

## Studying Properties of Expanded Graphite Coated With $\text{CoFe}_2\text{O}_4$ Particles, Application to Remove Oil Spills

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### Article history

Received: 26-May-2016

Revised: 06-June-2016

Available online: 04-Aug-2016

### Keywords:

$\text{CoFe}_2\text{O}_4$ ,  
Expanded graphite,  
Oil spills,  
Sorbent

### Abstract

The magnetic exfoliated graphite (EG) was prepared by coating  $\text{CoFe}_2\text{O}_4$  particles on the EG through sol-gel method. Properties of EG- $\text{CoFe}_2\text{O}_4$  were characterized by Scanning Electronic Microscopy (SEM), X-ray diffraction (XRD), Energy Dispersive X-ray (EDX), Nitrogen gas adsorption and desorption curves, and Vibrating Sample Magnetometer (VSM). The obtained results indicated that  $\text{CoFe}_2\text{O}_4$  particles deposited uniformly and effectively on EG. The as-synthesized EG- $\text{CoFe}_2\text{O}_4$  was found to have high sorption capacities for Fuel oil (FO), Diesel oil (DO) and Crude oil (CO), with the highest sorption capacity for FO, thus allowing it to be a promising material for oil spill treatment.

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### Introduction

Through the history, the oil spill has severely caused environmental damage to ocean water resources. A large amount of spilled oil has a significant negative influence on the ecosystem and put the life of human and living species at high risk. Therefore, developing new absorbents with high adsorption capacity and easy handling has become increasingly important and essential for cleaning water resources polluted by oils.

Expanded graphite (EG) with multi-porous structure has large specific surface area and low density. Thanks to this, EG has been considered as an important sorbent to tackle the above-mentioned issues [1,2]. Recently, some studies have reported several synthesis methods of EG from graphite intercalated compounds (GICs) in order to enhance its pores size range; they can be classified into three kinds of porous structures including worm-like particles, small wedge-shaped pores on the surface of the particles, and ellipsoidal pores inside the particles [3-7]. GICs was complex materials containing alkali metals and acid molecules such as  $\text{H}_2\text{SO}_4$ ,  $\text{FeCl}_3$ , Na-tetrahydrofuran (THF), K-THF and Co-THF inserted between oppositely charged carbon layers. In mentioned substances,  $\text{H}_2\text{SO}_4$  has drawn attention as an effectively intercalating agent to fabricate EG under ashock-thermal condition with low cost, large sorption capacity and high adsorption rate of spilled heavy oils [5]. However, EG's small particle size and high dispersion limit its recovery and recyclability in a large-scale water environment. In order to make it easier to control and recover, EG- $\text{CoFe}_2\text{O}_4$  has been developed by introducing  $\text{CoFe}_2\text{O}_4$  magnetic particles to EG [3,4]. EG- $\text{CoFe}_2\text{O}_4$  material successfully prepared by the sol-gel method had high magnetism. However, its adsorption capacity was not high enough for crude oil and required further improvement [6]. In this work, we introduce a new approach for synthesizing high-performance EG- $\text{CoFe}_2\text{O}_4$  from natural flake graphite by sol-gel method. EG- $\text{CoFe}_2\text{O}_4$  was

prepared using blended calcination method at a constant temperature in the furnace instead of thermal shock as in the previous studies [8,9]. The properties of EG- $\text{CoFe}_2\text{O}_4$  were characterized and its adsorption capacities were studied for crude, diesel and fuel oil. This method was found to significantly enhance oil adsorption of EG- $\text{CoFe}_2\text{O}_4$ .

### Experimental

#### Materials

Natural graphite powder (granule size > 1.25 mm and carbon content  $\geq 85\%$ ) was derived from Yen Bai province, Vietnam.  $\text{H}_2\text{SO}_4$  (pure 98%) and  $\text{H}_2\text{O}_2$  (30%),  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{NH}_4\text{OH}$  was obtained from commercial sources and used as received.

#### Preparation of samples

EG was synthesized by intercalation method using  $\text{H}_2\text{O}_2$  (30%) as an oxidizing agent and  $\text{H}_2\text{SO}_4$  (96%) as an intercalating agent. Flake graphite in 1 gram was added into the mixture of  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{O}_2$  following volume ratio 20:1,4 by glass rod for 60s. After intercalation time was 50 minutes, mixtures were continually washed with water on Buchner funnel until pH value reached at 3-4. The as-filtered mixtures were dried at  $80^\circ\text{C}$  and then transferred into a furnace at  $1100^\circ\text{C}$  in 60s to produce EG.

