Simple synthesis and characterization of cobalt ferrites on expanded graphite by the direct sol-gel chemistry for removal of oil leakage (fuel oil, diesel oil and crude oil)

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Abstract. The present work focused on the synthesis and characterization of cobalt ferrite (CoFe₂O₄) on expanded graphite (EG) via a simple sol-gel auto-combustion route for the removal of oil leakage. The morphological, structural, and surface charge properties of the calcined nanocomposites were determined by Scanning Electron Microscopy (SEM), X-ray diffraction (XRD), Energy dispersion X-ray analysis (EDX). Magnetic properties such as the magnetic saturation, coercivity and remanence were measured by a vibrating sample magnetometer (VSM) at room temperature, which presented that the expanded graphite and CoFe₂O₄ based composite exhibited typical magnetic behaviors. This research objective is to investigate the adsorption capacity of the magnetic CoFe₂O₄ decorated expanded graphite (EG-CoFe₂O₄) for diesel oil (DO), crude oil (CO) and fuel oil (FO) in water environment.

1. Introduction
In last decades, oil spills cause the most severe environmental pollution on the sea and river. The amount of spilled oil has a detrimental influence on aquatic life and human health. Therefore, the use of absorbents with large adsorption capacity and easy manipulation becomes important and essential for oils pollution treatment [1, 2]. It can be divided into three primary oil adsorbents including inorganic mineral materials, organic synthetic materials, and organic vegetable materials. Exfoliated graphite (EG) has been considered as efficient platform due to excellent performance such as high specific surface area, porosity, structure stability, low density and cost-efficiency [3-6]. Recent studies have shown that EG prepared from natural graphite flakes several synthesis methods of EG from graphite intercalated compounds (GICs) in order to enhance its pore size range. GICs were complex materials containing alkali metals and acid molecules such as H₂SO₄, FeCl₃, Na-tetrahydrofuran (THF), K-THF and Co-THF inserted between oppositely charged carbon layers [7-11]. However, the efficient collection of used absorbents for large-scale systems was limited lying on some EG’s drawbacks such as high dispersion and inconvenience to separation.
Magnetic nanoparticles have some advantages, such as separation by magnetic properties. It is typically more effective than filtration or centrifugation because the loss of the catalyst is reduced. Magnetic separation is simple, economical and favorable for industrial applications [12-14]. The nanosized spinel ferrites having structural formula MFe$_2$O$_4$ (M = Ni, Cu, Zn, Co, Mn, Mg, etc) have drawn considerable attention on the ground of fascinating structural, electrical and magnetic properties [15]. Among numerous ferrites, cobalt ferrites (CoFe$_2$O$_4$) has taken into account as a versatile magnetic material in many fields of biomedical applications, magnetic recording media, magnetic liquids, catalytic behavior, electrochemical stability and microwave absorbents [12-15]. Thus, the CoFe$_2$O$_4$ based composites may be considered as an efficient adsorbent to remove heavy oil in aqueous solution.

Nowadays, several chemical and physical techniques are used to synthesize ferrite nanoparticles including combustion method, solid state reactions, polyl technique, vapour deposition, sol-gel, thermal decomposition, microwave-assisted method solvothermal and hydrothermal synthesis [15-20]. Conventionally, the sol-gel and co-precipitation method are more popular in comparison to aforementioned methods and have used increasingly to fabricate nanocrystal ferrite with an equiaxial shape, well-controlled morphology and narrow particle size distribution [21, 22]. Although the advantage of co-precipitation technique allows preparation of material low temperature, sol-gel technique is effective and facile chemical route for ferrite nanoparticles lying on cost-efficient precursors and production of ultrafine and homogeneous particles in a short processing time [21, 23]. Thus, sol-gel method was found to be one of well-established approaches to fabricate CoFe$_2$O$_4$ included hybrid composites.

Based on these findings, in order to make it easier to control and recover EG, magnetic expanded graphite (MEG) has been developed by introducing CoFe$_2$O$_4$ magnetic particles to EG by the sol-gel method, which had high magnetism. The properties of EG-CoFe$_2$O$_4$ were characterized and its adsorption capacities were studied for crude, diesel and fuel oil.

