Study on Oil Absorption Properties of Magnetic Chitosan Stearic Acid Compound

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Abstract. The magnetic chitosan-stearic acid compound was prepared for using chitosan and stearic acid. The morphology, structure and hydrophobic property of the magnetic chitosan-stearic acid compound were characterized. The influences of oil type and temperature on its oil absorption performance were determined. The results shows that the magnetic chitosan-stearic acid compound has a fluffy structure with a contact angle of 133.65°, indicating that the compound has a good hydrophobic property. Different oils have various impact on the oil absorption performance of the magnetic chitosan-stearic acid compound. The magnetic chitosan-stearic acid compound has the best oil absorption to crude oil, with an oil absorption rate of 4.12 g/g. With the increase of temperature, the oil absorption rate first increases and then decreases. There is an optimal temperature for oil absorption, with a temperature of 40℃.

1. Introduction
In recent years, with the continuous development and utilization of offshore oil resources, the pollution of offshore oil spill comes to be a concern [1,2]. At present, the domestic and foreign methods for the treatment of offshore oil pollution include combustion treatment, microbial treatment, physical fence method, etc [3]. However, oil-absorbing materials are widely used and have broad application prospects [4,5]. It is not only energy efficient, low cost, but also easy to recycle, making it become an ideal oil-absorbing material [6,7].

Lin et al. used natural biodegradable chitosan to interact with the carboxyl group of stearic acid and introduced hydrophobic alkyl chains to prepare a hydrophobic compound adsorbent [8]. Guo et al. prepared and researched a magnetic chitosan-stearic acid material that was easily degradable and oil-absorbing, which could adsorb dozens of times of its own oil, easily degradable and variable in volume, providing a new method for automatic degreasing [9]. Lin et al. prepared hydrophobic and lipophilic chitosan stearic acid ionic compound by the reaction of sodium stearate solution and particle groups in chitosan hydrochloric acid solution. It was found that the ionic compound had a good oil absorption performance for diesel, crude and kerosene, and it became a new type of high-performance oil absorption material [10]. The above studies have produced ideal compound oil-absorbing materials, but the oil-absorbing effect of the material need to be further studied and analyzed.

In this paper, we used chitosan and sodium stearate as raw materials to prepare magnetic chitosan-sodium stearate compound oil absorption material. The morphology and characteristics of the compound were characterized by high-power microscope testing. The contact angle of the compound material was measured and analyzed. The influence of different oil types and temperature on the oil absorption performance of magnetic compound were analyzed.
2. Experimental

2.1 Materials and Instruments
Chitosan, glacial acetic acid, sodium stearate, ethanol, ammonia water, KBr and tetramethylammonium hydroxide (TMA, 25%) were purchased from Sinopharm Chemical Reagent Co., Ltd (Beijing, China, AR grade). FeCl₂·6H₂O were purchased from Sigma-Aldrich Trading Co., Ltd (Shanghai, China, AR grade). Magnetic Fe₃O₄ nanoparticles were purchased from Andi Metal Material Co., Ltd (Hebei, China). The crude oil was taken from Zhoushan Aoshan Petroleum Base (Zhoushan, China). Deionized water was made in the laboratory.

The instruments used in this study were as follows: 101-00BS electric heating constant temperature blast drying oven and DF-101S thermostat stirrer (Shanghai Lichen Bangxi Instrument Technology Co., Ltd. China), KQ-50B ultrasonic cleaner (Kunshan Meimei Ultrasonic Instrument Co., Ltd. China), VHX-5000 super depth of field three-digit digital microscope(Keyence, Japan), JEM2100F transmission electron microscope (Electronics Corporation, Japan), 6700FTIR Fourier spectrometer (FT-IR) (Nicolet, Thermo Fisher Scientific, America), and JY-82 contact angle measuring instrument (Chengde Dingsheng Testing Machine Testing Equipment Co., Ltd. China).

2.2 Experimental methods

2.2.1 Preparation of magnetic chitosan stearic acid compound
3 g Fe₃O₄ nanoparticles were weighed, and added into 1mol/L TMA aqueous solution, which had maintained at 3-4 ℃ for 24 hours. When Fe₃O₄ nanoparticles were absorbed by a magnet close to the bottom of the beaker, the beaker was tilted to pour out the TMA solution. Then, the Fe₃O₄ nanoparticles were washed with deionized water for 5-6 times for standby. The acetic acid aqueous solution with a mass ratio of 95% was prepared, and kept at 80 ℃ for 10 minutes in the thermostat water bath. 5 g chitosan was weighed, slowly added to the aqueous solution of acetic acid, and stirred for 3-5 minutes until the chitosan was completely dissolved. The washed Fe₃O₄ nanoparticles were added into chitosan acetic acid aqueous solution, and then ultrasonically vibrated for 3-4 minutes for standby.

100 mL deionized water was measured, and maintained kept at 80 ℃ for 10 minutes in the thermostat water bath. 4.5g sodium stearate was weighed, added into the deionized water, and stirred until the sodium stearate was completely dissolved. The prepared magnetic chitosan acetic acid solution was slowly added into sodium stearate solution in the high-speed stirring. After adding the magnetic chitosan acetic acid solution, the mixture was stirred for 4-5 minutes to demise the reaction. After the full reaction, the reaction product was filtered using non-woven fabric, washed with 80 ℃ hot water to remove unreacted reactants, and then dried in the drying oven at 60 ℃ for 3-4 hours to obtain magnetic chitosan stearic acid compound.

2.2.2 Characterization of magnetic chitosan stearic acid compound
The morphology of magnetic Fe₃O₄ nanoparticles was measured by JEM2100F transmission electron microscope. The spectrum of magnetic chitosan-stearic acid composite material was measured by Nicolet6700 Fourier spectrometer. The contact angle of the magnetic chitosan-stearic acid composite material was measured with JY-82A contact angle measuring instrument. The morphology of magnetic chitosan-stearic acid composite material was characterized by VHX-5000 ultra-depth-of-field microscope.

