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Preparation of Core-shell Magnetic Nanoparticles Carrier for Treatment of Emulsified Oil

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Preparation of Core-shell Magnetic Nanoparticles Carrier for Treatment of Emulsified Oil

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Abstract. The Fe_3O_4 nanoparticles was prepared by chemical co-precipitation method, and modified with polyethylene glycol and lauryl sodium sulfate to obtain amphiphilic magnetic core. Core-shell magnetic particles (CMP) were prepared by modified dispersion polymerization method. After characterization, the contact angle θ of material was 133.4°, and the specific surface area of CMP reached to 1032.43 m2/g. The absorption rate up to 27.1007 g/g, and the oil release rate was up to 96.19%, ensure it fully adsorptive to the emulsified oily wastewater. The saturated magnetization of MPP was 3.95 emu/g, showed strong magnetic response. It is beneficial for recovery and reuse the material. After 12 hour degradation of crude oil, CMP immobilized with petroleum oil degrading strains to treat emulsified oil was 13.86% higher than that of free bacterial cells. The results of this research provide a reference for the rapid adsorption and degradation of emulsified oil wastewater by immobilized microorganisms with novel magnetic materials.

Keywords. Nano-materials; Immobilization; Bioremediation; Emulsified oil; Wastewater treatment.

1. Introduction

Emulsified oil wastewater is a kind of oil-containing wastewater which is difficult to treat. It contains not only emulsified oils, but also a large number of surfactants, alkanes, aromatic hydrocarbons, ketones, halogenated hydrocarbons and nitrogen-containing compounds. At present, the emulsified oil wastewater degreasing methods mainly include demulsification, centrifugation, gravity sedimentation, flotation, electrolysis, adsorption, etc. [1,2]. These processes have better oil removal effect in practical applications， but the COD is still as high as several hundred or even several thousand, which cannot meet the requirements of emission standards. Therefore, it is particularly important to study new, fast and efficient water treatment methods.

Immobilized microbiology is applied to wastewater treatment, which is beneficial to increase the proliferation of microorganisms in the bioreactor, solid-liquid separation after reaction, improve the processing capacity of the system. Magnetic polymer particles are a new type of polymer material that not only has the excellent properties of polymer materials, but also has good magnetic responsiveness[3-5].The ingenious combination of immobilization technology and magnetic separation technology is a very active research direction in the field of bioengineering nowadays [6,7]. In the study of wastewater treatment, magnetic materials should have the characteristics of loose porosity, strong biological affinity, floatability and fluidization [8-10]. In this study, magnetic colloidal magnetic core [11,12] was prepared by dispersion polymerization method. The porous material of core-shell structure was synthesized under controlled conditions, and the immobilized microorganism was immobilized on magnetic material to prepare emulsified oil wastewater treatment agent for degrading emulsified oil wastewater.

2. Experimental materials and methods

2.1. Reagents and materials

Reagents ferrous chloride, absolute ethanol, hydrochloric acid, PEG, SDS, St, BPO, MAA, DVB, PAC, PASA, n-hexane, etc. were purchased from Sinopharm Group. Agar, peptone, beef extract, glucose, yeast extract powder were purchased from Beijing Aoboxing Company. Bacillus cereus was purchased from the China General Microorganisms Collection. Petroleum ($\rho_{20=}$ 889 kg m^{-3}), diesel (ρ_{20} = 822 kg m^{-3}), heavy oil was and emulsified oil.

2.2. Preparation of Core-shell Structure Magnetic Particles

Weigh $FeCl_3 \cdot 6H_2O$ (4 g) and $FeCl_2 \cdot 4H_2O$ (8 g) dissolved in 80 mL of deionized water, heated to 80℃ in a water bath, under the protection of nitrogen, 5 mL of 4 mol/L ammonia water was added drop by drop and stirred for 30 min to precipitate Fe^{3+} and Fe^{2+} .After cooling to room temperature, adding 2 g PEG and 3 g SDS dissolved in 50 mL deionized water to modify, stirring for 1 h. After the obtained black solution was flocculated with ethanol, Fe_3O_4 magnetic colloid was obtained, washed with dilute hydrochloric acid and deionized water until neutral, and then dried for storage. Dispense 100 mL of 7% PEG solution, heat to 70 °C in a water bath, add 12 g of Fe_3O_4 magnetic colloid, add 100 mL of absolute ethanol under the protection of nitrogen, and stir at 60 °C for 0.5 h. The mixed solution was heated to 80 °C, and 10 mL St with 4 g BPO, 2 mL MAA, 4 mL DVB, 12 mL n-heptane, 12 mL toluene, 1 g PAC, 1 g PASA were added in sequence, Using acetone as a good solvent, magnetic porous particles with styrene-acrylic acid copolymer as the main component were obtained by extracting 48 hours in Soxhlet extractor and drying 10 hours at 120℃.