2. Experimental details

2.1. Preparation of sample

Exfoliated graphite (EG) was prepared by chemical method using H$_2$O$_2$ and H$_2$SO$_4$ as oxidation and intercalating agents following the procedure described in our previous work [24]. EG-CoFe$_2$O$_4$ was prepared by adding magnetic CoFe$_2$O$_4$ on EG through the sol-gel route. The citric acid solution was added in mixture of Fe(NO$_3$)$_3$.9H$_2$O, Co(NO$_3$)$_2$.6H$_2$O (with molar ratio of Fe$^{3+}$/Co$^{2+}$= 1:2) following molar ratio of C$_3$H$_5$O$_7$::Fe$^{3+}$ as 4:1. The pH of solution was increased to about 7-8 by drop-wise adding ammoniac solution aiming to keep the sols stable. Subsequently, 1 g of the exfoliated graphite was added into the mixture and then vigorously stirred for about 30 minutes until EG not floating on the surface of solution. The temperature of solution was raised to 80°C for 4h to obtain a dark viscous liquid and then dried at 110°C for 24 hour. The as-prepared EG-CoFe$_2$O$_4$ composites were further calcined at temperatures range of 400-800°C for 1 hour at a heating rate of 10°C/min.

2.2. Characterization

The morphology of EG-CoFe$_2$O$_4$ was indicated by Scanning electron microscopy (SEM, Hitachi SU3500). The X-ray powder diffraction (XRD) of AC was implemented on D8 Advance Bruker powder diffractomter with a Cu–Kα excitation source. The diffraction spectra were recorded with scan rate of 0.02°/s. The angle range (2θ) was investigated between 0° and 50°. Energy dispersion X-ray analysis (EDX) spectrography was studied by Hitachi TM3000 with Oxford SwiftED3000 intrument. The magnetism of composites was performed on a GMW 3474-140 magnetometer equipped with a superconducting magnet to produce fields up to 16 Koe.
2.3. Evaluation of sorption capacity

For the dry system, EG-CoFe$_2$O$_4$ was added directly into blend of different oils and water solution contained in glass dishes at room temperature. After 6 minutes, blends of EG-CoFe$_2$O$_4$ and oil were recovered using permanent magnetic under glass dish. EG-CoFe$_2$O$_4$ was then separated and dried at room temperature to remove the water completely. The amount of adsorbed oil was calculated from the weight increase of EG-CoFe$_2$O$_4$ after adsorption, using the following equation:

$$\text{Adsorption capacity} = \frac{m_2 - m_1}{m_1} \text{ (g/g)}$$

where $m_1$ is the weight of EG-CoFe$_2$O$_4$ before oil adsorption (g), and $m_2$ is the weight of EG-CoFe$_2$O$_4$ after oil adsorption (g).

3. Results and discussion

Figure 1a shows the XRD pattern of the as-obtained EG-CoFe$_2$O$_4$ by using the acid sol-gel method. Diffraction peaks at 26.70° is ascribed to the main peak of natural graphite corresponding to (200) plane [25-27]. This suggests that the exfoliation of a carbon layer was not absolutely. The new peak at 35.45° and 30.01° can be attributed to CoFe$_2$O$_4$ crystalline incorporated into graphite layers in (311) and (220) plane, which imply that cobalt oxide and iron (III) oxide transformed into cobalt ferrite under high temperature [28, 29].

The elemental composition of the EG-CoFe$_2$O$_4$ was determined by Energy dispersion X-ray analysis (EDX) as shown inset of 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 results. In accordance with expectation, the total weight percent of Ni, Fe and O species was close to 10 wt%. Scanning electron microscopy (SEM) were used to observe the morphology of the samples under study. Figure 2 shows the SEM images of the as-prepared EG-CoFe$_2$O$_4$ composites. The samples were stacked closely, and no obvious layered structure for EG appeared in the observation view. The shape of EG-CoFe$_2$O$_4$ is rough due to even dispersion of CoFe$_2$O$_4$ magnetic nanoparticles on the EG surface. This is indicated that CoFe$_2$O$_4$ was successfully incorporated into EG sheets.
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Figure 2. SEM image of EG (A) and EG-CoFe$_2$O$_4$ (B), inset of Figure 2B shown the elemental compositions of EG-CoFe$_2$O$_4$.

Figure 3. (A) The simulated experiment for the magnetism of EG-CoFe$_2$O$_4$ and (B) Magnetization curves of EG-CoFe$_2$O$_4$.