2.2.3 Determination of Oil Absorption Properties
A certain amount of magnetic chitosan stearic acid compound was put into a non-woven bag, and the non-woven bag was soaked in crude oil to carry out the oil absorption tests for 24 hours. Then, the non-woven bag was taken out, and weighed after dripped for 5 minutes. At the same time, the empty non-woven bag was used as a blank control group. So, the oil absorption ratio of magnetic chitosan stearic acid compound was determined. The oil absorption ratio of the compound could be calculated by
formula (1):

\[ A = \frac{m_1 - m_2 - m_3}{m_2} \times 100\% \]  
(1)

Where A is the oil absorption ratio which reflected the oil absorption performance, \( m_1 \) is the total mass of compound and non-woven bag after oil absorption, g; \( m_2 \) is the mass of compound loaded in non-woven bag, g; \( m_3 \) is the mass of the nonwoven bag, g.

3. Results and Discussion

3.1 Characterization of magnetic chitosan stearic acid compound

The transmission electron micrograph of the magnetic Fe₃O₄ nanoparticle sample was shown in Figure 1(a). The nanoparticles had a very small cubic shape and a large specific surface area, which could provide a large surface energy. Therefore, they gathered together in large numbers to form larger aggregates. The morphology of the magnetic chitosan-sodium stearate composite oil absorption material was shown in Figure 1 (b). The magnetic composite oil absorption material aggregated into uniformly sized aggregates, showing a fluffy sponge-like structure. The fluffy tissue structure could be observed clearly from the figure, which provided a large specific surface area. It was shown that it had a better oil absorption performance.

The FT-IR spectra of magnetic chitosan stearic acid compound and chitosan stearic acid compound were shown in Figure 2. For magnetic and non-magnetic chitosan sodium stearate compounds, the absorption peak at 3451 cm⁻¹ was the stretching vibration of -OH in chitosan. The asymmetric stretching vibration peak of methylene (-CH₂) in the alkyl chain of sodium stearate was at 2925 cm⁻¹. The absorption peak at 2844 cm⁻¹ was the compound symmetric stretching vibration of chitosan and methylene in sodium stearate. The new absorption peak at 1712 cm⁻¹ was caused by the stretching vibration of carboxyl C=O formed by the interaction between chitosan and sodium stearate. The absorption peaks at 717 cm⁻¹ and 500 cm⁻¹ were the vibration region of Na-O. The above analysis showed that chitosan and sodium stearate were combined with each other. Compared with the non-magnetic compound, the magnetic chitosan-sodium stearate compound had an absorption peak of Fe-O bond at 588 cm⁻¹, indicating that the Fe₃O₄ nanoparticles existed in the compound.

![Figure 1. Morphology of magnetic Fe₃O₄ nanoparticles (a) and magnetic composite oil-absorption material (b).](image)
Figure 2. FT-IR spectra of magnetic chitosan-stearic acid and chitosan-stearic acid composite oil absorption material.

The contact angle drop diagram of magnetic and non-magnetic chitosan stearic acid compounds were shown in Figure 3. Through the measurement and calculation, the contact angles of non-magnetic and magnetic compounds were 133.65° and 136.69°, respectively. They both were greater than 90°, which indicated that the two compounds both had a good hydrophobicity, and the hydrophobic properties were not affected by the magnetism properties.

Figure 3. Contact angle of non-magnetic compound (a) and magnetic compound (b).

3.2 Influence of oil types on oil absorption properties
The influences of five kinds of crude oil (A), corn oil (B), gasoline (C), kitchen waste (D) and polluted oil and water (E) on the oil absorption performance of magnetic chitosan stearic acid compound in the same adsorption times was investigated, as shown in Figure 4. According to Figure 4, the higher the viscosity of oil, the better the oil absorption performance. The oil absorption ratio of crude oil was the highest (4.12g/g), and the one was the lowest (2.5g/g). However, the gasoline, as the only light oil, had a higher oil absorption ratio than the corn oil. The viscosity of the gasoline was far smaller than that of the corn oil whereas the oil absorption ratio was opposite. The reason was that the gasoline was volatile, and there would be a certain amount of volatilization in the experiment process, which led to higher oil absorption ratio of gasoline oil than actual oil absorption rate.
3.3 Influence of temperature on oil absorption properties

The influence of temperature on the oil absorption performance of the compound was obtained, as shown in Figure 5. The temperature had an obvious influence on the adsorption performance of the compound. The oil absorption ratio of the compound first increased rapidly and then reached stability with an increase of the temperature ranging from 20 to 60 °C. When the temperature reached 60°C, the oil absorption rate dropped significantly. This was because the viscosity of crude oil was reduced due to the higher temperature and it couldn’t be better adsorbed by the compound. The best oil absorption temperature of magnetic chitosan stearic acid compound was 40 °C.

4. Conclusions

In this study, a magnetic chitosan-stearic acid composite was prepared by using chitosan and stearic acid. The morphology, structure and hydrophobicity were characterized, and the effects of oil type and temperature on its oil absorption performance were analyzed. The conclusion is as follows:

(1) The magnetic composite material has a fluffy sponge structure with a large specific surface area and excellent oil absorption performance. It has a good hydrophobic property with a contact angle reached 133.65°.

(2) The magnetic composite material has the best oil absorption performance for crude oil with an oil absorption rate reached 4.12g/g. With the increase of temperature, the oil absorption performance increased first and then decreased. There is an optimal temperature for oil absorption. When the temperature is 40 °C, the oil absorption rate of magnetic composite material is the largest.

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