STUDY ON SYNTHESIS OF MnFe$_2$O$_4$/GNPs COMPOSITE AND APPLICATION ON HEAVY METAL REMOVAL

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ABSTRACT

Nowadays, composite materials between mixed-metal oxides and graphene are widely studied due to their multiple applications on different fields. MnFe$_2$O$_4$ is a magnetic material which has the ability to absorb toxic heavy metal in water. Graphene nanoplatelets (GNPs) with about 10 layers, is one of type of graphene. GNPs was used as matrix for the fine distribution of metal oxide nanoparticles. Surface area for the absorption process can be increased. Composite was synthesized using solvothermal method, in which mixed-metal oxide nanoparticles were directly formed in-situ from precursor salts onto GNPs surface. Synthesized material was analyzed using XRD, SEM and EDX methods to determine its properties. Heavy metal absorption capacity was also studied and showed good results.

Keywords: environmental treatment, MnFe$_2$O$_4$, GNPs, composite, solvothermal, heavy metal absorption.

1. INTRODUCTION

In Vietnam, the rapidly growing industrialization and the fast growing factories lead to water being contaminated toxic heavy metals. The exposure to these heavy metals is considered a major health risk due to their toxicity and carcinogenicity. Among them, lead is a common environmental pollutant. Lead exposure can occur from various routes like air, soil, commerical products and especially from water. Causes of lead contamination often linked to industrial use of lead, include factories and facilities that produce lead-acid batteries, lead wire and pipe, metal recycling and foundries. Lead builds up in the body can damage brain and kidneys; in severe cases anemia, coma and death may occur.

In recent years, nanoparticles of magnetic materials have been used to remove heavy metal from water. These materials are useful because of their invaluable magnetic properties, such as in magnetic seperation. Among them, MnFe$_2$O$_4$ have been proven to be a potential heavy metals absorbent. Manganese ferrite have spinel structure and its properties depend on morphology and size, which can be controlled by synthesis parameters [1]. Various methods are used to produce
MnFe₂O₄ nanoparticles, such as solid state reactions [2], combustion synthesis [3], thermal decomposition [4], coprecipitation [5] and hydrothermal method [6].

On the other hand, graphene nanoplatelets is multi-layered graphene, and thus it has many interesting properties [7]. GNP's has many oxygenated function groups and high surface area, which make it a good absorbent by nature. When combine together, MnFe₂O₄/GNP's composite is a promising candidate for heavy metal removal, as material can be easily separated out of the water being treated using a magnet.

In this paper, the MnFe₂O₄/GNP's composite was synthesized by hydrothermal method, in which the mixed-oxide particles were formed in-situ onto the GNP's surface. The purpose of this method is to distribute evenly and avoid the agglomeration of oxide particles, thus increase the surface area so the absorption process is more effective.

2. EXPERIMENTAL

2.1. Preparation

2.1.1. Materials

Mn(NO₃)₂ 50 % solution, Fe(NO₃)₃.9H₂O 98.5 %, Pb(OAc)₂.3H₂O 99 %, K₂S₂O₈ 99.5 %, H₂SO₄ 98 %, EtOH 99.7 %, dimethylformamide DMF 99.5 % AR grade, graphite 99 % China were used.

2.1.2. Preparation of GNP's

Graphite was first exfoliated partially by using method described in [8]. Typically, 2 g graphite was dispersed in 100 mL solvent mixture containing 75 % acetone and 25 % H₂O. The mixture then was sonicated at 40 kHz and 300 W for 4 hours. The mixture was slightly heated for solvent to evaporate to get the product.

Then, 2 g graphite from the first step was dispersed in 150 mL H₂SO₄ 98 % and then 10 g K₂S₂O₈ was added. Thereafter, the reaction mixture was stirred for 4 hours at room temperature. The GNP's product was then filtered out of the mixture, washed 3 times with ethanol, 3 times with water, and finally dried at 60 °C for 6 hours.

