyes have a complex structure that is often stable and resistant to biodegradation [11]. There are more than 10000 different commercial dyes used in the textile process; approximately 15% of the total production is lost as wastewater during dyeing processes [12]. Intermediate products from the degradation of dyes are considered to be a major health hazard to the environment, humans, and other organisms, especially aquatic organisms [13]. Therefore, toxic and persistent organic substances in wastewater need to be removed before being discharged into the environment. There are many methods of removing organic pollutants that have been reported [14–18].

TA is an azo dye with a characteristic $-\text{N}=\text{N}-$ bond [19]. Foods containing too high concentrations of TA will lead to human health hazards such as allergies and asthma, affect the nervous system, and more seriously increase the risk of death. According to international standards, the amount of TA allowed for human consumption is 7.5 mg/kg body-weight/day, in nonalcoholic beverages; TA should not exceed 0.01 g/mL [20, 21]. Nowadays, conventional treatment procedures are inadequate and disabled for handling the highly persistent hazardous materials; experiments are still being conducted to create a more effective method [22].

Typical researches on the electrolysis process for treatment of dyes were the electroactive persulfate process from aqueous solutions for removal of basic Violet 16 [6] and the anodic oxidation process with graphite anode coated with lead dioxide for degradation of methylene blue and real textile wastewater [9]. Photocatalysis showed to be an effective catalyst to remove dyes under irradiation. ZnO could remove phenol under UV-C light [22], nano zerovalent iron (nZVI) can degrade acid red 14 under UV-C light in the presence of H_2O_2 and persulfate ($\text{S}_2\text{O}_8^{2-}$) [23], copper oxide nanoparticles showed high activity with metronidazole antibiotic under UV light [24], and persulfate activated by UV

and ferrous ions could decompose dimethyl phthalate [25]. Adsorption was an efficient process for materials with a large surface area and easy recovery such as clinoptilolite zeolite [11], activated carbon [26], carbon nanotubes modified by nZVI [27], mesoporous magnetite/zeolite nanocomposite [28], $\text{Fe}^{\text{II}}\text{Fe}_2^{\text{III}}\text{O}_4/\text{GO}$ [29], $\text{Fe}_3\text{O}_4/\text{GO}$ [30], iron oxide/carbon nanocomposite [31], and magnetic chitosan/graphene oxide [32]. These materials are currently effective adsorbents for removing basic violet, methylene blue, nitrate, dimethyl phthalate, diphenyl phthalate, 2,4-dinitrophenol, lead, and fluoride. Other methods to enhance the removal of organic compounds in wastewater could be done by adding H_2O_2 to the decomposition process [33–35].

AOPs have been reported as promising technologies for the elimination of organic pollutants due to their high performance, simple operation, and inexpensive material [36] since AOPs were based on the generation of highly oxidizing radicals (hydroxyl radicals OH^\bullet , hydroperoxyl radicals HO_2^\bullet , and superoxide radicals $^\bullet\text{O}_2^-$) to degrade organic compounds into CO_2 , H_2O , and inorganic ions [37]. Also, photocatalysts and Fenton catalysts have proven to be highly effective in the aqueous medium and are suitable for applications in industrial wastewater treatment [1, 38–40].

Fenton catalysts with iron valences of 0, II, and III on silica-based materials were effective catalytic systems for oxidizing toxic and persistent organic substances. The $\text{Fe}_2\text{O}_3\cdot\text{SiO}_2$ composite was synthesized by the impregnation method for degrading tartrazine at 60 mg/L, and the degradation efficiency reached 98.5% in 80 min [1]. Interactive nanospheres in the $\text{Fe}_2\text{O}_3/\text{SiO}_2$ composite synthesized by the emulsion method could improve the catalytic performance, and the degradation efficiency of methylene blue approached 88% in 80 min [41]. The thin slice of iron-mesoporous silica prepared by ball milling followed by uniaxial pressing and calcination could adsorb and degrade methylene blue at efficient removal of 99.94% at the concentration of 1000 mg/L [42]. A mesoporous $\alpha\text{-Fe}_2\text{O}_3/\text{SiO}_2$ composite with a highly ordered mesostructure showed a high adsorption capacity of 90 mg/g and superior heterogeneous Fenton-like catalytic activity for removal of methylene blue; the removal efficiency was 100% at the concentration of 300 mg [43]. SiO_2 -encapsulated zero-valent iron nanoparticles were prepared for degradation of methylene blue; the degradation efficiency was 94.2% at the ethylene concentration of 16 mg/g [44]. However, these Fenton catalytic systems remained with some drawbacks including the difficulty of catalyst recovery, cost-intensive sludge processing, and disposal process, which limited working in the low pH range ($\text{pH} < 3$) [45–47]. This will create difficulties to adjusting the pH for the catalysis process and neutralizing the treated wastewater before being discharged into the environment.

Magnetic particles are commonly used for the Fenton process because they are easily separated from the solution by magnets after the reaction. In addition, Fe_3O_4 has the super magnetic property and both of Fe (II) and Fe (III) irons could activate H_2O_2 to produce strong oxidizing radicals that could enhance its catalytic ability [48, 49]. Moreover, the catalyst activity of Fe_3O_4 could also be improved

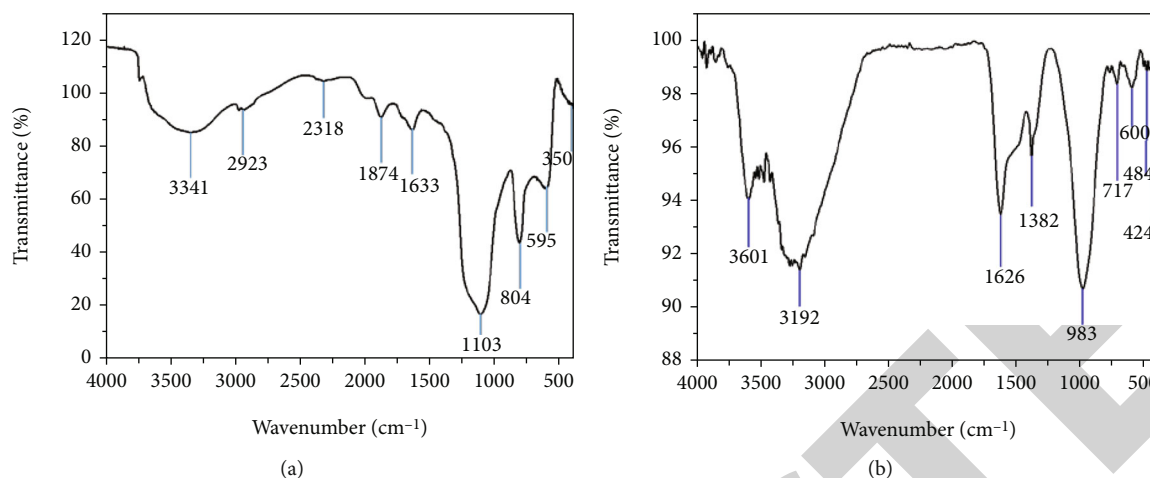


FIGURE 2: FT-IR spectra of (a) SiO_2 and (b) $\text{CuO}\cdot\text{Fe}_3\text{O}_4/\text{SiO}_2$ composite.

by combining it with noble metals [50–52] and transition metal oxides [53–55]. Surface interactions between metal oxide phases, crystal structure, phase structure, and synergistic interactions between components could be the causes for the enhanced catalytic ability in the wide pH range.

In this study, SiO_2 was prepared from rice husk (RH) with the assistance of CTAB and the $\text{CuO}\cdot\text{Fe}_3\text{O}_4/\text{SiO}_2$ composite was prepared by simple coprecipitation method to enhance the Fenton-like degradation of dyes in a wide range of pH in solution. As-prepared samples were characterized by XRD, N_2 adsorption/desorption isotherm, FT-IR, FE-SEM, EDS, and TEM. The catalytic performance of samples was evaluated by the oxidation of tartrazine (TA) in the presence of H_2O_2 . The effects of reaction conditions such as pH, H_2O_2 concentration, catalytic dosage, and initial TA concentration on the degradation of TA were carried out. The degradation kinetics were obtained from fitting the experimental profile with time by using the first-order kinetic model. Additionally, the reusability of catalyst was evaluated by cyclic experiment.

2. Materials and Method

2.1. Materials. Rice husk was obtained from a farm in Thai Binh province of Vietnam, the silica content was determined by mass analysis, and the result showed that rice husk contained 21.3 wt.% of silica. Cetrimonium bromide (CTAB) (99.0%), copper nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2\cdot 3\text{H}_2\text{O}$) (99.0%), iron(II) sulfate heptahydrate ($\text{FeSO}_4\cdot 7\text{H}_2\text{O}$) (99.0%), iron(III) chloride hexahydrate ($\text{FeCl}_3\cdot 6\text{H}_2\text{O}$) (99.0%), NaOH (99.0%), HCl (99.0%), and hydro peroxide (H_2O_2 99.0%) were obtained from Merck. Tartrazine (99%) was purchased from Sigma-Aldrich.

