OILY WASTEWATER TREATMENT BY MAGNETIC CARBON NANOTUBES NANOCOMPOSITE

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Abstract. A magnetic multi-wall carbon nanotube (MCNTs) nanocomposite was synthesized and was used as an adsorbent for removal of oil from aqueous solutions. The MCNTs nanocomposite was composed of commercial multi-wall carbon nanotubes and iron oxide nanoparticles. The property of this magnetic adsorbent was characterized by scanning electron microscopy, X-ray diffraction and VSM. Adsorption characteristics of the MCNT nanocomposite was examined using diesel oil (DO) as adsorbate. The sorption capacity was affected significantly by the initial concentration of DO, sorbent amount and contact time. Batch experiments were conducted to investigate the affect of different DO initial concentration (ranging from 0.2 to 1.0%) and contact time (10 to 90 min) to the removal efficiency. This MCNTs nanocomposite can be recycled conveniently from water with the assist of an external magnet because of their exceptional properties.
Keywords. Multi-wall carbon nanotube, adsorption, diesel oil removal, magnetic separation

1 INTRODUCTION

Carbon nanotubes (CNTs) have been the focus of extensive research in recent years due to their exceptional mechanical, thermal, and electrical properties. Because of their nanoscale dimensions and high surface area, CNTs could also be considered as efficient templates for the assembly and tethering of nanoparticles on their surface. Carbon nanotubes as new adsorbents have gained increasing attention of many researchers [1-2]. CNTs have been proven to possess great potential as superior adsorbents for efficient removing many kinds of organic and inorganic contaminants than activated carbon due to their large specific surface area, small size, and layered structures [3]. Although the adsorption capacity is increased using CNTs as adsorbents, it might be suffered from the inconvenience of tedious centrifugation separation process. To overcome this problem, functionalizing CNTs with magnetic nanoparticles can combine the features of magnetic nanoparticles and CNTs, which may result in novel chemical and physical properties, and thus promising applications [4-5]. In the present work, deposition of Fe_3O_4 nanoparticles on the outer surface of the nanotube was examined.

Oily wastewater is one of the most common sources of pollution generated by production in oil fields, oil refineries, ferrous and non-ferrous metallurgy, metal processing, mineral processing and chemical industries, as well as thermal energy and mining systems. Water pollution by waste oil has left an undesired impact on the environment and further risks to human health such as the risk of skin cancer from skin contact with used motor oils. A proper collection and treatment as well as the mitigation of any spills are therefore essential for the successful management of waste oils. The most commonly used methods for treatment of oily wastewater, before their disposal; include skimming, gravity separation, neutralization, flotation, adsorption, membrane process, coagulation and flocculation, electrochemical, emulsion breaking. Adsorption is one of the most effective processes of advanced wastewater treatment, which reduces trace hazardous organic and inorganic wastes left in effluents after the conventional treatment [6-8]. A wide range of adsorption materials, such as activated carbon, bentonite, peat, sand, coal, and fiberglass have been examined for oily wastewater treatment [9]. In this work, we aim at exploring the possibility to produce magnetic MWCNTs with exploitable characteristics as adsorbent for removal oily wastewater. This magnetic nanocomposite adsorbent was composed commercially available multi-wall carbon nanotubes and magnetic iron oxide nanoparticles for removal of oil contaminated in water.

2 MATERIALS AND METHODS

2.1 Materials

Multi-wall carbon nanotubes (MWCNT) with outer diameter 10–50 nm and length 1–10 μm was purchased from Institute of Materials Science (VAST, Vietnam). A stock solution of oil-contaminated water was prepared by mixing various amount of diesel oil (DO) with 1000 mL of water. The mixture was then stabilized in a blender at high speed for 15–20 min and sonicated for 10 min. The resultant solution was milky white and later used for adsorption test. All chemicals were analytical grade and used without further purification.

2.2 Preparation of MCNTs composite

0.15 g of multi-wall carbon nanotubes (MWCNT) was first dispersed in a solution mixture of concentrated H_2SO_4 and $HNO_3$with the volume ratio of 3:1. The suspension was stirred for 4 h at temperature of 60 ºC. Carboxylated multi-wall carbon nanotubes (named as MCNT-COOH) was washed with de-ionized water several times to reach neutral pH and dried at 110 ºC for 4 h. The synthesis of magnetic-multi-wall carbon nanotubes was performed by first adding 0.25g MCNT-COOH into 100 mL aqueous solution of 0.425g $(NH_4)_2Fe(SO_4)_2.6H_2O$ and 0.6275g $NH_4Fe(SO_4)_2.12H_2O$ (mol ratio of Fe^{2+}:Fe^{3+} =1:2) and stirred. 2.5 mL NH_4OH 8M was added to the solution and stirred for 30 min at 50 ºC. The magnetic-multi-wall carbon nanotubes (MCNTs) were collected by an external magnet. The resulting powder products were washed with ethanol three times and dried under vacuum for 24 h.

