Studying Of The Effect of Adsorption Conditions For The Removal Of Diesel Oil From Wastewater Using The Magnetic Exfoliated Graphite/$CoFe_2O_4$

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***Abstract*— Exfoliated graphite (EG) has known as excellent adsorbent in removing oil-contaminated water lying on its low density and multiporous structure. However, the utilization of EG is to bring some problems due to difficulty to gather it after adsorption. In order to restrict this shortcomings; the introduction of magnetic component, such as $CoFe_2O_4$ into adsorbent has been taken into consideration aiming easy recovery of the used adsorbents from wastewater under a magnetic field. The effect of the physical performance of as-obtained EG-$CoFe_2O_4$ as well as adsorption conditions to adsorption capacity was investigated in this study. The physical properties of as-obtained EG-$CoFe_2O_4$ were characterized by using modern techniques such as SEM, XRD, VSM and Nitrogen adsorption/desorption. Besides, the adsorption experiments for diesel oil were conducted under conditions including adsorption time, dosage of diesel oil, salinity and temperature. The results were found as 20 g dosage of diesel oil, 6 minutes adsorption time, 3.5% salinity and temperature at 30oC that allow obtaining the max adsorption capacity of as-synthesized EG-$CoFe_2O_4$ for diesel oil.**

Keywords—adsorption capacity, $CoFe_2O_4$, diesel oil, exfoliated graphite, wastewater.

I. INTRODUCTION

As oil consumption has increased annually throughout the world, a large amount of oil has been released into the environment during transportation and storage. Actually, this is disaster for humankind because of harmful affects on marine microorganism and living habitats through various plants, fishes and also water, resulting damages to environment. Common treatment techniques were applied for this oil spill accident such as in-situ burning, skimming, bioremediation, dispersion, and use of adsorbents. One of the solutions for removing massive spilled oil is the use of absorbents due to high efficiency, cost-effectiveness, easy and simple operation and feasibility for large-scale application. Thus, developing new absorbents with high capacity and easy handling has become increasingly important for water purification.

The research on recovery and recycle of spilled heavy oils by using carbon material, such as exfoliated graphite (EG) has been intensively explored [1-6]. EG has known as an important factor to treat oil spills due to its low density and porosity. Considered as an innovative approach, the incorporation of magnetic components, such as $CoFe_2O_4$, into the adsorbents has been found to facilitate phase separation under a magnetic field thus allowing easy collection of the used adsorbents from polluted water in large scale [7-9]. However, the adsorption efficiency significantly depends on the type and quantity of oil spill, weather conditions and surrounding environment. Practically, environmental impacts have profoundly influent affects on adsorption and recovery of oils. Thus, this study aim to preliminarily evaluate the influence of four factors such as adsorption time, temperature, salinity and oil dosage on adsorption of as-prepared EG/$CoFe_2O_4$. The adsorbent was prepared from available graphite source in Vietnam via atwo-stage process: (1) fabricating exfoliated graphite, (2) decorating $CoFe_2O_4$ particles on EG. The physical properties were analysed by SEM, XRD and VSM.

II. Materials and Methods

A. *Chemicals and Materials*

Natural graphite powder (granule size > 1.25 mm and carbon content ≥ 85%) was derived from Yen Bai province, Vietnam. H_2SO_4 (pure 98%) and H_2O_2 (30%), $Fe(NO_3)_3.9H_2O$, $Co(NO_3)_2.6H_2O$, $NH_4.OH$ were obtained from commercial sources and used as received. Diesel oil was offered from Petrovietnam Research and Development Center with a sulphur content not exceeding 0.5%.

B. *Preparation of EG-Fe$_3$O$_4$*

The EG was firstly synthesized by intercalation method using H_2O_2 as oxidizing agent and H_2SO_4 as intercalating agent as follows. 1 g of natural graphite flakes was added into 20 mL mixture of H_2SO_4 and H_2O_2 (20:1.4 v/v). After 50 minutes, the expanded mixture was continually washed with water until the pH value reached 5-6. Then, the resulting black powder was collected by vacuum filtering and dried at 80^{o}C for 24 h. The exfoliation was conducted in a microwave oven at the power of 720 W for 10s.