2.2. Synthesis of Porous SiO_2 . The synthesis of silica was modified from the previous report with the assistance of CTAB [56]. Typically, RH is removed from the soil with distilled water and then soaked in 0.5 M HCl for 30 minutes to remove metal impurities. After washing with distilled water to reach pH~7, RH was dried at 100°C for 24 h. Dry RH

was then burned at 600°C under airflow for 2 h to obtain rice husk ash (RHA). Subsequently, 5 g of RHA was added to an Erlenmeyer flask with 100 mL of 2 M NaOH; the mixture was heated and stirred continuously for 2 h to dissolve the silica from the ash. After cooling, the solution was filtered to remove the residues and obtain sodium silicate.

Porous SiO_2 was prepared from sodium silicate by the hydrothermal method. In a typical experiment, 40 mL of abovementioned sodium silicate was added into the mixture of 2.187 g of CTAB and 34 mL of 0.6 M HCl under stirring for 1 h; pH was controlled as 7.5–8.5 by using 6 M HCl. The mixture was aged at 50°C for 24 h. Subsequently, the white gel was transferred into an autoclave and heated up to 100°C for 48 h. The precipitate was washed with distilled water to remove surfactants and acids until neutral. The white solid was dried at 100°C for 12 h before heating at 600°C for 6 h to obtain SiO_2 powder.

2.3. Synthesis of the Porous $\text{CuO}\cdot\text{Fe}_3\text{O}_4/\text{SiO}_2$ Composite. The porous $\text{CuO}\cdot\text{Fe}_3\text{O}_4/\text{SiO}_2$ composite was prepared by the simple coprecipitation method. Typically, 2.156 g of $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$, 4.197 g of $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$, and 0.6655 g of $\text{Cu}(\text{NO}_3)_2\cdot 3\text{H}_2\text{O}$ were added into a beaker containing 200 mL of distilled water under stirring for 20 min; 0.2 g of SiO_2 was then added into the mixture. The pH of the mixture was adjusted to 10.0 by using 3 N NaOH solution and stirred at 60°C for 3 h to form the dark gel. The solid gel was carefully washed several times by distilled water and ethanol and then dried at 60°C at 12 h in an oven to obtain dark powder $\text{CuO}\cdot\text{Fe}_3\text{O}_4/\text{SiO}_2$ composite.

2.4. Characterization. The crystalline phase of samples was investigated by X-ray powder diffraction. XRD patterns were obtained by using a Bruker D8 Advance diffractometer (Germany) with $\text{Cu K}\alpha$ irradiation (40 kV, 40 mA). The 2θ ranging from 20 to 80° was selected to analyze the crystal structure. The morphology and size of the samples were observed by transmission electron microscopy (TEM, JEM-2010) and the emission scanning electron microscopy (FE-SEM, JEOL-7600F). The textural properties were measured

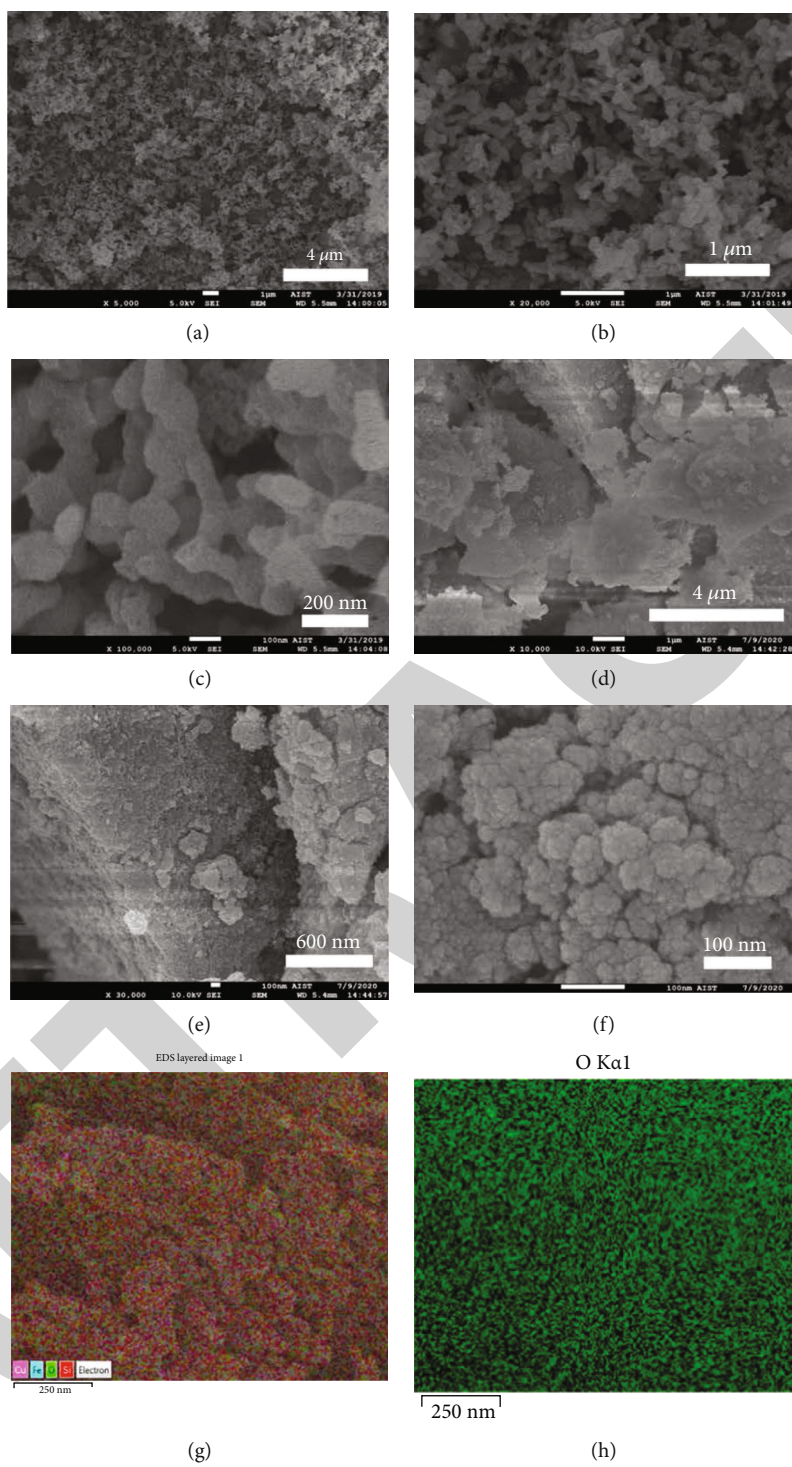


FIGURE 3: Continued.

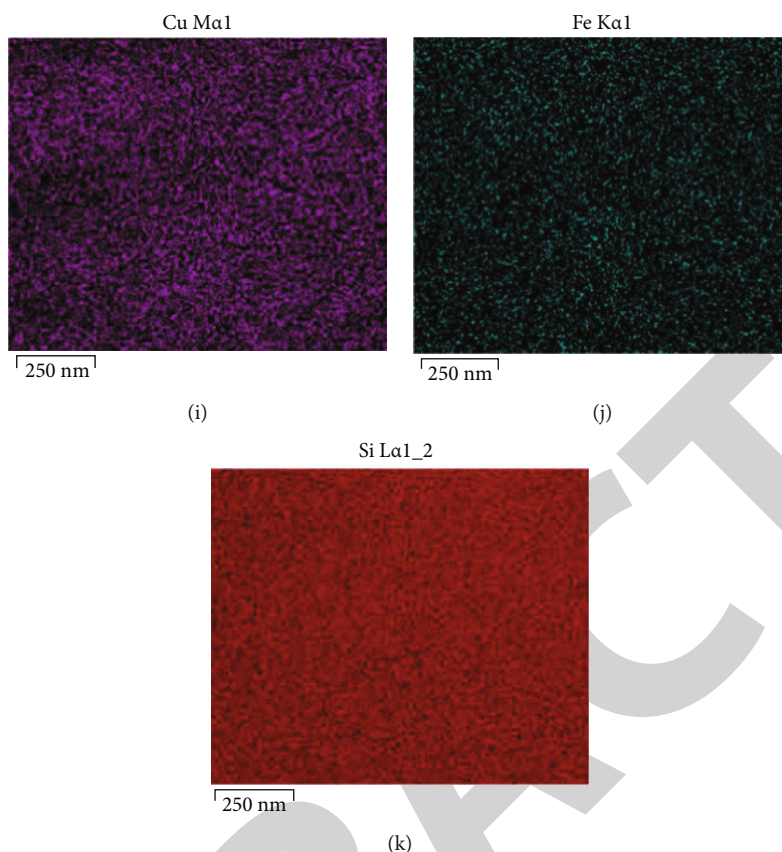


FIGURE 3: (a) FE-SEM images of SiO_2 , (d–f) FE-SEM images and (g) EDS image of $\text{CuO}\cdot\text{Fe}_3\text{O}_4/\text{SiO}_2$ composite, (h) O elemental map, (i) Cu elemental map, (j) Fe elemental map, and (k) Si elemental map of $\text{CuO}\cdot\text{Fe}_3\text{O}_4/\text{SiO}_2$ composite.

via N_2 adsorption/desorption isotherms using micromeritics (Gemini VII). The specific surface area was obtained by using the Brunauer-Emmett-Teller (BET) method; the pore volume and pore diameter were determined by the Barrett, Joyner, and Halenda (BJH) method.