2.3. Characterization test of samples

Scanning electron microscopy (EVO18, Zeiss, Germany) was used to characterize the morphology of the material. An X-ray diffractometer (Bruker D8 ADVANCE, Germany) was used for the determination of the material structure. Vibrating sample magnetometer (Lake Shore 7410, USA) was used to measure the magnetic properties of the prepared materials. Zeta potentiometer (Zeta 90 plus, Brookhaven, USA) was used to characterize the stability of colloidal dispersion. The contact angle measuring instrument (Easy-Drop, RUSS company, Germany) measures the surface contact angle. The specific surface area of the sample was measured by a specific surface and pore size measuring instrument (F-Sorb 3400, Jine Spectrum, Beijing).Gas chromatography (Shimadzu, Japan) was used to determine the degradation rate of emulsified oil by microorganisms.

Adsorption performance test: including material oil absorption capacity, oil retention capacity test. The quality of the sample before it is absorbed into the oil is recorded as m_1 , The sample is left to stand for about 30 s and weighed. The quality of the sample is recorded as m_2 .Continue to stand for 15 min and weigh again. The quality of the sample is recorded as m_3 .

3. Results and discussion

3.1. Adsorption performance test

A drop of heavy oil was added to a petri dish filled with water. As shown in Figure 1 (a) ~ (d), When the material is close to the heavy oil droplets from the side, the material will show obvious oil absorption;

Figures (e) and (f) are tested separately when the material is first injected and the oil droplets are first dropped. At this time, it can be observed that the material is quickly covered by the oil droplets when the material and the oil droplets are in contact, regardless of the order.

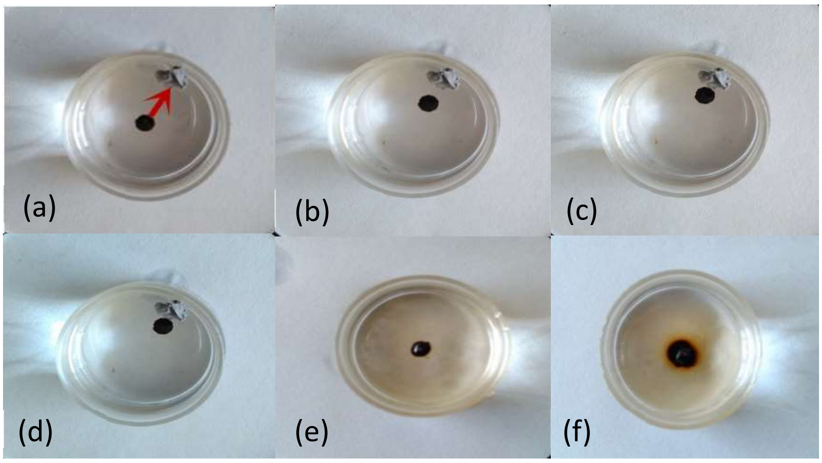

Figure 1 Lipophilic performance test of synthetic polymer materials

Test of oil absorption capacity and oil preservation ability of synthetic polymer immobilization materials for heavy polymer, crude oil and diesel oil:

$$k = \frac{m_2 - m_1}{m_1} \tag{1}$$

$$q = \frac{m_3 - m_1}{m_2 - m_1} \times 100\% \tag{2}$$

Calculate the final saturated oil absorption rate k (unit g/g) and the final slow release oil retention rate q (%) based on the mass according to formulas (1) and (2). Parallel experiments are performed 3 times and take average value. The results are shown in the table. 1.

