Superhydrophobic Fe$_3$O$_4$/OA Magnetorheological Fluid for Removing Oil Slick from Water Surfaces Effectively and Quickly

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ABSTRACT: Considering the severe impacts on the economic losses caused by oil spills, it is of great significance to develop an oil-absorbent material for removing the oil slick from the water surface effectively. As a new oil-absorbent material, magnetorheological fluid (MRF) has unsinkability, hydrophobicity, and lipophilicity, which could effectively remove the oil slick on the water surface while repelling water. Particularly, the prepared MRF shows a good response to external magnetic field. MRFs show high oil removal capacity in fresh water, deionized water, and salt water with efficiencies up to 94.39, 93.65, and 92.71%, respectively. Besides, Fe$_3$O$_4$/OA magnetic nanoparticles (MPs) could be reprepared into MRF by simple treatments. After the fifth cycle, the MRF prepared by the recovered Fe$_3$O$_4$/OA MPs still has high oil removal efficiency, and that means the Fe$_3$O$_4$/OA MPs has excellent reusability and stability. The method for preparing MRFs provided in this work is simple and effective, and the MRFs have a promising potential for cleaning oil slick.

1. INTRODUCTION

With the increase of oil explorations and sea transport activities, oil pollution has become a more and more severe problem year by year. Once oil spill occurs, oil films with low biodegradability will float on the water, which will damage the ecological environment seriously. Therefore, how to remove oil slick effectively has attracted worldwide attention.$^{1,2}$ The traditional methods used to solve this problem include mechanical collection,$^3$ chemical dispersants,$^4$ bioremediation,$^5$ in situ burning,$^6$ adsorption,$^7$ etc. On the basis of these methods, the removal of the oil slick can be realized, however, most of the methods are time-consuming and expensive processes, and even secondary pollutions will be generated. The impact of oil spills is tremendous, it has been reported that one ton of crude oil will spread on the water surface rapidly after spillage, forming an oil film of 12 km$^2$ in the area eventually.$^8$ It is important to increase the efficiency of the removal of oil slick, while first, it is necessary to prepare an oil-absorbing material with fast oil adsorption rate and high oil removal efficiency.

In recent years, the investigations of magnetic composite materials for oil removal have been increased significantly. Most of the magnetic composite materials concerned are hydrophobic and oleophilic. It can get rid of the oil slick quickly and efficiently without secondary pollution. The materials include, for example, modified magnetic nanoparticles (MPs)$^{9,10}$ modified hybrid sponges,$^{11,12}$ high oil-absorbing resins,$^{13,14}$ modified graphene aerogels,$^{15,16}$ etc.

It has been validated that the magnetic composite materials have the promising properties to remove the oil slick on the water surface. However, due to the inherent disadvantages, the available magnetic composite materials cannot be conveniently used in practice. For instances, the modified graphene aerogel is easy to collapse in the oil–water circulation operation,$^{17}$ because it is a brittle material. As for the modified hybrid sponges, although they have high absorption efficiency, the wide application in oil–water separation is limited due to their nonbiodegradability and nonreusability.$^{18}$

As a new type of a smart material,$^{19,20}$ magnetorheological fluids (MRFs) show good magnetic response to an external magnetic field. After modifications of the MPs in MRFs, MRFs become hydrophobic and oleophilic and also have unsinkable characteristics. Compared with other magnetic composite materials, MRFs are ecofriendly materials and show good oil removal performance. Rashin et al.$^{21}$ removed oil slick (motor oil) with the coconut oil-based MRF, and the oil removal efficiency was 91%. But coconut oil can cause secondary pollution and affect the reuse of oil slick. To avoid the
secondary pollution, Tian et al.\textsuperscript{22} used the lubricant oil-based MRF for removing oil slick (lubricant oil), and the efficiency of the lubricant oil-based MRF exceeds by 90%. However, these oil removal experiments of MRF are carried out on a fresh water surface, and the influence of water salinity was not investigated.

In this work, we developed a simple and practical approach to prepare Fe\textsubscript{3}O\textsubscript{4}/OA core–shell MPs. Fe\textsubscript{3}O\textsubscript{4}/OA MPs modified by oleic acid (OA) exhibit superhydrophobicity, superlipophilicity, and unsinkability. The morphology, surface, thermal stability, and magnetism of Fe\textsubscript{3}O\textsubscript{4}/OA MPs were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), contact angle measurement instrument, thermogravimetric analysis (TGA), and vibrating sample magnetometer (VSM). The ultrasonic dispersion method was used to distribute the MPs in a carrier fluid (lubricant oil) uniformly to prepare an oil-based MRF.