EG- $\text{CoFe}_2\text{O}_4$  was prepared by adding magnetic particles  $\text{CoFe}_2\text{O}_4$  to EG through the sol-gel process. In details, a mixture of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (with amolar ratio of  $\text{Fe}^{3+}/\text{Co}^{2+} = 1:2$ ) was homogeneously dissolved in citric acid solution. In order to keep the sols stable, the pH of the solution was fixed to about 7-8. Then 1 g of the EG was added into the mixture and then stirred again for about 30 minutes or until the floating EG disappeared on the surface of the solution. The obtained composites were further baked at  $600^\circ\text{C}$  for 1 hour and at a heating rate of  $10^\circ\text{C}/\text{min}$ .

### Characterization

The morphology of EG-CoFe<sub>2</sub>O<sub>4</sub> samples was studied by SEM of Hitachi SU3500. X-ray diffraction patterns were recorded in a Siemens D5000 Diffractometer with a CuK<sub>α</sub> radiation (1.5406 Å) at a scan velocity of 2° (2θ) min<sup>-1</sup>. Energy dispersion X-ray analysis (EDX) spectrography was performed by Hitachi TM3000 and Oxford SwiftED3000 instrument. Measurements of the static magnetic moment were conducted on a GMW 3474-140 magnetometer equipped with a superconducting magnet to produce fields up to 16 Koe.

### Evaluation of adsorption capacity

EG-CoFe<sub>2</sub>O<sub>4</sub> was added directly into mixtures of different oils and water contained in Petri dishes at room temperature. After 6 minutes, mixtures of EG-CoFe<sub>2</sub>O<sub>4</sub> and oil were recovered using permanent magnetic under the dish. EG-CoFe<sub>2</sub>O<sub>4</sub> was then separated and dried at room temperature to remove the water completely.

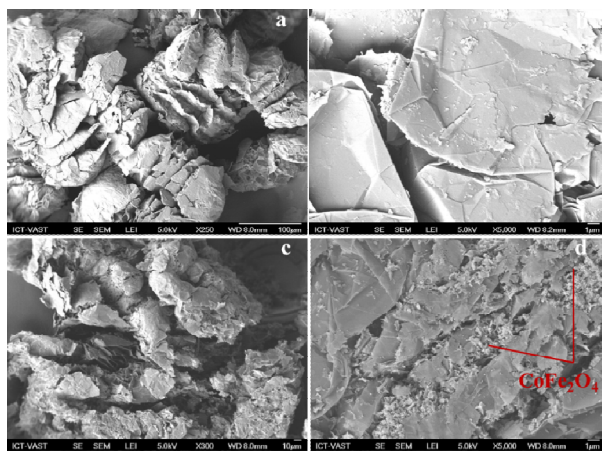
The amount of adsorbed oil was calculated from the increased weight of EG-CoFe<sub>2</sub>O<sub>4</sub> after adsorption with the following equation:

$$\text{Adsorption capacity} = \frac{m_1 + m_2}{m_1}$$

where  $m_1$  is the weight of EG-CoFe<sub>2</sub>O<sub>4</sub> before oil adsorption (g),  $m_2$  is the weight of EG-CoFe<sub>2</sub>O<sub>4</sub> after oil adsorption (g).

## Results and Discussion

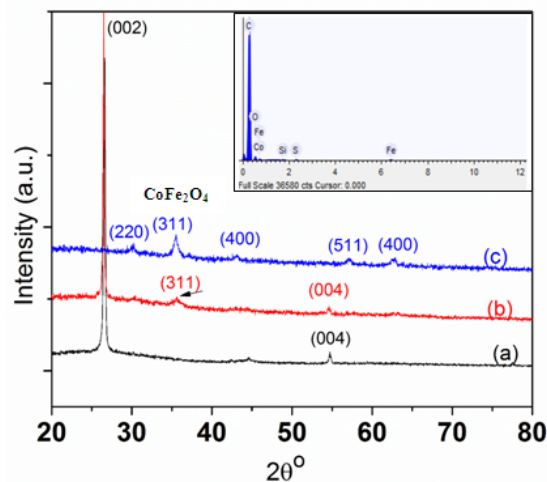
Figure 1 shows the morphology of EG and EG-CoFe<sub>2</sub>O<sub>4</sub> by SEM analysis. It can be seen that EG and EG-CoFe<sub>2</sub>O<sub>4</sub> have worm-like and multilevel pore structures. The EG's surface is smooth and its myrmekitic textures are observed in Figure 1b. In comparison with EG, the shape of EG-CoFe<sub>2</sub>O<sub>4</sub> is rough (Figure 1d) given that the small sized CoFe<sub>2</sub>O<sub>4</sub> agglomerates dispersed uniformly on the EG surface. This is evidence indicating the successful addition of CoFe<sub>2</sub>O<sub>4</sub> during preparation.