Table 1 Test results of adsorption performance of materials prepared for different oils

No	Oil	m1(g)	m2(g)	m3(g)	k (g / g)	q (%)
1	Heavy oil	0.1505	4.2292	4.0738	27.1007	96.19
2	Crude oil	0.1499	2.6614	2.3158	16.7545	86.24
3	Diesel oil	0.1503	1.4522	1.1617	8.6620	77.69

From Table 1, it can be seen that the adsorptive capacity of the prepared materials to three kinds of oil is quite different, which indicates that the variety of oil is related to the adsorptive capacity.

3.2. Static contact angle test

In order to test the micro-lipophilic hydrophobic properties of the carrier material, the contact angle of the carrier material was tested. The test results are shown in Fig. 2.

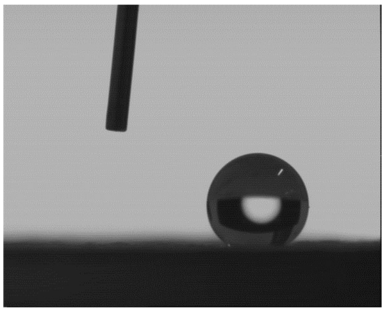

Figure 2 Static contact angle photo of the material

According to the Young's equation, the degree of wetting of the material can be measured by the magnitude of the contact angle θ. The display value of the contact angle of the carrier material prepared in this study is 133.4°, ranging from 90° to 150°, approaching 150°.The prepared material exhibits hydrophobicity in terms of hydrophilicity and hydrophobicity, and also indicates that the prepared carrier has good hydrophobicity and is suitable as an immobilized microbial material.

3.3. x-ray diffraction characterization

Figure 3 is an X-ray diffraction pattern of the prepared magnetic material. It can be seen from the figure that 30°, 36°, 43°, 54°, 57°, 63°, 71° and 74° correspond to the diffraction characteristic peaks of the eight crystal faces of $Fe3O4$, respectively.), (311), (400), (422), (511), (440), (620), and (523), respectively. Since the diffraction peaks in the XRD spectrum are sharp and there are no other peaks, therefore, it can be confirmed that the magnetic material prepared by the experiment contains $Fe3O4$ composition. Calculate by Scherrer formula $D = \frac{k\gamma}{B\cos\theta}$, where K is the Scherrer constant, D is the average thickness of the grains perpendicular to the crystal plane direction, B is the half-height width of the diffraction peak of the measured sample, θ is the diffraction angle, and γ is the X-ray wavelength 0.1540 nm. The calculated average particle size D is about 50 nm.

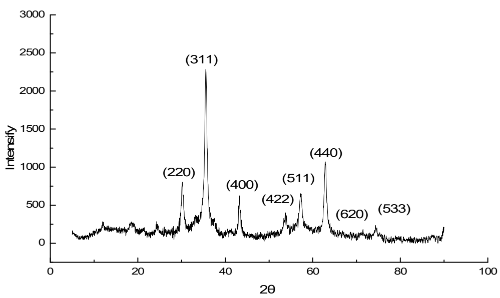

Figure 3. XRD spectrum

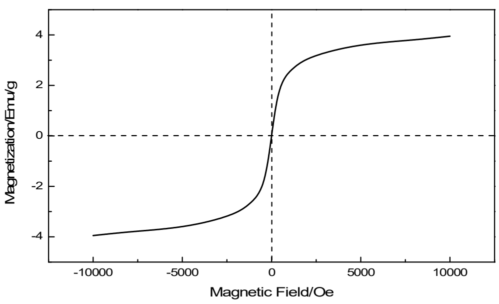

Figure 4. Hysteresis loop diagram at room temperature

3.4. Magnetic test

Figure 4 shows the room temperature hysteresis loop of the magnetic particle carrier at 300 K at room temperature. It can be seen from the figure that the coercivity of the magnetic particle is zero, showing a typical superparamagnetism. The specific saturation magnetization of the magnetic particles is 3.95 emu/g, which proves that the magnetic composite particles have strong magnetic responsiveness, which is beneficial to the recovery and reuse of the immobilized microbial materials after use.