Furthermore, two variables were selected as the influencing factors, namely the mass of the MRF (0.5, 1, and 2 g) and the type of water surfaces (fresh water, deionized water, and salt water). By carrying out the oil slick removal experiments, we obtained the oil removal efficiency of MRF under the influence of the variables mentioned above. Based on the multicycle experiments, the reusability of the Fe\textsubscript{3}O\textsubscript{4}/OA MPs was investigated.

2. RESULTS AND DISCUSSION

2.1. Microstructure and Morphology. The XRD diffraction patterns of Fe\textsubscript{3}O\textsubscript{4}/OA magnetic nanoparticles (MPs) are assigned near (220), (311), (400), (511), and (440). It is a typical reflection of the cubic structure of Fe\textsubscript{3}O\textsubscript{4} (JCPDS no. 19-0629), indicating that Fe\textsubscript{3}O\textsubscript{4} microspheres were formed. It can be noted that there are no secondary peaks in the XRD patterns, which means that the sample has high purity. In addition, the intensity of each diffraction peak of Fe\textsubscript{3}O\textsubscript{4}/OA MPs is weaker than that of Fe\textsubscript{3}O\textsubscript{4} microspheres, which is attributed to the oleic acid (OA) coated on the surfaces of Fe\textsubscript{3}O\textsubscript{4} microspheres. It can also be found that the coating of OA does not affect the formation of Fe\textsubscript{3}O\textsubscript{4} microspheres.

Besides, the average size of Fe\textsubscript{3}O\textsubscript{4}/OA MPs was calculated by the Debye–Scherrer equation.\textsuperscript{23,24}

\[ D = \frac{k\lambda}{\beta\cos\theta} \]  

where \( D \) is particle diameter, \( \lambda \) is the X-ray wavelength of 0.154056 nm, \( k \) is the Scherrer constant, \( \theta \) is the Bragg angle, and \( \beta \) is the peak width at half maximum of the diffraction peak. The average size of Fe\textsubscript{3}O\textsubscript{4}/OA MPs is about 16.4 nm.

Figure 2 shows the SEM images of Fe\textsubscript{3}O\textsubscript{4}/OA MPs. It can be seen from Figure 2 that the size of Fe\textsubscript{3}O\textsubscript{4}/OA MPs is 18 nm approximately. The result is in good accordance with the result calculated by the Debye–Scherrer equation. Besides, the shape of the Fe\textsubscript{3}O\textsubscript{4}/OA MPs is spherical-like, which is mainly attributed to the use of NH\textsubscript{4}H\textsubscript{2}O\textsubscript{2} as the alkali source to regulate the pH of the Fe\textsuperscript{3\textsuperscript{+}}/Fe\textsuperscript{2\textsuperscript{+}} mixture.\textsuperscript{25}

The oil removal capacity of Fe\textsubscript{3}O\textsubscript{4}/OA MPs depends on the size and shape of the particles, as well as the thickness of the OA coated on the surface of Fe\textsubscript{3}O\textsubscript{4} microspheres. Therefore, Fe\textsubscript{3}O\textsubscript{4}/OA MPs were further characterized by TEM. It can be seen from Figure 3 that the OA layer exists on the surface of Fe\textsubscript{3}O\textsubscript{4} microspheres. The black areas present Fe\textsubscript{3}O\textsubscript{4} microspheres, while the bright areas present OA. It was found that Fe\textsubscript{3}O\textsubscript{4} microspheres are coated with OA to form a typical core–shell structure. OA not only prevents the agglomeration of Fe\textsubscript{3}O\textsubscript{4} microspheres in the magnetorheological fluid (MRF) but also improves the hydrophobic and lipophilic properties of Fe\textsubscript{3}O\textsubscript{4} microspheres.