In the next step, $CoFe_2O_4$ nanoparticles were then introduced to the EG surface by the following procedure. A mixture of $Fe(NO_3)_3.9H_2O$, $Co(NO_3)_2.6H_2O$ (with molar ratio of Fe^{3+}/Co^{2+}= 1:2) were 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 ^{o}C for 1 hour and at a heating rate of 10 ^{o}C/min.

C. *Adsorption studies*

For oil adsorption, 0,2 g of EG-$CoFe_2O_4$ was added directly into mixtures of diesel oil (DO) in petri dishes at room temperature. After adsorption time, mixtures of EG-$CoFe_2O_4$ and oil were recovered using magnetic permanent placed under the dish. EG-$CoFe_2O_4$ 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-$CoFe_2O_4$ after adsorption with the equation:

$$Adsorption\ capacity = \frac{m_2 - m_1}{m_1}$$

Where m_1 is the weight of EG-$CoFe_2O_4$ before oil adsorption (g), m_2 is the weight of EG-$CoFe_2O_4$ after oil adsorption (g).

D. *Characterization methods*

The X–ray powder diffraction (XRD) of AC was implemented on D8 Advance Bruker powder diffractometer with a Cu–Kα excitation source. The diffraction spectra were recorded with scan rate of 0.02^o/s. The angle range (2θ) was investigated between 0^o and 50^o. The morphological study of material surface was identified by scanning electron microscope (SEM) technique on the instrument S4800, Japan. SEM morphology was recorded utilizing an accelerating voltage source of 10 kV. Measurements of static magnetic moment were conducted on a GMW 3474-140 magnetometer equipped with a superconducting magnet to produce fields up to 16 Koe.

III. Results and Discussion

A. *Characterization of EG-Fe$_3$O$_4$*

Figure 1A shows the morphologies of EG-$CoFe_2O_4$ (3:1 weight ratio) as investigated by SEM. It can be seen that the exfoliated graphite sheets are densely decorated with nanosized $CoFe_2O_4$ without large aggregations. The light nanoparticles of $CoFe_2O_4$ were found to effectively distribute over the wrinkled surface of EG leading to increase its surface roughness. Based on the enlarged image shown in Figure 1A, the magnetic nanoparticles were partially covered by the new carbon layer produced in the high-temperature exfoliation. This proves successful addition of nanosized $CoFe_2O_4$ into EG during preparation.

The crystalline structures of EG/$CoFe_2O_4$ composite were analysed by XRD, as shown in Figure 1B. A strong sharp diffraction peak at 2θ = 26.6^o is attributed to plane (0 0 2) of the EG as found on the presence of graphite lattices in the composite [12]. In addition, two diffraction peaks at 35.5^o and 56.9^o are ascribed to plane (311) and (511) of the $CoFe_2O_4$ structure [13-14]. These observations suggest that $CoFe_2O_4$ was successfully modified on the surface of expanded graphite sheets. The magnetic properties of as-prepared EG–$CoFe_2O_4$ composite at room temperature were characterized by using VSM. As displayed in Figure 1C, the S-like curve was correlated to the magnetization hysteresis loops of composite. It is clearly observed that saturation magnetization of EG-$CoFe_2O_4$ reach at 32 emu/g. According to the above analyzed results, the $CoFe_2O_4$ were successfully introduced to the EG surface and loaded it with magnetic characteristic sufficient for further application.