3.5. Immobilized microorganisms

The surface morphology of the prepared material and the immobilized microorganisms is shown in Fig. 5.It can be seen from the figure that the surface of magnetic particles with dense and interconnected holes, is suitable for immobilization of microorganisms degrading emulsified oil. A large number of rod-shaped microorganisms are attached to the surface and pores of the material, indicating that the microorganisms exhibit a good growth and proliferation state on the carrier, which also indicates that the carrier material has good bioaffinity and is suitable for the growth and reproduction of microorganisms.

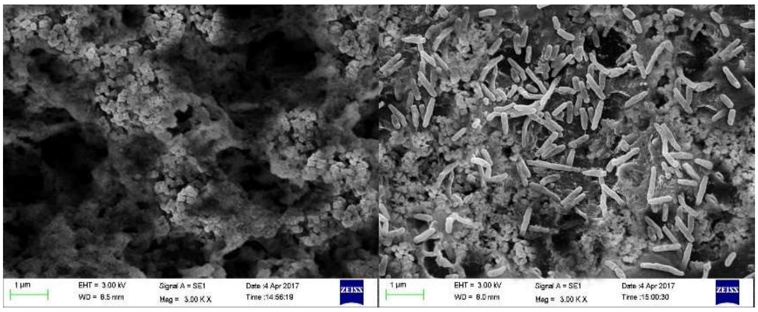

Figure 5. SEM diagram of magnetic particles

3.6. Analysis of adsorption mechanism

The Fe_3O_4 magnetic nanoparticles were prepared by chemical coprecipitation method. The reaction formula is: $2Fe^{3+} + Fe^{2+} + 8OH^- \rightarrow Fe_3O_4 + 8H_2O$, and the particles were modified with PEG and SDS to make them amphiphilic, and a magnetic colloid was obtained. The magnetic particles of the core-shell structure were prepared by a dispersion polymerization method using a magnetic colloid as a magnetic core. The core-shell structure is combined by nesting relationship, thus maintaining the amphiphilicity of the particles to the greatest extent, and the porous particles are obtained by controlling the conditions of the porogen. The porous structure enables the hydrophilic magnetic core to be in contact with the outside through the pores, and the hydrophobic shell layer has an adsorption property to the emulsified oil, thereby reflecting the parental properties of the material. The material's specific surface area meter test readings show a specific surface area as high as 1032.43 m^2 / g. The main principle of the material's strong adsorption capacity and large adsorption capacity is that the hydrophobic outer shell has affinity for the emulsified oil, and the adsorbed emulsified oil droplets are captured by the pores of the surface of the material, and the inner space of the material is rich and the specific surface area is large. The oil adsorption capacity of the material is further improved.

3.7. Petroleum degradation effect

The microorganism and the culture solution were mixed at a volume ratio of 1:10 to prepare a bacterial suspension, and the crude oil, the surfactant, and the water were mixed at a volume ratio of 10:1:100 and ultrasonically treated to prepare an emulsified oil. The degradation rate of GC-FID on immobilized, direct-release (free state) petroleum-degrading microorganisms is calculated by the following formula:

$$R_d = \frac{X_c - X_s}{X_C} \times 100\% \tag{3}$$

Among them, R_d is the degradation rate of emulsified oil, X_c is the content of blank emulsified oil, X_s is the residual oil contained in each sample after degradation.

After 12 hours of degradation test, the degradation rates of free and immobilized microorganisms were calculated to be11.83% and13.47%, respectively. After the immobilization of petroleum-degrading microorganisms, the degradation rate of emulsified oil was significantly increased in a short period of time, and the degradation rate of emulsified oil was 13.86% higher than that of free-degrading microorganisms within 12 hours.

4. Conclusion

Through the characterization and application of materials, the following conclusions are obtained:

(1) By preparing Fe_3O_4 magnetic nanoparticles and modifying them to obtain amphiphilic magnetic colloidal magnetic cores. The magnetic particles of the core-shell structure were prepared by a dispersion polymerization method, the oil adsorption capacity of the material is further improved.

(2) The material has a specific saturation magnetization of 3.95 emu/g, and the magnetic particles have excellent magnetic response properties, which facilitates material recovery and reuse.

(3)The immobilized microorganism by the prepared material has better deoiling effect in treating wastewater containing emulsified oil. After the microorganism was immobilized, the degradation efficiency increased by 13.86%.

Acknowledgments

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