2.5. Fenton-Like Catalyst Test. The batch test was used to evaluate the TA degradation efficiency of the prepared catalyst. 50 mg of the catalyst was added to 100 mL of the dye solution and a certain amount of H_2O_2 . The pH of the solution was adjusted by adding 0.1 M HCl or 0.1 M NaOH. At different time intervals, approximately 2 mL of the mixture was withdrawn and filtered using a syringe filter ($0.45\ \mu\text{m}$ PTFE membrane). The dye concentration was analyzed using a UV-vis spectrophotometer (Agilent 8453) at 426 nm. The degradation efficiency (DE) and rate constant (k_{ap}) of TA in the catalyst were calculated by equations (1) and (2) as follows:

$$\text{DE} (\%) = \frac{C_0 - C_t}{C_0} \times 100\%, \quad (1)$$

$$\ln \frac{C_0}{C_t} = k_{\text{ap}} \times t \quad (2)$$

where k_{ap} (s^{-1}) is the rate constant, C_0 is the initial concentration of TA, C_t is the concentration of TA in time, and t is

reaction time presented by min and s for equations (1) and (2), respectively.

3. Results and Discussion

3.1. Characterization. The X-ray diffraction patterns of SiO_2 and the $\text{CuO}\cdot\text{Fe}_3\text{O}_4/\text{SiO}_2$ composite are shown in Figure 1. The peak at 2θ of 22.8° was attributed to the amorphous silica [57]. The XRD analysis of the composite was relatively different from SiO_2 . The diffraction peak of SiO_2 almost disappeared in the composite. The low-intensity peaks at 2θ of 35.6 and 62.2° could be assigned to Fe_3O_4 (PDF#88-0886) [58]. There were no signals of CuO observed for the composite. However, the composition of the metals in the composite is shown in the EDS result below. This result implied that Fe_3O_4 and CuO oxides were formed only at low crystallinity after the synthesis process by salts and with a short aging time.

FT-IR transmittance spectra of SiO_2 and the $\text{CuO}\cdot\text{Fe}_3\text{O}_4/\text{SiO}_2$ composite are presented in Figure 2. For observation of SiO_2 , the broad peak from $3000\text{--}3700\ \text{cm}^{-1}$ was assigned to the presence of O-H stretching vibration of Si-O-H and adsorbed water (H-O-H) [1]; the peak at $1633\ \text{cm}^{-1}$ could be attributed to the vibration bending of O-H. The intense bands at 1103 , 804 , and $595\ \text{cm}^{-1}$ were associated with the asymmetric and symmetric of Si-O-Si, Si-O, and Si-OH bonds, respectively, as seen in Figure 2(a).

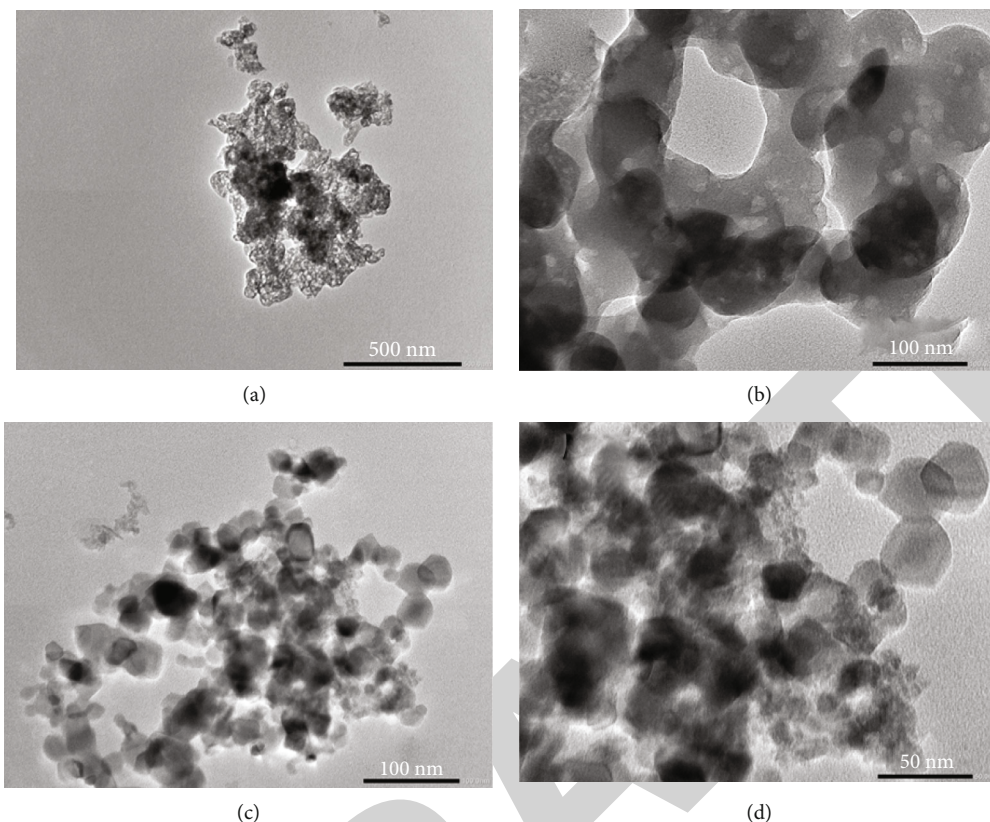


FIGURE 4: (a, b) TEM images of SiO_2 and (c, d) TEM images of $\text{CuO}\cdot\text{Fe}_3\text{O}_4/\text{SiO}_2$ composite.

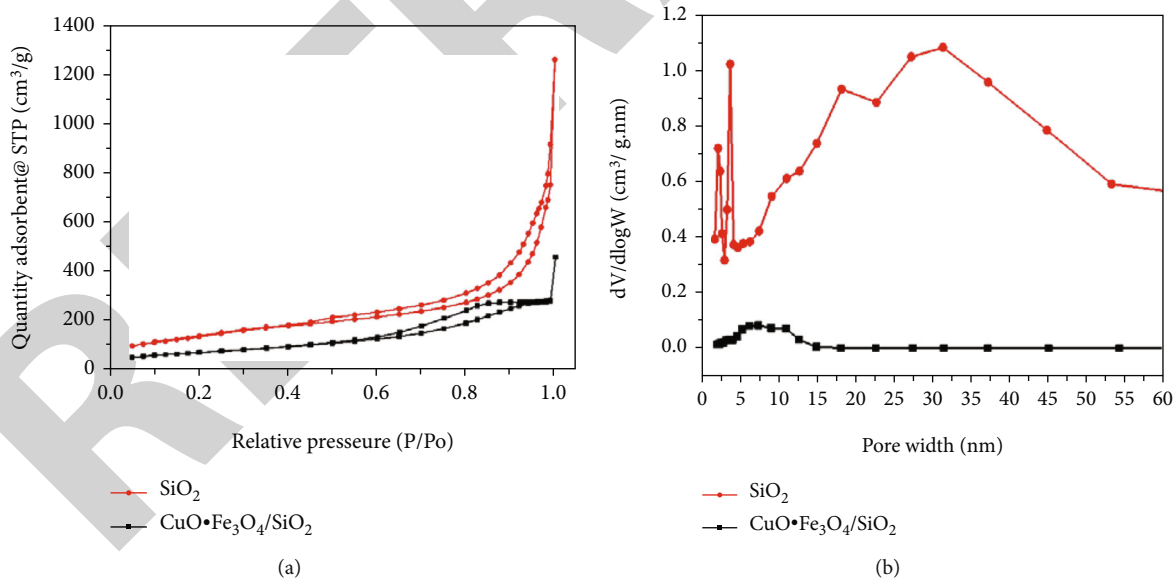


FIGURE 5: (a) N_2 adsorption/desorption isotherms and (b) pore size distributions of SiO_2 and $\text{CuO}\cdot\text{Fe}_3\text{O}_4/\text{SiO}_2$ samples.