2.3 Characterizations

An X-ray diffraction was carried out in X'Pert Pro MRD (PANanalytical, The Netherlands) at room temperature with Cu-K□radiation (λ = 0.154nm) and an incident angle (2θ), ramping from 2 to 800 at a rate of 50 seconds/step. Magnetic measurement of the product was conducted on a vibrating sample magnetometer (VSM-5 Model, MicroSense Co.,Ltd.). Scanning Electron Microscope (SEM) and Fourier transform infrared spectroscopy (FT-IR) were used to characterize the morphology and structure of the prepared materials. The FT-IR spectra were recorded with a Bruker Tensor 27 spectrometer (Germany) and the range of the scanning wave numbers was 500–4000 cm^{-1}. The SEM photographs were investigated using Hitachi S-4800 Scanning Microscope (Japan).

2.4 Adsorption experiments

Adsorption kinetic experiments were conducted in a set of Erlenmeyer flasks (100 mL) containing 0.1 g of MCNT nanocompostie and 30 mL different concentrations of oil (0.2 to 1% v/v) in water to determine the minimum time required for adsorption to reach a steady-state condition at a fixed pH (=7.0). The aliquots were taken from the suspension at different time intervals and treated with a magnet to separate the MCNT nanocomposite adsorbents from the solution. Treated samples were collected at various time intervals and analyzed for COD. To investigate the effect of adsorbent dosage, different doses of MMWCNT nanocomposite adsorbents were added to each Erlenmeyer flasks with constant time.

3 RESULT AND DICUSSION

3.1 Preparation and Characterizations of Nanocomposite

The FT-IR spectrum of prepared nanocomposites were indicated in Figure 1. The successful coating of Fe_3O_4 on the CNT surface can be seen in the spectroscopic analysis. Several typical peaks of Fe_3O_4 were observed in the spectrum of MCNTs, inferring the coexistence of Fe_3O_4 in the structure of the synthesized nanocomposite. As can be seen, the typical adsorption peak at 3418 cm^{-1} indicated the stretching vibration of O-H bonds. The characteristic peaks at 1113 cm^{-1} and 1572 cm^{-1} was belonged to C–C and C=C bounds in MWCNT, respectively. The strong peak at around 1632 to 1700 cm^{-1} was related to the C=O groups. For the bare MWCNT materials, only the weak –OH stretching was observed; COO^- stretching and metal stretching vibrations were not found. It is believed that binding of Fe_3O_4 to CNT surface increased its hydroxyl and COO^- groups. Finally, as the result, the FI-TR graph demonstrated the existence of Fe_3O_4 nanoparticle in nanocomposite, which was relative to the results of XRD patterns.

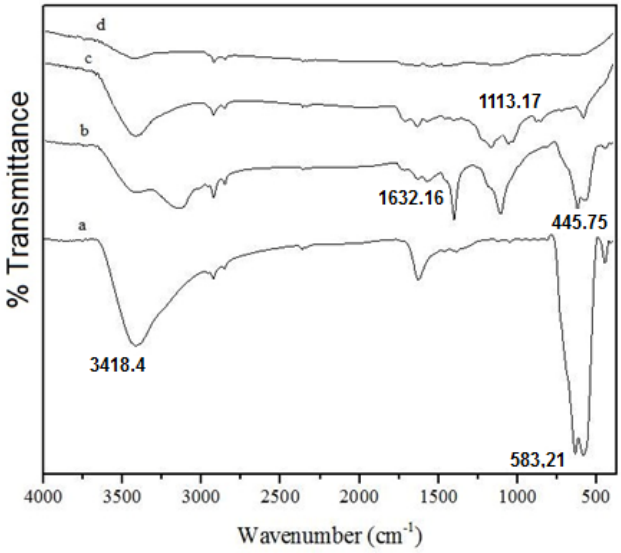

Figure 1. FT-IR of Fe_3O_4 (a), MCNTs (b), MCNT-COOH (c) và MWCNTs (d)

The results exhibited a typical broad reflection at 2θ of 27, 36 and 42° which can be attributed to reflection of amorphous carbon composed of polycyclic aromatic carbon sheets of similar to that of pure MWCNTs. Additionally, the other diffraction peaks at 30.3, 33, 42.1, 59 and 62.5 ° can be indexed as planes of Fe_3O_4 (data not shown).

