An Initial Evaluation on the Adsorption of SO\textsubscript{2} and NO\textsubscript{2} over Porous Fe\textsubscript{3}O\textsubscript{4} Nanoparticles Synthesized by Facile Scalable Method

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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\textsubscript{2}), sulfur dioxide (SO\textsubscript{2}), 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\textsubscript{2} and H\textsubscript{2}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\textsubscript{3}O\textsubscript{4} nanostructured material is a potential candidate due to its stability, high surface area, and easy synthesis [9]. Some researchers have pointed out that Fe\textsubscript{3}O\textsubscript{4} 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\textsubscript{3}O\textsubscript{4} as an adsorbent for the removal of nitrogen dioxide and sulfur dioxide.

The removal of SO\textsubscript{2} and NO\textsubscript{2} 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 SO2 and NO2 in fires due to its flammable nature.

In this work, Fe3O4 nanoparticles were prepared by a facile scalable method and applied as an adsorbent for the adsorption of NO2 and SO2. The material was characterized by a number of analytical techniques. The Fe3O4 nanoparticles exhibited good adsorption abilities in the removal of SO2 and NO2.

2. Experimental Section

2.1. Synthesis of Fe3O4 Nanoparticles. All chemicals were of analytical grade. Iron(III) chloride hexahydrate (FeCl3·6H2O), iron(II) chloride tetrahydrate (FeCl2·4H2O), ammonia solution 25% (NH3·H2O), 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 (Fe3O4) nanoparticles were prepared by the following coprecipitation method [16–18].

In brief, FeCl3·6H2O (0.05 mol, 13.52 g) and FeCl2·4H2O (0.03 mol, 5.96 g) were dissolved in 100 mL DI water with a Fe2+/Fe3+ 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 Fe3O4 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 N2 adsorption/desorption at 77K 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 microscopy (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 at a heating rate of 10°C/min, 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 Fe3O4 nanoparticles were exposed to dried SO2 and NO2 at a particular time in the fixed bed reactor under ambient temperature. These gases were mixed with nitrogen as a carrier gas (5% SO2 or NO2 in the N2 atmosphere). The Fe3O4 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⁻¹ 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 SO2 and NO2.

3. Results and Discussion

3.1. Characterization of Fe3O4 Nanoparticles. The porous, interconnected Fe3O4 nanoparticles were synthesized using a facile scalable method. The mixture solution of FeCl3 and FeCl2 was prepared with a Fe2+/Fe3+ molar ratio of 0.6. The used Fe27/Fe28 molar ratio is higher than the Fe27/Fe28 molar ratio in Fe3O4 because a part of Fe28 oxidized to Fe29 will lead to the lower Fe28/Fe29 molar ratio. The increase of Fe28 concentration can attain the ideal Fe28/Fe29 molar ratio of ~0.5. Then, the ammonium solution was added dropwise into the solution until pH = 11.0 to achieve Fe3O4 nanoparticles with high purity. Figure 1 shows the X-ray diffraction (XRD) patterns of the synthesized Fe3O4. All peaks were indexed to cubic Fe3O4 (JCPDS: 01-088-0315) without any impurity phase. However, γ-Fe2O3 has the same crystal structure and a lattice spacing as Fe3O4. To distinguish Fe3O4 from γ-Fe2O3, the d value of lattice spacing of (311) was calculated by Bragg’s equation. The d-spacing value (311) of Fe3O4 was calculated to be 2.5249 Å, similar to the value of 2.52516 Å (standard cubic Fe3O4: 01-088-0315). As reported by Iida et al. [18], the standard d-spacing value (311) of γ-Fe2O3 is 2.5177 Å (γ-Fe2O3, JCPDS: 00-039-1346). It can infer that the phase of the obtained material is completely matched with the phase of the standard cubic Fe3O4.