The band in $3000\text{--}3700\text{ cm}^{-1}$ of the composite was split into two peaks, which shifted to a smaller wave number. The intense bands at 983 and 717 cm^{-1} came from Si-O-Si vibration. In addition, the bands at 484 and 424 cm^{-1} could be assigned to vibrations of Si-Cu-O and Si-Fe-O, respectively, as seen in Figure 2(b), which confirmed that SiO_2 is indeed bound with CuO and Fe_3O_4 .

Figure 3 FE-SEM images of SiO_2 and the $\text{CuO}\cdot\text{Fe}_3\text{O}_4/\text{SiO}_2$ composite. The structure of SiO_2 was observed as resembling clouds; the uniformly sized SiO_2 particles of about $100\text{--}200\text{ nm}$ were gathered together to form a porous structure, in Figures 3(a)–3(c). Meanwhile, the arrangement of metal oxide particles was tight in the composite and them being placed in the channels of SiO_2 , in Figures 3(d)–3(f).

TABLE 1: Textural properties of as-synthesized SiO_2 and as-synthesized $\text{CuO}\bullet\text{Fe}_3\text{O}_4/\text{SiO}_2$ composite.

Sample	S_{BET} (m^2/g)	Pore volume (cm^3/g)	Average pore size (nm)
SiO_2	496.4	1.154	9.3
$\text{CuO}\bullet\text{Fe}_3\text{O}_4/\text{SiO}_2$	248.6	0.420	6.2

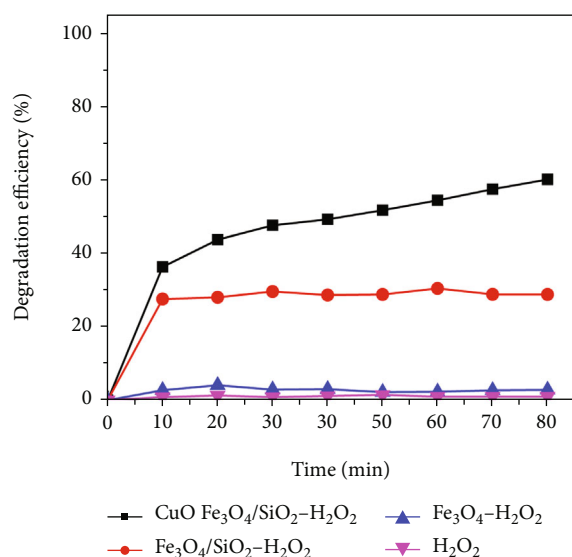


FIGURE 6: Oxidative degradation of tartrazine in the different catalytic systems. The reaction conditions: dosage catalyst of 0.5 g/L, tartrazine concentration of 50 mg/L, H_2O_2 concentration of 12 mM, and pH = 5.

EDS image and elemental maps indicated that Cu and Fe were evenly dispersed in the composite (Figures 3(g)–3(k)), although there was no signal of CuO observed in the XRD (Figure 1).

SiO_2 with a porous structure was observed in the TEM images, in Figures 4(a) and 4(b). There were two types of pores; small pores were formed inside the silica particles after burning the CTAB, and large pores were generated by the arrangement of the silica particles. These could facilitate the dispersion of metal oxide particles on the surface of the silica. As seen in Figures 4(c) and 4(d), the spherical particles of CuO and Fe_3O_4 with a size of about 20–50 nm were uniformly dispersed in the composite. As the result, the porosity and the adsorption capacity of the $\text{CuO}\bullet\text{Fe}_3\text{O}_4/\text{SiO}_2$ composite were decreased. However, its catalytic activity was expected to increase due to the presence of metal oxides.

The N_2 adsorption/desorption isotherms of as-prepared samples are shown in Figure 5. It can be observed in Figure 5(a) that the N_2 adsorption/desorption isotherms of SiO_2 and $\text{CuO}\bullet\text{Fe}_3\text{O}_4/\text{SiO}_2$ exhibited as the IV isotherm with an H_3 hysteresis loop from the IUPAC classification, indicating the presence of the mesoporous structure in the sample. However, the hysteresis loop of the $\text{CuO}\bullet\text{Fe}_3\text{O}_4/\text{SiO}_2$ composite was lowered than that of SiO_2 , showing a remarkable reduction in the surface area of the composite; the surface areas were $496.4 \text{ m}^2/\text{g}$ and $248.6 \text{ m}^2/\text{g}$ for silica and the composite, respectively. The pore size distribution of SiO_2 was in

the range of 2–60 nm, showing the bimodal peak in the range of 2–6 nm and the broad peak in the range of 20–55 nm. This is in complete agreement with the results from the abovementioned TEM. While the large pores ranging from 20–55 nm of the $\text{CuO}\bullet\text{Fe}_3\text{O}_4/\text{SiO}_2$ composite disappeared, small pores of the composite remained and its pore size distribution concentrated in the range of 2–15 nm, in Figure 5(b). The average pore sizes of silica and composite were 9.3 and 6.2 nm, and the pore volumes of silica and composite were 1.154 and $0.420 \text{ cm}^3/\text{g}$, respectively, in Table 1.

3.2. Degradation of Dyes

3.2.1. The Effect of the Catalytic System. The catalytic activity of the as-prepared samples was examined by the oxidation of TA under reaction conditions: dosage catalyst of 0.5 g/L, TA concentration of 50 mg/L, H_2O_2 concentration of 12 mM, and pH = 5. As indicated in Figure 6, the DE value was only 1% in H_2O_2 within 80 min, which proved that TA was a highly persistent compound and it was difficult to degrade in H_2O_2 even though it was a strong oxidizing agent. The degradation of TA for the $\text{Fe}_3\text{O}_4\text{-H}_2\text{O}_2$ system was also negligible. The DE value increased to 20.1% for the $\text{Fe}_3\text{O}_4/\text{SiO}_2\text{-H}_2\text{O}_2$ system and increased to 60.2% for the $\text{CuO}\bullet\text{Fe}_3\text{O}_4/\text{SiO}_2\text{-H}_2\text{O}_2$ system. The porous structure and large specific surface of SiO_2 (Table 1) could facilitate the dispersion of Fe_3O_4 , leading to an increase in the catalytic capacity of $\text{Fe}_3\text{O}_4/\text{SiO}_2$, whereas the simultaneous presence of CuO and Fe_3O_4 oxides on the surface of SiO_2 could enhance the catalytic ability of the $\text{CuO}\bullet\text{Fe}_3\text{O}_4/\text{SiO}_2$ composite.

3.2.2. Effect of the Initial pH. The pH in the solution is a vital factor affecting the catalytic removal of dyes in an aqueous solution. It not only affects the surface charge and functional group structure but also affects the rate formation of the OH^\bullet radical. In this study, the effect of pH in the solution on the degradation of TA in the catalytic systems was investigated at the pH in the solution from 3 to 7 under the fixed other conditions; the results are shown in Figure 7. The catalytic performance of the $\text{Fe}_3\text{O}_4\text{-H}_2\text{O}_2$ and $\text{Fe}_3\text{O}_4/\text{SiO}_2\text{-H}_2\text{O}_2$ systems was strongly dependent on the pH in the solution. The DE values of the $\text{Fe}_3\text{O}_4\text{-H}_2\text{O}_2$ and $\text{Fe}_3\text{O}_4/\text{SiO}_2\text{-H}_2\text{O}_2$ systems at pH 3 in 80 min were 98.2 and 85.2%, respectively. The catalytic performance was sharply reduced with the increase of the initial pH. The DE values for the $\text{Fe}_3\text{O}_4\text{-H}_2\text{O}_2$ system were 2.9 and 1.0%; these were 27.2 and 18.7% at pH 5 and 7 for the $\text{Fe}_3\text{O}_4/\text{SiO}_2\text{-H}_2\text{O}_2$ system, respectively, in Figures 7(a) and 7(b). These results were consistent with previous studies; the Fenton catalyst of iron oxides showed to be effective at an acidic environment (pH 3–4) [59, 60]. Meanwhile, the degradation of TA in the $\text{CuO}\bullet\text{Fe}_3\text{O}_4/\text{SiO}_2\text{-H}_2\text{O}_2$ system was less affected by pH than