2.1.3. MnFe₂O₄ and MnFe₂O₄/GNP's composite synthesis

Calculated amount of Mn(NO₃)₂ 50 % solution and Fe(NO₃)₃.9H₂O was measured and dissolved in 60 mL dimethylformamide solvent so that concentration of Mn²⁺ and Fe³⁺ was 0.02 M and 0.04 M, respectively. The mixture was stirred for 30 minutes and then transferred to an 80 mL autoclave reactor, sealed and heated for 24 hours. Two different experiments were conducted at 150 °C and 200 °C. Products were then filtered, washed 3 times with ethanol and water, before being dried at 60 °C for 6 hours.

MnFe₂O₄/GNP's composite was formed by a similar process. First, 0.05 g GNP's was dispersed in 60 mL DMF in 30 minutes at 40 kHz and 300 W. Second, Mn(NO₃)₂ and Fe(NO₃)₃ was added in the same amount as previous experiment. Last, the procedure was conducted at 200 °C for 24 hours.

2.1.4. Lead solutions
AR grade lead (II) acetate trihydrate was used to prepare stock solution of 400 mg/L. This solution was diluted to get desired concentration at 200 mg/L, 100 mg/L, 40 mg/L, 20 mg/L, 10 mg/L.

2.2. Material characterization

The chemical composition of the material was characterized by Energy-dispersive X-ray spectrometry (EDX) using Hitachi S-4800. The phase composition was determined by powder X-ray diffraction (PXRD) method on X’Pert Pro. XRD patterns were recorded using CuKα radiation (λ = 1.5406 Å). MnFe₂O₄ material has cubic crystal structure, space group 227: Fd-3m, lattice parameter a = 8.5 Å [9]. The magnetic property of materials was checked simply by using a magnet. The morphology of the material was characterized by scanning electron microscope (SEM) using Hitachi S-4600. Lead concentration of after-treatment solution was measured by atomic absorption spectroscopy (AAS) using contrAA 700.

2.3. Study on Pb²⁺ absorption

Adding 0.01 g MnFe₂O₄/GNPs composite to 30 mL solution of each concentration prepared above. The mixture was sonicated at 300 W and 40 kHz for 10 minutes, before being left for 20 hours to reach absorption equilibrium.

The amount of absorbed metal ion is calculated using the equation: qₑ = V.(C₀-Cₑ)/m, where qₑ (mg/g) is the amount of absorbed metal ions at equilibrium, C₀ and Cₑ are initial concentration and equilibrium concentration, respectively (mg/L), V (mL) is the volume of the Pb²⁺ solution and m (g) is the mass of the absorbent. The Langmuir isotherm between the amount of absorbed metal ion and the concentration at equilibrium can be expressed by:

\[ qₑ = \frac{bqmCₑ}{1+bCₑ} \]

where b is the Langmuir constant. This equation can be rewritten as:

\[ \frac{Cₑ}{qₑ} = \frac{Cₑ}{qm} + \frac{1}{bqm} \]

so qₘ can be calculated as 1/tanα from the plot between Cₑ/qₑ and Cₑ.

3. RESULTS AND DISCUSSION

3.1. Material characteristics

The material phase was identified by PXRD method (Figure 1a). Results showed that synthesized GNPs still has characteristic peak of graphite, that is 26.7° corresponding to (002) face (♦ symbol) of graphite but much lower intensity. The decrease of intensity indicate a loss of crystallinity, as the result of the exfoliation of graphite. In addition, GNPs formation was also indicated by great volume expansion and lower density.