The magnetic property plays a crucial role in magnetized materials. It is given that the magnetic response ability of materials to an external magnetic field to promote their application. In present work, the incorporation of CoFe$_2$O$_4$ aims to enhance magnetism of exfoliated graphite which been found to facilitate phase separation under a magnetic field thus allowing easy collection of the used adsorbents from polluted water. To characterize the magnetic performance of materials, the magnetization measurements were performed at room temperature with the applied field of 16000 Oe. The
magnetism of EG, CoFe$_2$O$_4$ and EG-CoFe$_2$O$_4$ prepared by sol-gel methods are shown in Figure 3. The obtained results showed the magnetic value of EG near the zero. The addition of CoFe$_2$O$_4$ nanoparticles into EG significantly increased the magnetic value of composite. It can be observed that the hysteresis loops of EG-CoFe$_2$O$_4$ based composite show the characteristics of ferromagnetic materials. The magnetism of EG-CoFe$_2$O$_4$ reaches at 32 emu/g. However, the magnetism of EG-CoFe$_2$O$_4$ is lower than CoFe$_2$O$_4$ magnetic value (45 emu/g) due to the magnetic barrier of graphite layer with sharp edges for magnetic response to an external magnetic field [30].

Adsorption efficiency of porous adsorbents heavily depend on the specific surface area and pore volume. Hence, the adsorption capacity is expected to be higher for the larger surface area and microporous volume. The change in textural properties of graphite upon modification was investigated by N$_2$ adsorption measurement. The detailed parameters as found in Table 1 showed the pore volume (supermicro-meso pores) and BET surface area of EG-CoFe$_2$O$_4$ determined to be 0.153 cm$^3$/g and 192.30 m$^2$/g respectively which are higher than those of the unmodified EG (0.122 cm$^3$/g and 147.46 m$^2$/g). It is given that decomposition of acid citric molecules in the sample calcination stage producing defects and large holes and two-step calcining process in the EG-CoFe$_2$O$_4$ fabrication. Figure 4 shows the selected adsorption and desorption isotherms of EG-CoFe$_2$O$_4$ material. Inset of Figure 4, the mesopore networks with a wide range of mesopores sizes were emerged owing to exfoliation process and pore radius 8-30Å pores contributes mainly to the total mesopore volume.

Table 1. Properties of EG and MEG.

| Sample        | $S_{BET}$ (m$^2$/g) | Pore radius (Å) | Pore volume (cm$^3$/g) |
|---------------|---------------------|------------------|------------------------|
| EG            | 147.46              | 13.70            | 0.122                  |
| EG-CoFe$_2$O$_4$ | 192.30             | 14.00            | 0.153                  |

Figure 4. Nitrogen adsorption/desorption isotherms curve of EG-CoFe$_2$O$_4$ and Insets: pore size distributions.

The adsorption capacities of the as-prepared EG-CoFe$_2$O$_4$ 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 5 showed that EG-CoFe$_2$O$_4$ has the highest adsorption capacity, and also fastest sorption rate, for FO (54.13 gFO) followed by CO (50.79 gCO) and DO (43.35 gDO). This is explained lying on the
glutinosity and density property of FO and CO are higher than that of DO reported in previous research [31-33].

![Figure 5](image-url)

**Figure 5.** (A) Procedure of oil adsorption: (i) EG-CoFe$_2$O$_4$ immersed in oil and water blend, (ii) using permanent magnetic to keep EG-CoFe$_2$O$_4$ containing oil, (iii) EG-CoFe$_2$O$_4$ after adsorption and (B) the adsorption capacities of EG-CoFe$_2$O$_4$.

4. Conclusions
In brief, the EG-CoFe$_2$O$_4$ was prepared via a facile two-step process: the expansion of graphite by intercalation method using H$_2$O$_2$ and H$_2$SO$_4$ and the decoration of magnetic CoFe$_2$O$_4$ on EG by sol-gel method. The obtained results showed that the CoFe$_2$O$_4$ nanoparticles were deposited efficiently and evenly on the EG layers. The specific surface area and magnetism of the EG-CoFe$_2$O$_4$ were obtained at 303.05 m$^2$/g and 32.00 emu/g, respectively. The adsorption capacity for FO, DO and CO was found to be about 54.13gFO, 43.35gDO and 50.79 gCO per 1g of EG-CoFe$_2$O$_4$ adsorbent, thus allowing it to be a promising material for oil pollution treatment.

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