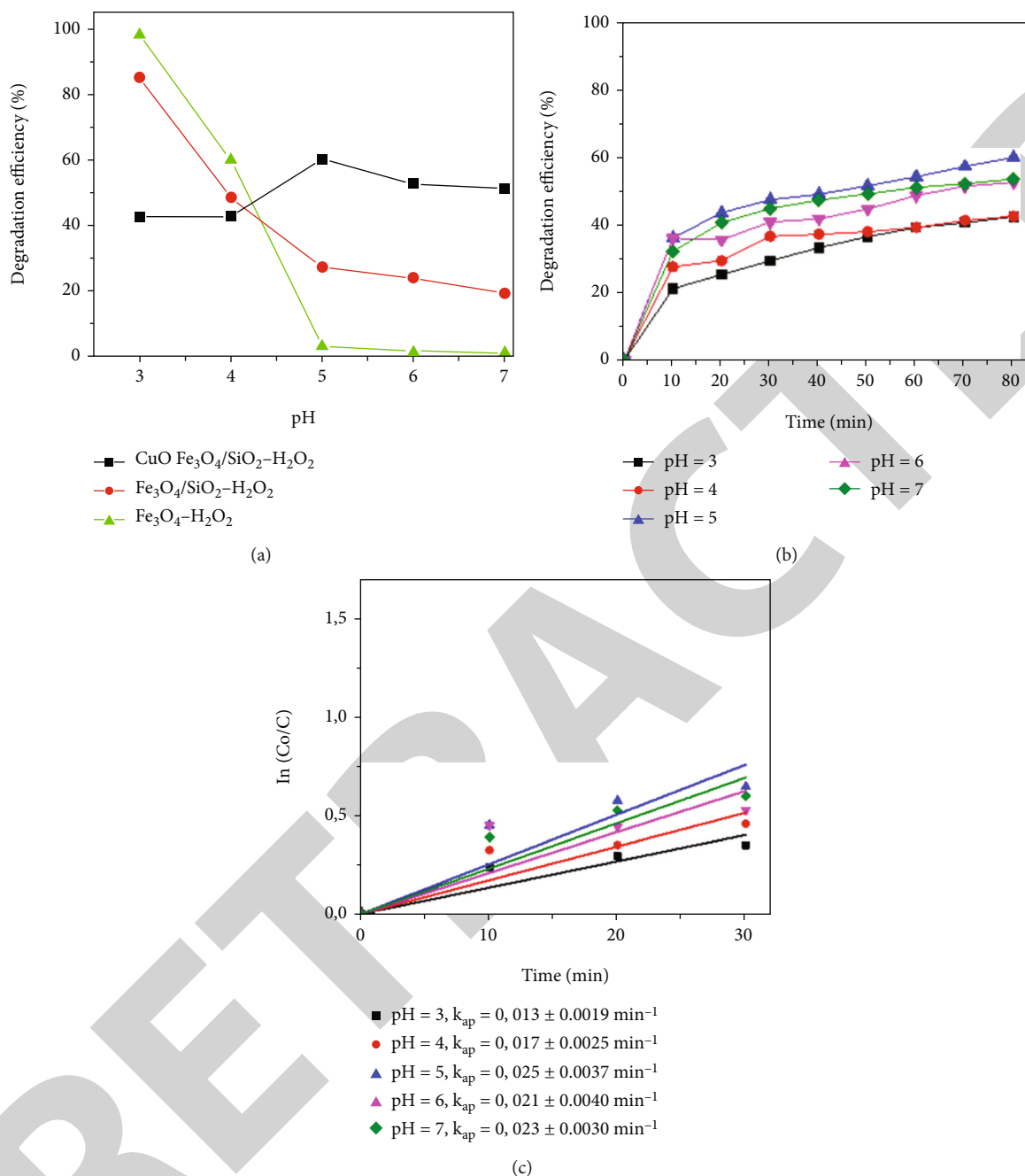


FIGURE 7: (a) Degradation efficiency of tartrazine in the different catalytic systems and pHs, (b) degradation of tartrazine in CuO•Fe₃O₄/SiO₂ at the different initial pHs, and (c) fitting plots.

in the Fe₃O₄-H₂O₂ and Fe₃O₄/SiO₂-H₂O₂ systems. It could work in a wide pH range from 3 to 7, and the catalytic activity was strongest with a reaction rate of 0.025 min⁻¹ at pH 5, in Figure 7(c). The enhancement of catalytic efficiency in the neutral-pH region could be explained by the following reasons: the supporter SiO₂ could expand the pH-active zone of the Fenton catalyst since SiO₂ has multiple hydroxyl groups on the surface. The surrounded -OH groups might chelate with the Fe²⁺ and Fe³⁺ ions to form the weak chelation, benefiting the Fenton reaction at neutral pH [40, 61]. Alternatively, the formation of [Cu(H₂O)₆]²⁺ was concur-

rent with the generation of [Fe(H₂O)₆]³⁺, which was soluble in the Fenton reaction cycle, which enhanced generating hydroxyl radicals even at high pH [59].

3.2.3. Effect of H₂O₂ Concentration. The effect of the H₂O₂ concentration on the catalytic performance of the CuO•Fe₃O₄/SiO₂-H₂O₂ system was investigated by increasing the H₂O₂ concentration up to 180 mM at the fixed other conditions (TA concentration of 50 mg/L, dosage catalyst of 0.5 g/L, and pH 5). The degradation efficiency and fitting plots are presented in Figure 8. The absence of H₂O₂ in the

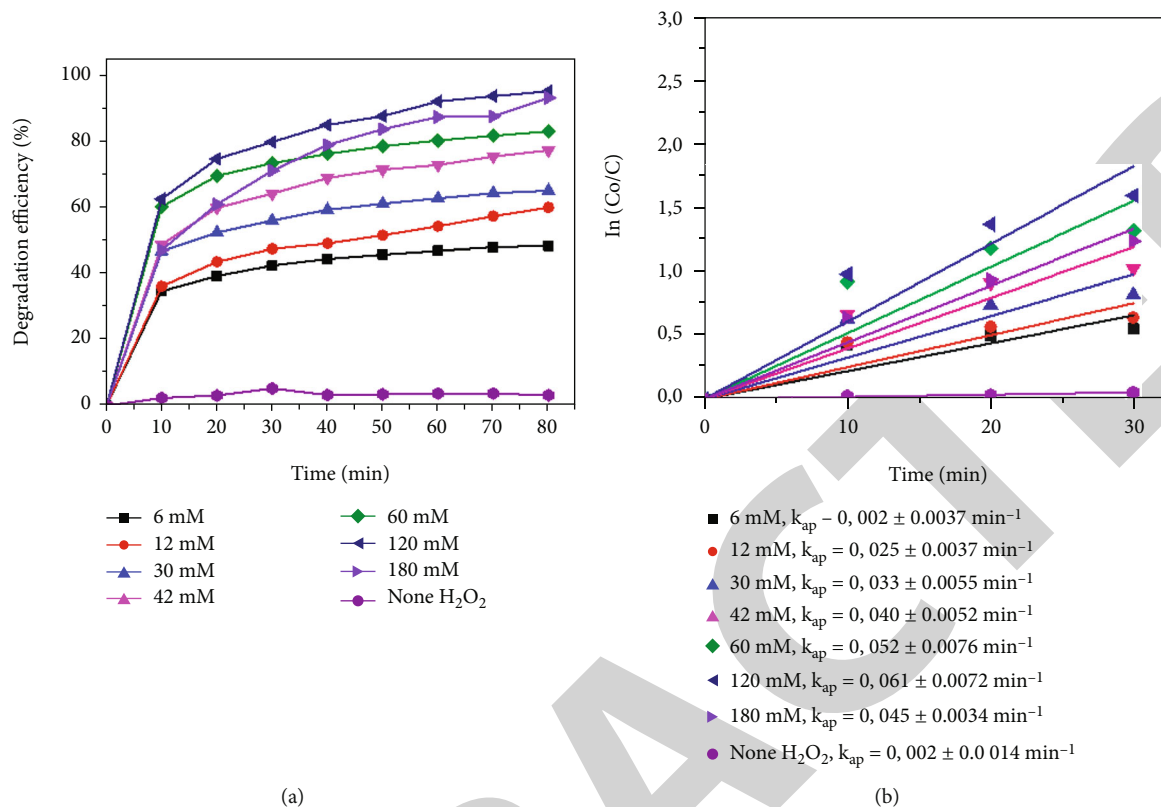


FIGURE 8: (a) Oxidative degradation of tartrazine at the different H₂O₂ concentrations and (b) fitting plots. The reaction conditions: dosage catalyst of 0.5 g/L, tartrazine concentration of 50 mg/L, and pH=5.