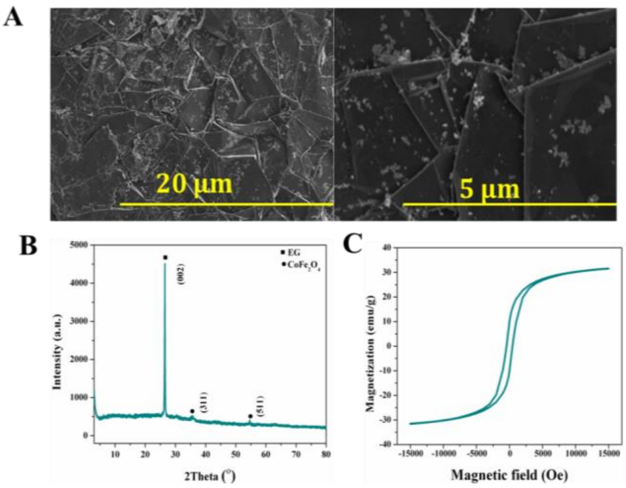

Figure 1. The physical properties of EG/$CoFe_2O_4$ (A) SEM, (B) XRD and (C) VSM

The pore volume and specific surface area of the as-synthesized EG/$CoFe_2O_4$ are 0.153 cm^3/g and 192.30 m^2/g, respectively. These results are expected to bring great efficiency for oil adsorption. The detailed parameters can be found in Table 1.

Table 1. Properties of EG/$CoFe_2O_4$

	S_{BET} (m^2/g)	Pore radius(A^o)	Pore volume (cm^3/g)
EG-$CoFe_2O_4$	192.30	14.00	0.153

B. Preliminary studies of adsorption conditions of diesel oil by the magnetic EG-$CoFe_2O_4$

In initial tests, the effect of four factors including adsorption time, dosage, temperature and salinity on adsorption capacity of EG-$CoFe_2O_4$ for DO were analyzed following single-factor experimental studies. Figure 2-5 presents the obtained results during testing. The adsorption time was firstly studied at 3.5% salinity, 30^{o}C temperature and using 15 g diesel oil in the different adsorption time at 2 min, 4 min, 5 min, 6 min, 7 min, 8 min. As observed from Figure 2, the adsorption capacity at the above different times is 41.3; 41.8; 41.78; 42.12; 41.48 and 40.65 g DO for 1 g adsorbent, respectively. The experimental results reveal that oil adsorption is remained stable with the increase of adsorption time.

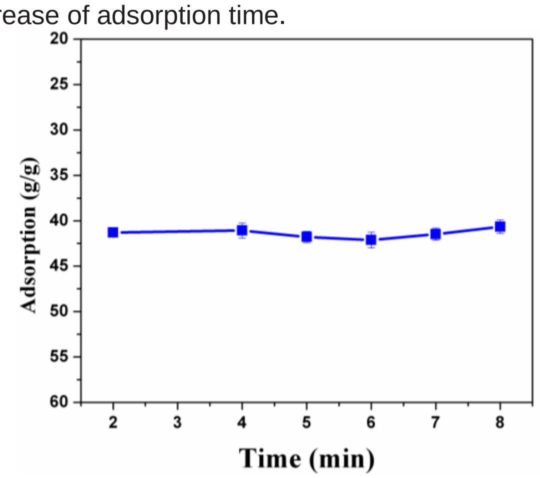

Figure 2. Adsorption of diesel oil under different adsorption time

The second factor was the temperature in adsorption solution conducted in the range from 10 ^{o}C to 30 ^{o}C. 0.2 g EG/$CoFe_2O_4$ was added into petri dish containing the 100 ml water with 3.5 % salinity and 15 g DO. As shown in Figure 3, the removal of diesel oil was increased when raising temperature. In fact, the adsorption capacity is 33.42 g/g at the temperature of 10 ^{o}C while the value at 30 ^{o}C is 42.12 g/g. This explained that the decrease in temperature caused a significant increase in oil viscosity especially for the heavier oils [15]. At high temperature, oil is expected to easily diffuse to inside pore of EG/$CoFe_2O_4$, resulting to surge the adsorption capacity. However, it is difficult to control the temperature of the oil spill area.