In order to investigate the contribution of Fe_3O_4 nanoparticles and magnetic property of the composite, a vibrating sample magnetometer was used in this study. In Figure 2, the results of magnetization curves of MCNTs and Fe_3O_4 were presented. Interestingly, the magnetization curve of MCNTs proved the representation of Fe_3O_4 in the structure of the composite. The curves also revealed the superparamagnetism of Fe_3O_4 and MCNTs nanocomoposite. The saturation magnetization value of Fe_3O_4 was greater than that of MCNTs, 45 *emu*/g and 35 *emu*/g respectively. The loss of the saturation magnetization of MCNTs nanocomposite may be explained by the influence of ingredient of CNT after coating with Fe_3O_4. Therefore, it can be concluded that the saturation magnetization of the MCNTs nanocomposite varies with the contents of Fe_3O_4 and CNT. It was observed that, after dispersion of MCNTs in oily aqueous solution, the MCNTs nanocomposite was mixed with the oily aqueous solution and shaking the mixture for some time. The MCNTs nanocomposite can be easily separated from the aqueous solution within few minutes by placing a permanentmagnet near the glass bottle (Figure 3).

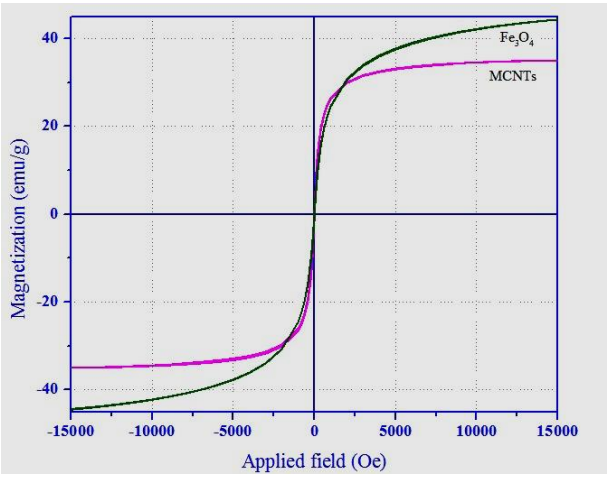

Figure 2. VSM of Fe_3O_4 and MCNTs

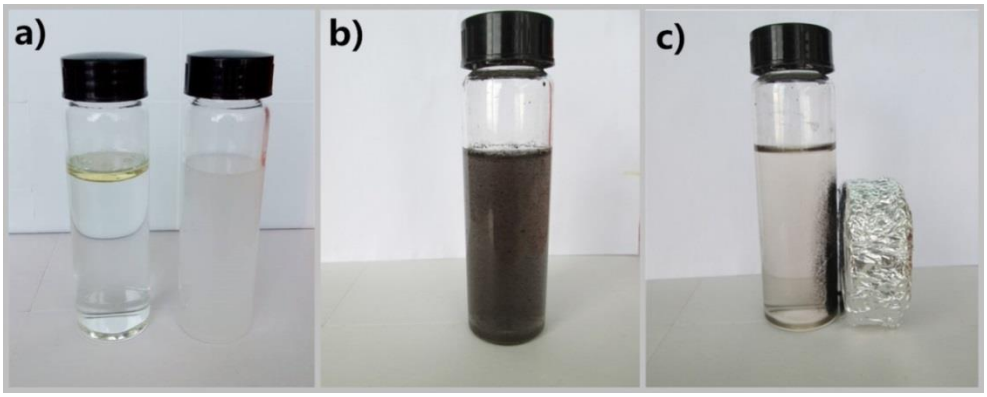

Figure 3. Oil-water mixture (a), Mixture of oil water emulsion and MCNT (b) and Separation by a magnet for reuse (c)

The morphologies of the MWCNTs and the synthesized MCNTs adsorbent were obtained by SEM. The results confirmed that iron oxide nanoparticles were successfully coated on the surface of MWCNTs to form multi-wall carbon nanotube iron oxide nanocomposites (Figure 4). These nanocomposites were explored as adsorbents for removal of DO from aqueous solution.