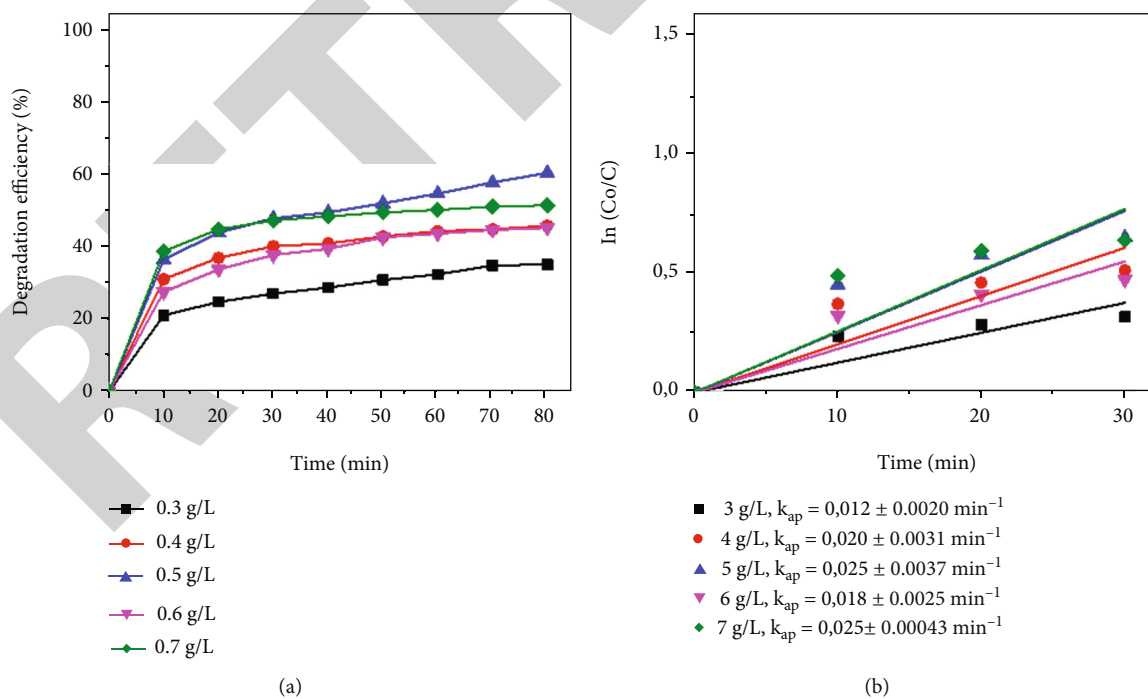


FIGURE 9: (a) Oxidative degradation of tartrazine at the different catalyst dosages and (b) fitting plots. The reaction conditions: tartrazine concentration of 50 mg/L, H₂O₂ concentration of 12 mM, and pH = 5.

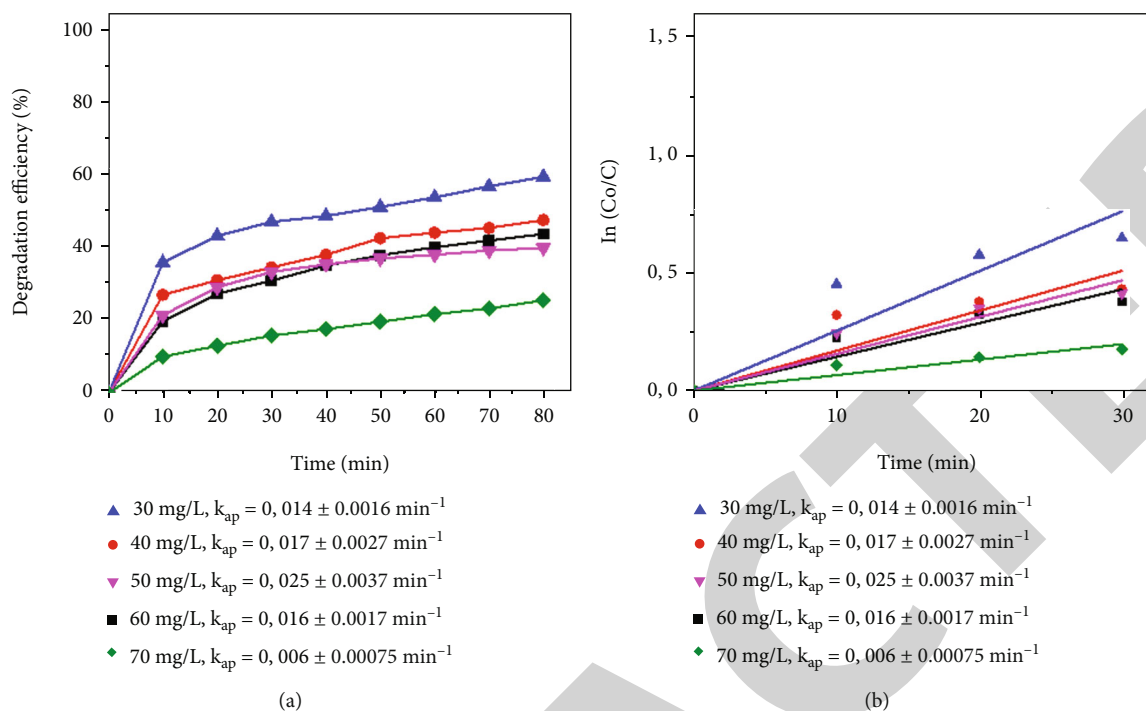


FIGURE 10: (a) Oxidative degradation of tartrazine at the different concentrations of tartrazine and (b) fitting plots. The reaction conditions: dosage catalyst of 0.5 g/L, H_2O_2 concentration of 12 mM, and pH = 5.

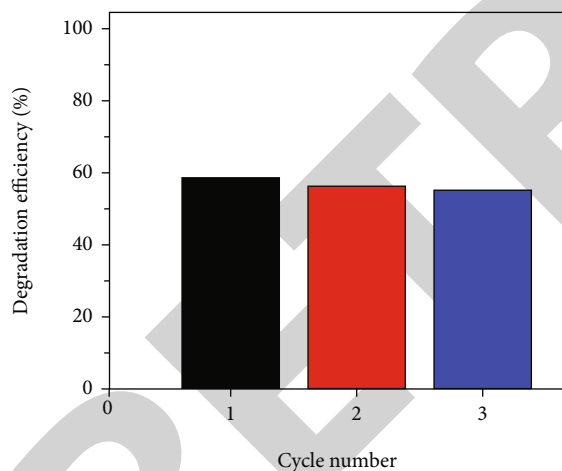
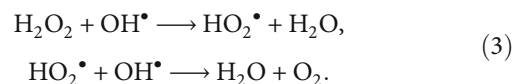


FIGURE 11: Reusability test of as-synthesized $CuO \cdot Fe_3O_4/SiO_2$ catalyst. Reaction condition: tartrazine concentration of 50 mg/L, dosage catalyst of 0.5 g/L, H_2O_2 concentration of 12 mM, and pH = 5.

solution led to low the degradation reaction, and the DE and the reaction rate were 3.2% and 0.002 min^{-1} , respectively. These values significantly increased to 48.6% and 0.022 min^{-1} , respectively, in the presence of H_2O_2 at 6 mM. When the concentration of H_2O_2 increased, the DE and reaction rate gradually increased, which achieved 93.3% and 0.061 min^{-1} , respectively, at 120 mM. The increase of the concentration of H_2O_2 could increase rate generation of the hydroxyl radical. However, further increasing the concentration of H_2O_2 to 180 mM, the catalytic performance was

reduced and the DE and reaction rate were 92% and 0.045 min^{-1} , respectively. When the concentration of H_2O_2 exceeded the critical level, the reaction rate and degradation efficiency decrease since the residual H_2O_2 molecules could act as hydroxyl radical recovery agents; OH^\bullet can recombine to form HO_2 and O_2 as expressed in equation (3) [62].



3.2.4. Effect of the Catalyst Dosage. The effect of the catalyst dosage on photocatalytic performance was studied to determine the optimum amount of photocatalyst added to the catalytic process. In this study, the catalyst dosage varied from 0.3 up to 0.7 g/L under the fixed conditions (TA concentration of 50 mg/L, H_2O_2 concentration of 12 mM, and pH 5); the results are presented in Figure 9. The reaction increased when raising the catalyst dosage from 0.3 to 0.5 g/L, showing the increase of DE within 80 min from 34.9 to 60.1%. However, the reaction was declined at the higher catalyst dosage than 0.5 g/L; the DE values were 44.9 and 51.1% for the catalyst dosages of 0.6 and 0.7 g/L, respectively. The obtained results are related to the number of active sites on the catalyst surface, which increase with the addition of the catalyst, leading to enhanced photocatalytic performance. Meanwhile, the high catalyst concentration ($>0.5 \text{ g/L}$) can lead to agglomeration of the reaction sites thereby slowing the TA removal efficiency [63, 64]. In addition, quenching of OH^\bullet radicals by excess iron ions in the reaction process, equation (4) [1], may also be