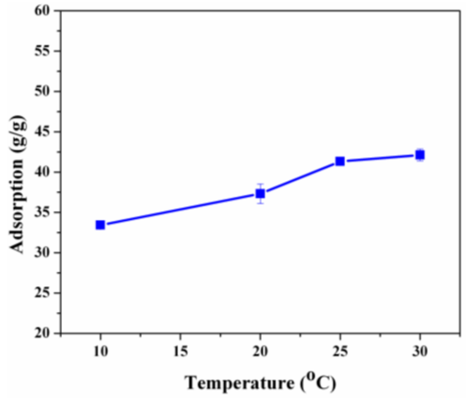

Figure 3. Adsorption of diesel oil under different temperature

Then, the oil dose floating on top of water was studied in 15 g, 20 g, 25 g, 30 g, 35 g. For testing, 0.2 g EG/$CoFe_2O_4$ was added in the petri dish including different diesel dosage at salinity of 3% and temperature of 30 ^{o}C. After adsorption at 6 minute, the result was seen in Figure 4. When the floating oil weight increases correlating to adsorbent dosage decrease, the adsorption capacity is thereby decreasing. In detail, the value at 15 g oil is 42.12 g/g whereas the value gains 36.1 g/g at 35 g oil. This showed that the adsorbent provided more porosity to adsorb more diesel oil when oil dose were less on the surface.

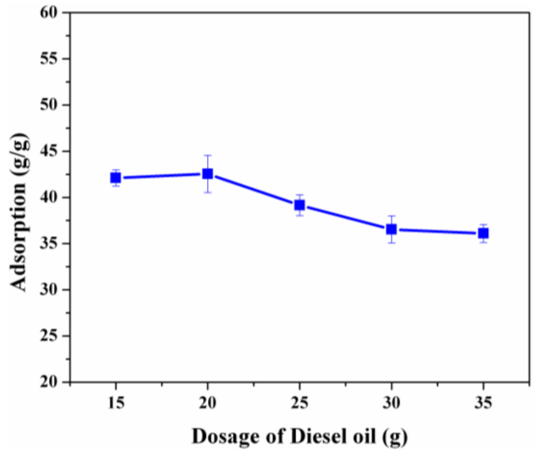

Figure 4. Adsorption of diesel oil under different oil dosage

Salinity was finally investigated in the range from 0.5 % to 3.5%. As shown in Figure 6, the removal of diesel oil slowly increased with varying the salinity. In particular, the salinity value at 0.2 %, 0.5 %, 1 %, 2 % and 3.5% is 39.92, 40.72, 40.82, 41.92, 42.12 g DO per 1 g adsorbent. The reason could be that the solubility of diesel was decreased in the more salinity water, so diesel was easily adsorbed by EG/$CoFe_2O_4$. The result indicated that salinity was favorable to adsorption. Overall, the two factors including dosage of diesel oil and temperature could affect the adsorption volume.

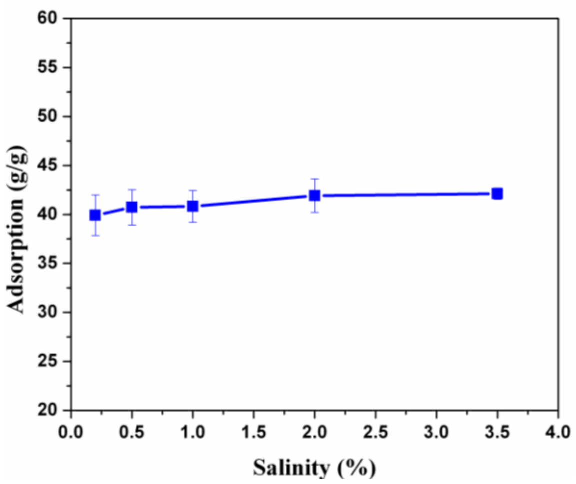

Figure 5. Adsorption of diesel oil under different salinity

IV. Conclusions

In this study, the magnetic EG/$CoFe_2O_4$ composites were succesfully synthesized via chemical method for applications in removal of diesel oil using the low-cost, abundant natural graphite source of Viet Nam. The as-synthesized EG/$CoFe_2O_4$ composites possess magnetic characteristic due to loading $CoFe_2O_4$ on EG. Based on preliminary analysis, the highest adsorption of the EG/$CoFe_2O_4$ for diesel oil in experimental conditions fixed at adsorption time at 6 minute, salinity of 3.5% and temperature at 30^{o}C and 20g diesel oil that allows where the adsorption time and salinity were considered as important factors.

Acknowledgment

This research is funded by Foundation for Science and Technology Development Nguyen Tat Thanh University, Ho Chi Minh City, Vietnam.

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