Figure 1b shows XRD patterns of MnFe₂O₄. From lattice parameters [9], the peaks at angles 2θ = 30°, 35.3°, 42.8°, 56.4° and 61.9°, correspond to (022), (113), (004), (115) and (044) faces (★ symbol), respectively. MnFe₂O₄ was synthesized without GNPs to optimize the reaction conditions. At elevated temperature and with the presence of water, DMF was hydrolyzed:
HCON(CH₃)₂ + H₂O → HCOOH + NH(CH₃)₂ (1)

Also above boiling point, DMF decomposed as reaction:

HCON(CH₃)₂ → CO + NH(CH₃)₂ (2)

Dimethylamine was liberated, thus increase pH of the solution:

NH(CH₃)₂ + H₂O → NH₂(CH₃)₂⁺ + OH⁻ (3)

At high pH, precursor salts were hydrolyzed to form hydroxides:

Fe³⁺ + 3 OH⁻ → Fe(OH)₃ (4)
Mn²⁺ + 2 OH⁻ → Mn(OH)₂ (5)

These hydroxides immediately lose water to form oxides at reaction temperature, at Fe³⁺: Mn²⁺ ratio 2:1 manganese ferrite is formed:

Mn(OH)₂ + 2 Fe(OH)₃ → MnFe₂O₄ + 4 H₂O (6)

This crucial process determined the outcome of the products. Both hydroxides have to be formed simultaneously for reaction (6) to occur; otherwise, oxides of each metal were formed separately. Checking by using a magnet showed that only experiment with at 200 °C yields magnetic products. Because Fe³⁺ is much more easily hydrolyzed than Mn²⁺, if the pH rising was not fast enough, hydrolyzation of Fe³⁺ ions was preferred, so the main products were Fe₂O₃ (Figure 1c). This is the case when performing experiment at lower reaction temperature (150 °C). At 200 °C, DMF decomposition rate was significantly faster, so both iron and manganese nitrate salts hydrolyzed simultaneously with molar ratio 2:1 to form the desired MnFe₂O₄ product. These conditions were chosen to perform next experiment with addition of GNP.

Figure 1. XRD patterns of a. MnFe₂O₄/GNPs composite, b. Fe₂O₃ formed at 150°C, c. MnFe₂O₄ synthesized at 200 °C, d. GNP.

Figure 1d shows XRD patterns of MnFe₂O₄/GNPs composite. Aside from peaks of MnFe₂O₄, a peak at 26.7° was characteristic of GNP indicating that the composite was
composed of both phases.

The morphology of synthesized GNPs and the composite material was characterized by scanning electron microscope (SEM) (Figure 2).

Figure 2a,b show that the obtained GNPs has layer structure similar to that of graphite, but with interlayer distance much wider, of about one micron and each layer thickness of about 20 nm. The large distance between each sheet contributed to the high surface area of material, and is a neccesary condition for Fe$^{3+}$ and Mn$^{2+}$ to blend in while ultrasonicated mixture of GNPs and salt precursors. Under hydrothermal condition, these salts deposited in-situ onto the surface of GNPs layers, as seen in Figure 2c,d. In Figure 2c, it can be clearly seen that GNPs interlayer distance and layer thickness was unchanged, so hydrothermal process did not effect GNPs itself, but merely filled the gap between sheets with the mixed-oxides. The MnFe$_2$O$_4$ size and shape can be seen in Figure 2d. The mixed-oxides crystal is uniform, narrow crystal size distribution of about 30 nm. Compared to hydrothermal method in [6], the oxides particles were formed by in-situ method had more well-defined shape. The reason is in this method, the crystal has more time to growth, in which face (001) is preferred, result in slightly larger size but well-defined octahedral shape.

Figure 2. SEM images of GNPs (a, b), MnFe$_2$O$_4$/GNPs composite side view (c), MnFe$_2$O$_4$/GNPs composite top view (d).
The chemical composition of the material was analyzed by Energy-Dispersive X-ray (EDX) spectrometry and the results obtained are shown in Figure 3. It can be seen that the composition varies on different areas. The mixed-oxides do not distribute evenly onto the GNP\text{s} surface. However, elemental ratio between Fe and Mn in each area is roughly 2:1, which confirms the formation of MnFe$_2$O$_4$. Note that the oxygen content is always larger than theoretical amount in the oxides (4 times Mn content or 2 times Fe content). The exceeding amount (roughly 20 \%) is contributed to O in oxygenated GNP\text{s} and from water adsorbed into the material.