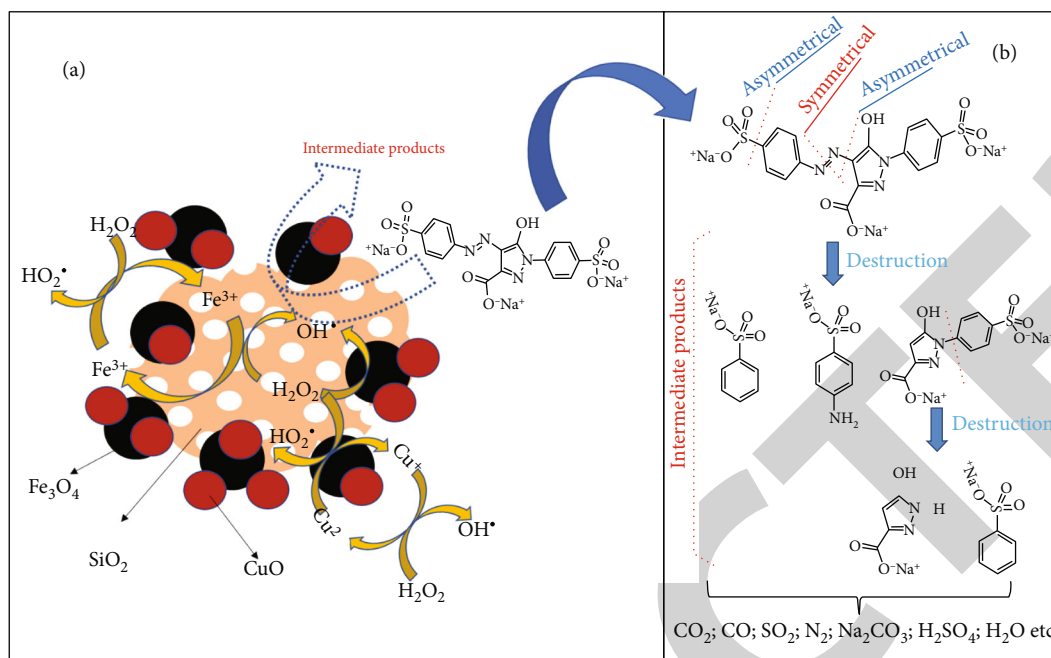
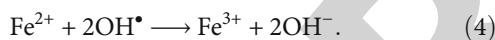


FIGURE 12: (a) The reaction mechanism of tartrazine on the $\text{CuO}\cdot\text{Fe}_3\text{O}_4/\text{SiO}_2$ composite and (b) possible route to the destruction of tartrazine in as-synthesized $\text{CuO}\cdot\text{Fe}_3\text{O}_4/\text{H}_2\text{O}_2$ system.

responsible for the result [1].



3.2.5. Effect of the Initial Dye Concentration. The influence of the initial dye concentration on the catalytic efficiency of the $\text{CuO}\cdot\text{Fe}_3\text{O}_4/\text{SiO}_2$ composite was demonstrated in the TA concentration range of 30–70 mg/L under fixed conditions (dosage catalyst of 0.5 g/L, H_2O_2 concentration of 12 mM, and pH 5), and the obtained results are presented in Figure 10. It indicated that the optimum TA concentration was 50 mg/L; the DE and reaction rate reached 60.1% and 0.025 min^{-1} , respectively. At lower concentrations, the frequency of collisions between the TA molecules and the catalyst surface was low, leading to a slow reaction [65]. At concentration above 50 mg/L. The degradation efficiency was decreased with an increase in TA concentration. Which could be assigned to either the low ratio of $[\text{OH}^\bullet]/[\text{TA}]$ at a similar catalyst dosage and H_2O_2 concentration or the block of the interaction of dyes molecules with active sites of the catalyst due to the competition of intermediates generated in the dye degradation process [66].

3.3. Reusability of the Catalyst and Reaction Mechanism Discussion. For a catalyst, reproducibility is one of the important parameters to advance to commercial application. At the end of each experiment, the catalyst was filtered and washed alternately with distilled water and ethanol 2–3 times and then dried in the oven at 80°C for 12 h for the next cycle. The DE slightly decreased after each cyclic experiment. The efficiency of the 3rd reuse was 55.1%, equivalent to 93.5% of the first use, in Figure 11.

The mechanism of oxidative degradation of TA by H_2O_2 in the $\text{CuO}\cdot\text{Fe}_3\text{O}_4/\text{SiO}_2$ catalyst is proposed in Figure 12. Porous SiO_2 acts as a supporter; the good adsorption can increase the interaction between H_2O_2 and the catalyst surface. Therefore, the formation of free radicals occurs rapidly. $\text{SiO}_2\text{-Fe}^{2+}/\text{Fe}^{3+}$ may activate H_2O_2 , leading to the formation of hydroxyl (OH^\bullet) and perhydroxyl (HO_2^\bullet) radicals according to reaction (5). In addition, the OH^\bullet and HO_2^\bullet radicals can be created by $\text{SiO}_2\text{-Cu}^{2+}$ via reaction (6). And, the OH^\bullet and HO_2^\bullet radicals oxidize TA to form CO_2 , H_2O , and other byproducts based on reaction (7). However, OH^\bullet plays a significant role in the oxidation of organic pollutants because it has higher oxidation potential than HO_2^\bullet [67]. The fragmentation mechanism of TA can be proposed in Figure 12(b) including the cleavage of the symmetrical and asymmetrical azo bonds by the OH^\bullet radical [1].

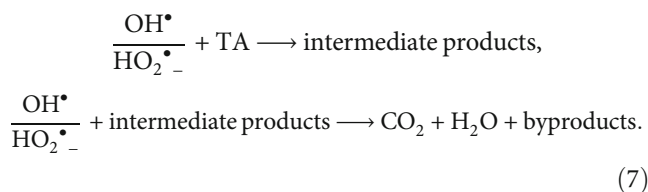
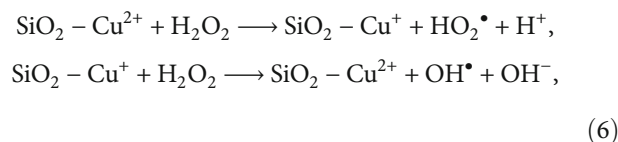
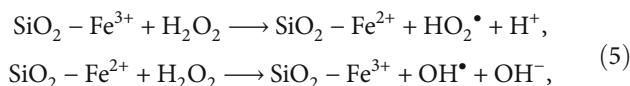
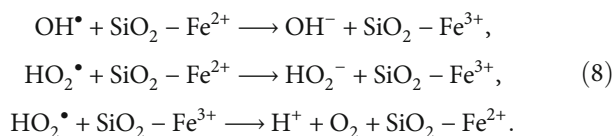


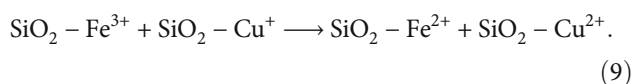
TABLE 2: Comparison of the removal efficiency of the dyes by different catalysts.