**Figure 1:** SEM images of EG and EG-CoFe<sub>2</sub>O<sub>4</sub> (a) EG, (b) detail view of EG, (c) EG-CoFe<sub>2</sub>O<sub>4</sub>, (d) detail view of EG-CoFe<sub>2</sub>O<sub>4</sub>

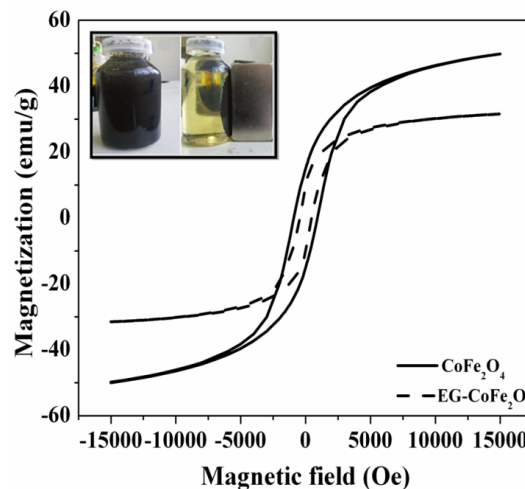
The elemental compositions of EG-CoFe<sub>2</sub>O<sub>4</sub> determined by EDX are shown in inset Figure 2. The EDX spectrum illustrated not only the primary ingredient of C but also others such as Co, Fe and O peaks which are in good agreement with the XRD result (Figure 2). As can be observed from Figure 2, the diffraction peak at  $2\theta=26.7^\circ$  is attributed to atypical characteristic of natural graphite corresponding to the stacked arrangement of carbon layers in the (200) plane [10,12]. This suggests that the carbon layers were not absolutely exfoliated in EG and EG-CoFe<sub>2</sub>O<sub>4</sub> structure.

However, the new peak at  $35.45^\circ$  in EG-CoFe<sub>2</sub>O<sub>4</sub> attributed to the (311) plane of the added crystalline CoFe<sub>2</sub>O<sub>4</sub> and imply that Co<sub>3</sub>O<sub>4</sub> and Fe<sub>2</sub>O<sub>3</sub> were successfully transferred to CoFe<sub>2</sub>O<sub>4</sub> under high temperature.



**Figure 2:** XRD pattern of EG-CoFe<sub>2</sub>O<sub>4</sub>, inset of (Figure 2) shown the elemental compositions of EG-CoFe<sub>2</sub>O<sub>4</sub>

The presence of CoFe<sub>2</sub>O<sub>4</sub> particles in samples has magnetism on EG is showed in inset Figure 3. The plot of magnetization (M) as a function of applied field (H) for EG and EG-CoFe<sub>2</sub>O<sub>4</sub> is shown in Figure 3. The magnetic properties of a material depend on the particle size, shape and quantity of CoFe<sub>2</sub>O<sub>4</sub>. It can be observed that magnetism of EG-CoFe<sub>2</sub>O<sub>4</sub> reach at 32 emu/g. Although its magnetic value is lower than the CoFe<sub>2</sub>O<sub>4</sub> magnetic value (46 emu/g), this result further demonstrate the deposition of CoFe<sub>2</sub>O<sub>4</sub> in EG as well-agreed with the SEM result.



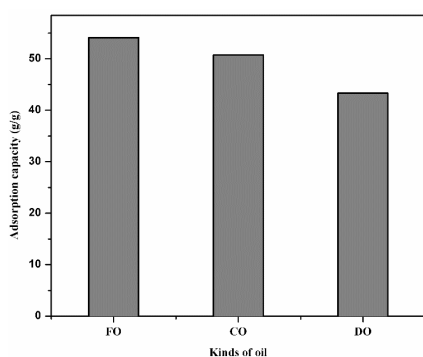
**Figure 3:** Magnetization curves of EG-CoFe<sub>2</sub>O<sub>4</sub>, inset of (Figure 3) shown the simulated experiment for the magnetism of EG-CoFe<sub>2</sub>O<sub>4</sub>

Adsorption occurs whenever a solid surface is exposed to a liquid. Therefore, oils adsorption capacity of the samples significantly depends on the specific surface area which means that the adsorption capacity is expected to be greater for the higher surface area. The pore volume and surface area of the as-synthesized EG-CoFe<sub>2</sub>O<sub>4</sub> are 0.153 cm<sup>3</sup>/g and 192.30 m<sup>2</sup>/g, respectively which are higher than those of the unmodified EG. It can be explained that acid citric molecules were decomposed in the sample calcination stage thus producing defects and large holes in the EG-CoFe<sub>2</sub>O<sub>4</sub>. The detailed parameters can be found in Table 1.