![Figure 3. Energy-dispersive X-ray (EDX) spectroscopy of MnFe$_2$O$_4$/GNP\text{s} material.](image)

| Area | Element content, % | 
|------|------------------|
|      | C    | O    | Fe   | Mn  |
| 1    | 20.13| 54.31| 14.25| 9.30|
| 2    | 22.55| 58.28| 14.13| 7.10|
| 3    | 29.10| 59.55| 11.29| 8.70|
| Average | 27.25| 59.85| 14.80| 8.35|

**Table 1.** Pb$^{2+}$ absorption capacity of the MnFe$_2$O$_4$/GNP\text{s} material.

| No. | C$_0$, mg/L | C$_e$, mg/L | q$_e$, mg/g | C$_e$/q$_e$, g/L |
|-----|-------------|-------------|-------------|-----------------|
| 1   | 10          | 0.4         | 28.8        | 0.014           |
| 2   | 20          | 1.5         | 55.5        | 0.027           |
| 3   | 40          | 4.2         | 107.4       | 0.039           |
| 4   | 100         | 20.2        | 239.4       | 0.084           |
| 5   | 200         | 111.0       | 267.0       | 0.416           |
| 6   | 400         | 295.0       | 315.0       | 0.937           |

Figure 4 was plotted from data in Table 1 between C$_e$ and C$_e$/q$_e$ to estimate maximum lead absorption capacity of the composite. The fitting line has R$^2$ value close to 1 so it is reliable. As mentioned above, the maximum absorption value is the reciprocal of the fitting line’s tangent, and
can be calculated as \[ q_{\text{in}} = (0.0031)^{-1} = 322.6 \text{ mg/g}. \] This result is comparable with the results from [6].

\[ \begin{align*}
\gamma &= 0.0031x + 0.0269 \\
R^2 &= 0.9968
\end{align*} \]

*Figure 4. Graph of Langmuir isotherm equation.*

As metal oxides containing oxygen atoms at outer surface of the crystals, Pb\(^{2+}\) ions can be attracted by electrostatic force with the negative charged oxygen. Lead also has affinity toward metal oxides because of the hydroxide groups that remain on the surface. In this case, it is especially true when the oxides were formed in hydrothermal environment. The remain of these hydroxide groups can also be noticed, that XRD peaks of oxides prepared hydrothermally often have low intensity, as the hydroxide decrease the crystallinity of the product. These hydroxide groups can perform a substitute reaction with lead, in which hydrogen atoms are replaced with Pb atoms, thus absorbing a good amount of lead in the process. GNP\(_s\) provide a template for the metal oxides to deposite on, evenly distribute those particles and by doing so increase the surface exposure of the material. On the other hand, GNP\(_s\) also has a minor contribution to the absorption of lead atoms. By possessing various oxygenated groups: epoxy, hydroxide, carboxylate, which have the same absorption mechanism as of the metal oxides, GNP\(_s\) served the dual purposes as a template and an absorbent.

4. CONCLUSION

By using solvothermal method, graphene nanoplatelets and its magnetic composite MnFe\(_2\)O\(_4\)/GNP\(_s\) were succesfully synthesized, as confirmed by XRD method. The condition of reaction was studied and 200 °C was the proper temperature, at lower temperature, undesired products were formed instead. The morphology and size of crystal were examined by SEM show that MnFe\(_2\)O\(_4\) has octahedral shape with size of about 30 nm, was in-situ deposited between layers of GNP\(_s\) sheets. Combining both material’s ability to remove lead ion from water, lead absorption capacity of this composite was tested and the maximum absorption reached about 322.6 mg/g.

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210
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