Moreover, TPRCO profiles of synthesized Fe3O4 further proved that the obtained material was pure Fe3O4. As shown in Figure 2, TPRCO profiles illustrated two distinct peaks of the reduction process, corresponding to two-step reduction of Fe3O4 → FeO and FeO → Fe. There was no peak of the Fe2O3 → Fe3O4 reduction process, referring that there was no presence of Fe2O3 in the synthesized material. The reduction temperature of the two-step reduction was approximately 285°C (Fe3O4 → FeO) and 595°C (FeO → Fe). These reduction reactions can be described as follows [19–21]:

\[
\text{Fe}_3\text{O}_4 + \text{CO} \rightarrow 3\text{FeO} + \text{CO}_2
\]

\[
\text{FeO} + \text{CO} \rightarrow \text{Fe} + \text{CO}_2
\]

According to these reports [19–21], the reduction of Fe3O4 by carbon monoxide starts in the temperature range of ~509–807°C, which was higher than the reduction temperature of Fe3O4 in our study. The lower reaction temperature can be explained due to nanometer-sized Fe3O4, reacting with carbon monoxide more easily than crystalline Fe3O4.

The morphology of Fe3O4 was observed using FE-SEM. As shown in Figure 3(a), Fe3O4 exhibited a uniform granular shape with nanoparticles interconnected to each other. The Fe3O4 nanoparticles have a diameter of ~10 nm. Besides, the
interconnected Fe₃O₄ nanoparticles formed void spaces which intercalated among Fe₃O₄ 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 Fe₃O₄ particles was calculated to be ∼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 Fe₃O₄ nanoparticles with the narrow particle-size distribution and the nanosize of Fe₃O₄ [23]. The particle-size distribution of Fe₃O₄ changes from 7 to 13 nm, revealing the good uniform of Fe₃O₄ nanoparticles. The nanometer-sized Fe₃O₄ was expecting to achieve a high specific area. The porous structure of Fe₃O₄ was characterized using N₂ adsorption-desorption isotherms. As shown in Figure 3(c), isotherm adsorption of Fe₃O₄ 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 Fe₃O₄. Via BET and BJH analysis, the specific area, average pore diameter, and pore volume of Fe₃O₄ were determined to be approximately 115.90 m²/g, 10.63 nm, and 0.30 cm³/g, respectively. The relatively high pore size of the Fe₃O₄ 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°C/min from room temperature to 700°C to evaluate the purity of Fe₃O₄ materials again, as shown in Figure 3(d). The weight gain near 100°C was attributed to the oxidation of Fe₃O₄ to γ-Fe₂O₃. 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 Fe₃O₄, making them react with oxygen more easily than crystalline Fe₃O₄. Nevertheless, the temperature near 100°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 Fe₃O₄ in the obtained sample was estimated to be 2.21 and 97.79%, respectively (Figure 3(d)).

3.2. Adsorption Ability of Fe₃O₄ Nanoparticles. Figure 4 shows the adsorption abilities of Fe₃O₄ after exposing to NO₂ in conditions of the study. As shown in Figure 4(a), the intensities of the IR features after 15 minutes exposure to NO₂ start to change, suggesting that the amount of NO₂ was adsorbed on the surface of Fe₃O₄. The adsorption of NO₂ at room temperature leads to an intensity increase of the 1386 cm⁻¹ band, corresponding to the band of nitrate (NO₃⁻) [26]. The adsorption mechanism of NO₂ on the Fe₃O₄ surface was reported by Eltouny et al. [27] via the following equations:

\[
\begin{align*}
2\text{NO}_2 \text{ (gas)} & \rightarrow 2\text{NO}_2 \text{ (adsorbed)} \\
2e^- + 2\text{NO}_2 \text{ (adsorbed)} & \rightarrow 2\text{NO}_2^- \text{ (adsorbed)} \\
\text{NO}_2^- \text{ (adsorbed)} + \text{NO}_2^- \text{ (adsorbed)} & \rightarrow \text{NO}_3^- \text{ (adsorbed)} + \text{NO} \text{ (gas)} + e^- \\
\text{NO}_3^- \text{ (adsorbed)} + \text{NO}_2 \text{ (gas)} & \rightarrow \text{NO}_3^- \text{ (adsorbed)} + \text{NO} \text{ (gas)}
\end{align*}
\]