Catalyst/adsorbent	Reaction conditions	Observation	Reference
As-synthesized CuO•Fe ₃ O ₄ /SiO ₂ /H ₂ O ₂ , Fenton-like catalyst	[cat.] = 0.5 g/L, [H ₂ O ₂] = 12 mM, pH = 5, [TA] = 50 mg/L, T = 30°C	93.3% of dye was removed within 80 min and 55.1% in the third cycle	This work
Fe ₂ O ₃ •SiO ₂ /H ₂ O ₂ , Fenton-like catalyst	[cat.] = 0.5 g/L, [H ₂ O ₂] = 12 mM, pH = 3, [TA] = 50 mg/L, T = 30°C	98.5% of dye was removed within 80 min and 86.7% in the third cycle	[1]
Sodium alginate/Fe ₃ O ₄ , Fenton-like catalyst	[cat.] = 5 g/L, [H ₂ O ₂] = 100 ppm, pH = 5, [BPA] = 20 ppm, T = 30°C	95% of BPA was removed within 120 min	[69]
Al, Fe-pillared clays, Fenton-like catalyst	[cat.] = 5 g/L, [TA] = 50 mg/L, [H ₂ O ₂] = 0.12 M, T = 75°C	97.5% of dye was removed within 240 min	[70]
Powder-activated carbon/Fe ₃ O ₄ , Fenton-like catalyst	[cat.] = 0.3 g/L, pH = 3, [H ₂ O ₂] = 3 mL/L, [metronidazole] = 50 mg/L	96.12% of metronidazole was removed within 90 min	[71]
Fe electrode; electro-Fenton	[H ₂ O ₂] = 0.32 mM/L, [NaCl] = 0.3 mg/L, pH = 3, [diazinon] = 20 ppm, δ = 5.14 mA/cm ²	100% of diazinon was removed within 34.49 min	[72]
SS316/β-PbO ₂ anode, electro-Fenton, and sono-electro-Fenton	[FeSO ₄] = 0.24 g/L, [NaCl] = 0.1 g/L, pH = 5.3, [H ₂ O ₂] = 30 mg/L, [diazinon] = 45.6 mg/L, voltage = 13.8 V	92% of diazinon was removed; 73.2% of COD and 67.4% of TOC were reduced after 75 min	[73]
SS316/β-PbO ₂ , Fenton, and electro-Fenton	[FeSO ₄] = 0.3 g/L, [H ₂ O ₂] = 0.12 mg/L, [oxytetracycline] = 20 mg/L, pH = 3.53, δ = 3.85 mA/cm ²	Oxytetracycline was removed at 84.7%, 73.4%, and 98.2% in electrochemical, Fenton, and electro-Fenton processes, respectively, after 42 min	[74]
3D/SEF/PAC/Fe ₃ O ₄ , sono-electro-Fenton	[cat.] = 5 g/L, [H ₂ O ₂] = 0.2 mL/L, [FeSO ₄] = 0.08 mg/L, [2, 4 - D] = 50 mg/L, pH = 3, δ = 5 mA/cm ² , [Na ₂ SO ₄] = 0.3 g/250 mL	96.2% of 2,4-dichlorophenoxyacetic acid was removed, and 92.31% of COD and 86.5% of TOC were reduced after 60 min	[75]
Fe electrode-sodium persulfate, electro-Fenton	[cat.] = 0.09 g/L, [Na ₂ S ₂ O ₈] = 0.9 g/L, [NaCl] = 0.2 g/L, [BV16] = 45 mg/L, pH = 5, U = 11.43 V	95% of dye was removed, and 57.14% of COD was reduced after 48.5 min	[10]
Graphite/β-PbO ₂ anode, electrochemical degradation	pH = 5.75, δ = 10 mA/cm ² , [Na ₂ SO ₄] = 78.8 mg/L	96.2% of methylene blue was removed after 50 min	[13]
UVC/Na ₂ S ₂ O ₈ /Fe ²⁺	[SPS] = 0.601 mM, [Fe ²⁺] = 0.075 mM, [dimethyl phthalate] = 5 mg/L, pH = 11	97% of dimethyl phthalate was removed, and 64.2% of TOC was reduced within 90 min	[25]
UV/ZnO, photocatalyst	[cat.] = 0.15 g/L, pH = 5, [phenol] = 10 mg/L, UV lamp = 125 W	94.2% of phenol was removed after 30 min	[22]
Au/ZnO/H ₂ O ₂ photocatalyst	[cat.] = 0.5 g/L, [H ₂ O ₂] = 50 mM, pH = 6, [dye] = 10 mg/L, Hg lamp = 250 W	99.2% of dye was removed after 30 min	[76]
Magnetic zeolite nanocomposite (MZNC) (zeolite : Fe ₃ O ₄ = 2 : 1), adsorption	[ads.] = 1 g/L, pH = 3, T = 50°C	96.12% of dimethyl phthalate was removed within 20 min, and the removal efficiency was 70.63% in the tenth cycle	[28]
Magnetic iron oxide/graphene oxide (MGO), adsorption	[ads.] = 0.334 g/L, pH = 5.38, [diethyl phthalate] = 4.241 mg/L	100% of diethyl phthalate was removed within 3.723 min	[29]
GO-Fe ₃ O ₄ , adsorption	[ads.] = 0.178 g/L, pH = 4.45, [2, 4 - dinitrophenol] = 50.10 mg/L, ultrasound frequency = 40.02 kHz	89.94% of 2,4-dinitrophenol was adsorbed, and the adsorption of the reuse adsorbent in both systems after 10 th consecutive cycles was reduced by about 22%	[30]
Clinoptilolite zeolite/Fe ₃ O ₄ nanoparticles, adsorption	[ads.] = 0.5 g/L, [BV16] = 25 mg/L, pH = 7, mixing speed = 250 rpm	99% of dye was removed after 45 min	[11]
Lignin-containing cellulose (LCNF), adsorption	[ads.] = 0.3 g/L, [Pb] = 10 mg/L, pH = 6, T = 25°C	99% of Pb was removed after 60 min	[77]

In addition, with the appearance of free radicals, Fe^{3+} and Fe^{2+} ions will be regenerated according to equation (8) [1, 36]. However, this process is quite slowly.



On other hand, the standard redox potential value of $\text{Fe}^{3+}/\text{Fe}^{2+}$ ($E^\circ = 0.77 \text{ V}$) is larger than that of $\text{Cu}^{2+}/\text{Cu}^+$ ($E^\circ = 0.17 \text{ V}$). Therefore, the presence of $\text{Cu}^{2+}/\text{Cu}^+$ will promote the regeneration of Fe^{3+} and Fe^{2+} according to equation (9) [36, 68] as follows:



3.4. Comparison with Other Catalysts. The catalytic performance of the as-prepared $\text{CuO}\bullet\text{Fe}_3\text{O}_4/\text{SiO}_2$ composite was compared with other catalysts recently studied on the removal of persistent organic compounds in water such as Fenton [1, 69–71], electro-Fenton [10, 13, 25, 72–75], photocatalyst [22, 76], and adsorption [11, 28–30, 77]. The reaction conditions and decomposition efficiency of these catalysts are listed in Table 2. The removal efficiency is dependent not only on the type of catalyst and the nature of the organic compound but also on the temperature, the stirring rate, the pH of the solution, the reaction time, and the concentration of the reactants. Therefore, direct comparison among catalysts is a challenge but the relative performance of the $\text{CuO}\bullet\text{Fe}_3\text{O}_4/\text{SiO}_2$ catalyst can be evaluated indirectly.

In Table 2, in comparison with the catalytic mechanism as a Fenton-like system, the DE of as-prepared $\text{CuO}\bullet\text{Fe}_3\text{O}_4/\text{SiO}_2$ was lower but the pH range for reaction occurred was wider than that of $\text{Fe}_2\text{O}_3/\text{SiO}_2$, sodium alginate/ Fe_3O_4 , Al, Fe-pillared clays, and powder-activated carbon/ Fe_3O_4 . The electron-Fenton system using the Fe electrode, SS316/ $\beta\text{-PbO}_2$, 3D/SEF/PAC/ Fe_3O_4 , Fe electrode-sodium persulfate, and graphite/ $\beta\text{-PbO}_2$ anode had a high degradation rate, but these processes required additional conditions associated with the reaction such as the addition of electrolyte, application of the current, and designing the appropriate electrode. Photocatalysts based on ZnO or Au/ZnO have a faster degradation rate of tartrazine than $\text{CuO}\bullet\text{Fe}_3\text{O}_4/\text{SiO}_2$, but the oxidation reaction took place at a low dye concentration, 10 mg/L. Adsorbents of GO- Fe_3O_4 , magnetic zeolite nanocomposite, clinoptilolite zeolite/ Fe_3O_4 nanoparticles, and lignin-containing cellulose had relatively high removal of organic compounds, but their poor reuse was a limitation for these materials. Therefore, the $\text{CuO}\bullet\text{Fe}_3\text{O}_4/\text{SiO}_2$ composite prepared by the simple coprecipitation method is expected to reduce the cost of the catalyst for large-scale application.

4. Conclusion

Mesoporous SiO_2 was successfully prepared from RH with the assistance of CTAB. Silica had an amorphous structure with a relatively large surface area of $496.4 \text{ m}^2/\text{g}$ and a relatively high pore volume of $1.154 \text{ cm}^3/\text{g}$. The $\text{CuO}\bullet\text{Fe}_3\text{O}_4/\text{SiO}_2$ composite was successfully prepared from obtained silica by a simple coprecipitation method for oxidizing dye. Metal oxide particles, Fe_3O_4 and CuO , of poor crystallinity and spherical shape with a particle size of approximately 20–50 nm, were well dispersed on the porous structure of SiO_2 . These could reduce the textural values of the $\text{CuO}\bullet\text{Fe}_3\text{O}_4/\text{SiO}_2$ composite; the surface area, pore volume, and average pore size of the composite were $248.6 \text{ m}^2/\text{g}$, $0.420 \text{ cm}^3/\text{g}$, and 6.2 nm, respectively.

The effects of reaction conditions such as catalyst dosage and initial dye concentration on the catalytic performance of the composite were studied. The reusability of the catalyst was investigated by cyclic experiments. The adsorption ability of the composite was decreased; however, the catalytic efficiency of the composite for oxidizing dye could be enhanced. The degradation of TA for the $\text{Fe}_3\text{O}_4\text{-H}_2\text{O}_2$ system was also negligible. The DE was increased to 60.2% for the $\text{CuO}\bullet\text{Fe}_3\text{O}_4/\text{SiO}_2\text{-H}_2\text{O}_2$ system. Porous SiO_2 acted as a supporter; the good adsorption could increase the interaction between H_2O_2 and the catalyst surface. Therefore, the formation of free radicals occurred rapidly. The $\text{SiO}_2\text{-Fe}^{2+}/\text{Fe}^{3+}$ from Fe_3O_4 might activate H_2O_2 leading to the formation of hydroxyl (OH^\bullet) and perhydroxyl (HO_2^\bullet) radicals. In addition, the presence of $\text{Cu}^{2+}/\text{Cu}^+$ could promote the regeneration of Fe^{3+} and Fe^{2+} . As the result, the catalytic efficiency of $\text{CuO}\bullet\text{Fe}_3\text{O}_4/\text{SiO}_2$ could be enhanced in the wide pH range of 3–7.

Data Availability

The research 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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