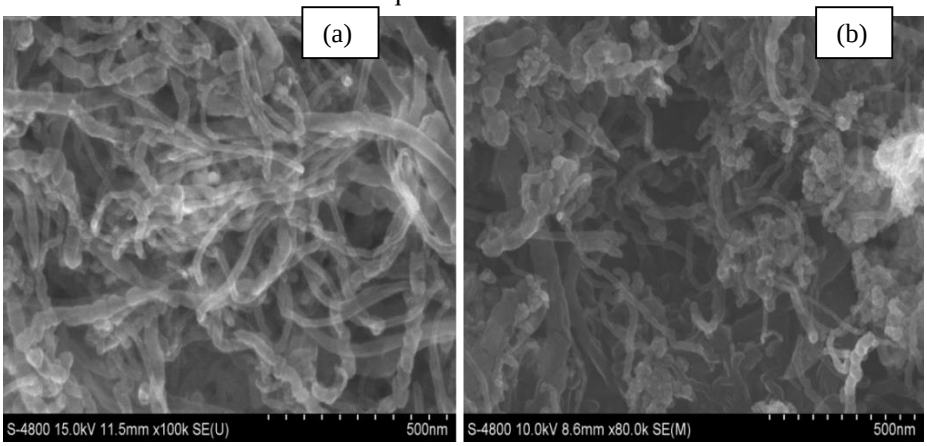

Figure 4. Scanning electron micrographs of MWCNTs (a) and MCNT nanocomposite (b)

3.2 Adsorption Test

3.2.1 Effect of contact time and initial oil concentration

The adsorption capacity and reuse performance of MCNTs for diesel oil was investigated in this study. The study on effect of shaking time and initial concentration on removal efficiency was performed with synthetic oily wastewater ranging from 0.2 to 1.0% (v/v). The results were shown in Figure 5. As can be seen, the DO removal efficiency increased fast with the increasing of adsorbed time in the range of 0-30 min for the concentration of DO from 0.2 to 1.0%. After 30 min, the DO removal efficiency increased slightly with increasing of adsorbed time until 60 min and achieved adsorption equilibrium in about 90 min. This can explain due to at the early stages, the number of holes on the surface of the material is quite large, so the DO molecules are easily adsorbed on the materials. Adsorption process takes place continuously; resulting in DO molecules gradually fill the cavities on the surface and inside tube of the material. The removal efficiencies were from 57.6 to 89.5% and 84.3 to 98.4% for 30 and 90 min contact time, respectively. Additionally, an increase in the initial DO concentration leads to the decrease in the removal efficiency of DO (Figure 6). However, amount of DO adsorbed increases from 268.13 to 386.9 mg/g with the increase in the concentration of DO from 0.2 to 1.0%. The higher initial concentration provides an important driving force to overcome all resistances of the oil between the aqueous and solid phases, thus increasing the uptake. In addition, increasing the initial oil concentration increases the number of collisions between oil and the adsorbent, which enhances the adsorption process. Additionally, the results show the adsorption isotherm of DO on the magnetic nanocomposite was fitted with the Langmuir model.

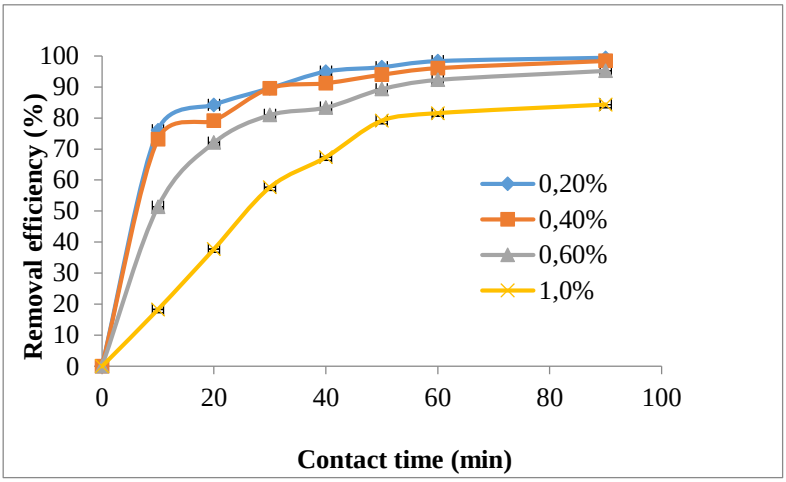

Figure 5. Effect of contact time on removal of DO by MCNTs (Room temperature, pH =7, 0.1 g of MCNT nanocompostie and 30 mL different concentrations of oil in aqueous solution)