(2)

The intensity of this peak increases as the time exposing to NO₂ gas increases, suggesting that the larger amount of NO₂ was adsorbed. The uptake of NO₂ by the Fe₃O₄ nanoparticles was shown in Figure 4(b). The amount of NO₂ adsorbed by the Fe₃O₄ reached the saturation level after 60 minutes of exposure. The mass of NO₂ adsorbed by the Fe₃O₄ after 60 minutes of exposure was recorded at 108.5 mg/g of Fe₃O₄. The high adsorption values of the Fe₃O₄ sample were owing to its larger pore volume and high surface area. Furthermore, the presence and mass of NO₂ in the Fe₃O₄ sample were also measured by SEM-EDX.
analysis. As shown in Figure 4(c), the signal of N, Fe, and O elements was detected in the Fe$_3$O$_4$ 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$_3$O$_4$. This result was similar to the adsorption mass of NO$_2$ by the Fe$_3$O$_4$ in Figure 4(b). The morphology of the Fe$_3$O$_4$ 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$_3$O$_4$ 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$_3$O$_4$ sample. Furthermore, the XRD pattern of Fe$_3$O$_4$ after exposing with NO$_2$ (Figure 4(b) inset) did not show any change, compared with the XRD pattern of Fe$_3$O$_4$ (Figure 1). The good stable structure can retain the adsorption ability after the regeneration and repeating the NO$_2$/Fe$_3$O$_4$ adsorption many times.

The adsorption abilities of Fe$_3$O$_4$ were further examined with the SO$_2$ gas. Figure 5 shows the adsorption ability of Fe$_3$O$_4$ with SO$_2$. Figure 5(a) shows the FTIR spectra obtained after exposing the Fe$_3$O$_4$ 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$_3$O$_4$ sample. The adsorbed amount of SO$_2$ was displayed in Figure 5(b). The mass of SO$_2$ adsorbed by the Fe$_3$O$_4$ was recorded to 40.5 mg/g of Fe$_3$O$_4$ at the saturation level after 60 minutes of exposure. Moreover, the presence and the adsorption mass of SO$_2$ in the Fe$_3$O$_4$ sample was evaluated by SEM-EDX analysis (Figure 5(c)). The signal of the S element was found to be
Figure 4: (a) FTIR of Fe₃O₄ samples after exposing to NO₂ gas at the particular time; (b) NO₂ adsorption on Fe₃O₄ samples; (c) SEM-EDX spectra; (d) FE-SEM image of Fe₃O₄ after 60 min of exposure to NO₂. Inset in Figure 4(b) shows the XRD pattern of Fe₃O₄ after 60 min of exposure to NO₂.

Figure 5: Continued.
1.95 % wt. of SO₂ in the sample, corresponding to 3.90 % wt. in the sample after 60 minutes of exposure. This quantity was calculated to \( \sim 40.6 \text{ mg/g of Fe}_3\text{O}_4 \), similar to the obtained adsorption of Fe₃O₄ in Figure 5(b). The surface of the Fe₃O₄ sample after 60 minutes of exposure with SO₂ was analyzed using FE-SEM measurement. As shown in Figure 5(d), the highly porous structure of Fe₃O₄ was sustained, and no significant change was realized (compared with Figure 3(a)). Moreover, the phase state of Fe₃O₄ (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

Fe₃O₄ nanoparticles have successfully been synthesized via the facile scalable method, in which Fe₃O₄ nanoparticles well achieved a porous structure with the high specific area and purity. The Fe₃O₄ nanoparticles exhibited good adsorption with toxic gases. The surface of the Fe₃O₄ nanoparticles adsorbed high amounts of SO₂ and NO₂ of 40.5 mg/g of Fe₃O₄ and 108.5 mg/g of Fe₃O₄, 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 Fe₃O₄ 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.

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