**Table 1:** Properties of EG and EG-CoFe<sub>2</sub>O<sub>4</sub>

	S <sub>BET</sub> (m <sup>2</sup> /g)	Pore radius (Å <sup>o</sup> )	Pore volume (cm <sup>3</sup> /g)
EG	147.46	13.70	0.122
EG-CoFe <sub>2</sub> O <sub>4</sub>	192.30	14.00	0.153

The sorption capacities of the prepared EG-CoFe<sub>2</sub>O<sub>4</sub> for heavy oils were evaluated using 3 kinds of common heavy oils including fuel oil (FO), diesel oil (DO) and crude oil (CO). The results in Figure 4 showed that EG-CoFe<sub>2</sub>O<sub>4</sub> has the highest sorption capacity for FO (54.13 g/g) followed by CO (50.79 g/g) and DO (43.35 g/g). The main reason is that the glutinosity and density property of FO and CO are larger than that of DO [9]. The adsorption capacity of the as-synthesized EG-CoFe<sub>2</sub>O<sub>4</sub> for heavy oils is considerably higher than those reported in the previous studies [7-9]. These results demonstrate the high efficiency of this method.

**Figure 4:** The adsorption capacities of EG-CoFe<sub>2</sub>O<sub>4</sub>

In order to explore the possibility of desorption and recovery oils from the used EG-CoFe<sub>2</sub>O<sub>4</sub>, the recovery of DO oil was conducted by filtration under mild pressure. Under mild suction of the used adsorbents, the DO oil could be recovered without serious disruption of the bulk morphology of EG-CoFe<sub>2</sub>O<sub>4</sub> [11].

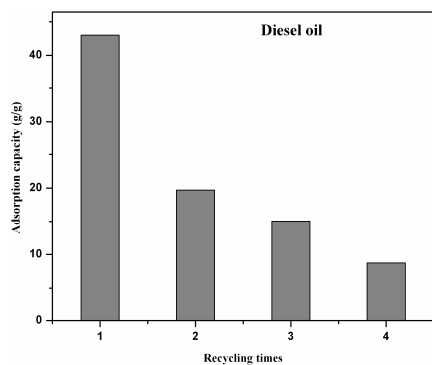
**Figure 5:** Changes in adsorption capacity of EG-CoFe<sub>2</sub>O<sub>4</sub> after recovery cycles

Figure 5 showed the changes in adsorption capacity of the EG-CoFe<sub>2</sub>O<sub>4</sub> after three reuse cycles. After the first suction cycle, the adsorption capacity for DO was 43 g/g and about 82% of the adsorbed oil was recovered. Then, the adsorption capacity along with the amount of recovered oil significantly decreased with increasing cycling times. After recovery, the water content in the recovered DO according to ASTM D95 test standard was always lower than 250 ppm, revealing a high-quality of recovered oil from the EG-CoFe<sub>2</sub>O<sub>4</sub> material.

## Conclusions

In this study, the magnetic CoFe<sub>2</sub>O<sub>4</sub> incorporated EG was synthesized based on the Vietnamese natural graphite flakes followed by application in sorption of heavy oils. The analysis results of SEM, EDS and XRD and VSM indicate that the uniform CoFe<sub>2</sub>O<sub>4</sub> particles were well dispersed in EG. The EG-CoFe<sub>2</sub>O<sub>4</sub> offered the highest sorption capacity for FO (54.13 g/g) and slightly lower values for CO and DO (50.79 and 42.12 g/g, respectively). The high adsorption capacities as well as high-quality of recovered oils enable the magnetic EG-CoFe<sub>2</sub>O<sub>4</sub> as-prepared from this improved approach to be one of the most promising materials for large-scale clean up of oil pollution.

## Acknowledgements

This research is funded by Foundation for Science and Technology Development Nguyen Tat Thanh University

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