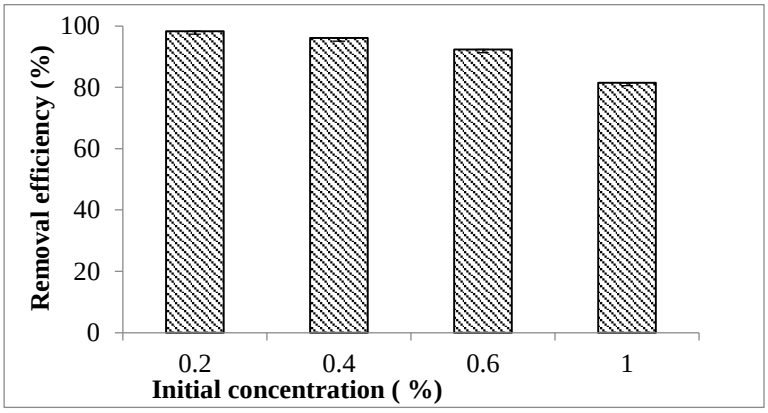

Figure 6. Effect of initial concentration on removal of DO by MCNTs (Room temperature, pH =7, 0.1 g of MCNT nanocomposite, time: 60 min and 30 mL different concentrations of oil in aqueous solution)

3.2.2 Effect of MCNTs dosage

It was observed that the percentages of DO adsorbed increased when the MCNTs dosage was increased over the range 0.05 to 0.25 g (Figure 9). The removal efficiencies of DO increased from 74.6 to 99.8% for dosage of 0.05 to 0.25, respectively. The reason might be based on van der Waals interactions occurring between the hexagonally arrayed carbon atoms in the graphite sheet of MCNTs and the aliphatic backbones of DO.

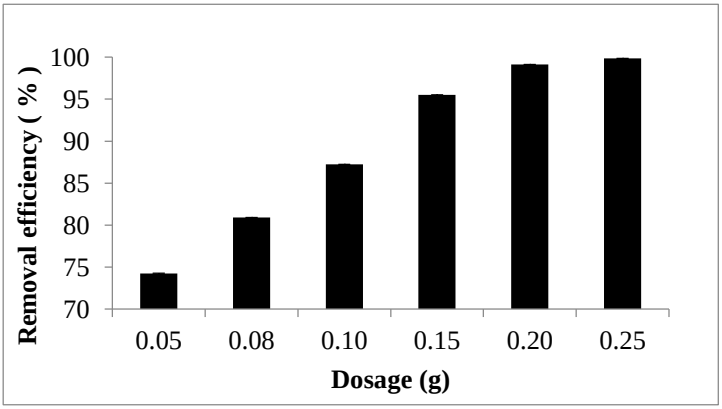

Figure 8. Removal efficiency of DO onto different amounts of MCNTs (Room temperature, pH =7, time: 60 min and 30 mL different concentrations of oil in aqueous solution)

4 CONCLUSIONS

In this contribution, a magnetic multi-wall carbon nanotube adsorbent for effective DO removal has been prepared. The structures of nanocomposite were characterized by FT-IR, XRD, VSM and SEM. The batch studies clearly suggest that MCNTs exhibits almost 100% adsorption at lower concentration of DO. The COD value is 899.3 mg/L and 5.57 mg/L for 0.2% DO in water before and after removal by prepared material, repsectively. The oil adsorption capacity of MCNTs increased with the increasing of contact time and MCNTs dosage.

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XỬ LÝ NƯỚC THẢI NHIỄM DẦU BẰNG VẬT LIỆU ỐNG NANO TỪ TÍNH

Tóm tắt. Vật liệu nanocomposit từ tính của ống nanocarbon đa lớp (MCNTs) được tổng hợp và sử dụng làm chất hấp phụ để loại bỏ dầu khỏi dung dịch nước. Vật liệu MCNTs được tổng hợp nên từ ống nanocarbon đa lớp và các hạt nano oxit sắt. Đặc trưng của vật liệu này được xác định bằng kính hiển vi điện tử quét, nhiễu xạ tia X và VSM. Các đặc tính hấp phụ của vật liệu nano MCNTs đã được kiểm tra bằng cách sử dụng DO như chất hấp phụ. Hiệu suất hấp phụ bị ảnh hưởng đáng kể bởi nồng độ DO ban đầu, lượng MCNTs và thời gian tiếp xúc. Các thí nghiệm khảo sát ảnh hưởng đến hiệu quả loại bỏ DO bao gồm: Nồng độ DO ban đầu (từ 0,2 đến 1,0%) và thời gian tiếp xúc (10 đến 90 phút). Vật liệu nano MCNT này có thể được tái chế một cách thuận tiện từ nước với sự trợ giúp của một nam châm bên ngoài vì các đặc tính đặc biệt của chúng.

Từ khóa. Ống nanocacbon, loại bỏ dầu diesel, từ tính, dầu loang

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