2.2. Thermal Stability Analysis. The accurate OA content of the Fe\textsubscript{3}O\textsubscript{4}/OA MPs was measured by a thermogravimetric analyzer. Fe\textsubscript{3}O\textsubscript{4}/OA MPs were heated from 20 to 800 °C at a heating rate of 10 °C/min. Figure 4 shows the weight loss of Fe\textsubscript{3}O\textsubscript{4}/OA MPs at different temperatures. As can be seen in Figure 4, the curve shows three steps of weight loss, and the reason is that the obtained Fe\textsubscript{3}O\textsubscript{4}/OA MPs are coated with bilayer OA-coated.\textsuperscript{26,27} In the first step, Fe\textsubscript{3}O\textsubscript{4}/OA MPs show mild weight loss of about 0.58 wt % from 0 to 100 °C, which can be attributed to the evaporation of the absorbed water. In the second step, it was found that the weight loss is about 10.35 wt % at a range from 100 to 500 °C. In the third step, the significant weight loss of Fe\textsubscript{3}O\textsubscript{4}/OA MPs reached at 7.70 wt % from 500 to 780 °C. The weight loss for the second and third steps is due to the thermal degradation of OA. The higher thermal degradation temperature shows that Fe\textsubscript{3}O\textsubscript{4}/OA MPs have excellent thermal stability, which indicates that Fe\textsubscript{3}O\textsubscript{4}/OA MPs have good adaptability in high-temperature environments. It should be noted that the OA in the inner layer and the OA in the outer layer are connected through the chemical interaction.\textsuperscript{28} Considering the presence of the absorbed water in the Fe\textsubscript{3}O\textsubscript{4}/OA MPs, the weight loss of the OA finally obtained was 18.05 wt %. Thus, it can be verified that the Fe\textsubscript{3}O\textsubscript{4} microspheres are well coated with OA.

Saber et al.\textsuperscript{29} proposed that smaller MPs can remove oil slick on the water surface more effectively since the specific surface area of MPs in increased. Therefore, on the one hand, it is necessary to reduce the size of MPs, and on the other hand, the thickness of the OA coating should be increased as much as possible. In our previous work,\textsuperscript{22} the size of prepared Fe\textsubscript{3}O\textsubscript{4}/OA MPs was 12.3 nm, and the thermal weight loss of OA is 14.5 wt %, and the MPs have shown high oil removal efficiency. While in the present work, the size of Fe\textsubscript{3}O\textsubscript{4}/OA MPs is 16.4 nm, and the thermal weight loss of OA is 18.05%.
which indicates that the OA coating gets thicker. The increase of the OA coating mainly results from the water bath heating at 80 °C used in the preparation process. It is convinced that the Fe3O4/OA MPs developed in this work may have better oil removal performance on water.

2.3. Magnetic Properties Study. The magnetic properties of Fe3O4/OA MPs are significant in recovering the oil–MRF mixture. Therefore, the magnetic properties of Fe3O4 microspheres and Fe3O4/OA MPs were measured in fields from −20 to 20 kOe by using a vibrating sample magnetometer, and the hysteresis loops were obtained. As shown in Figure 2, the magnetization curves of Fe3O4 microspheres and Fe3O4/OA MPs have no hysteresis and are reversible. The saturation magnetization of Fe3O4/OA MPs and Fe3O4 microspheres were 65 and 77 emu/g, respectively. It is reasonable that the saturation magnetization value of Fe3O4/OA MPs is lower than that of Fe3O4 microspheres, because the OA coatings will reduce the saturation magnetization of Fe3O4/OA MPs. The MRF prepared by Fe3O4/OA MPs has good magnetic response performance. Thus, the oil–MRF mixture can be recovered by a magnet after adsorbed thoroughly.

Figure 2. SEM images for Fe3O4/OA MPs.

Figure 3. TEM images for Fe3O4/OA MPs.
2.4. Surface Properties Study. The hydrophobicity and lipophilicity of Fe₃O₄/OA MPs were tested using a contact angle measurement instrument. The contact angles were measured by adding 5 μL of the water droplet and lubricant oil droplet to the bed of Fe₃O₄/OA MPs. As shown in Figure 6a, the water droplet stays on the bed of Fe₃O₄/OA MPs and does not penetrate the surface. It remains an original shape of water droplet, which means that Fe₃O₄/OA MPs have great hydrophobic properties. Figure 6b exhibits that the left and right water contact angles of Fe₃O₄/OA MPs are 152.47° and 153.31°, respectively.

To our knowledge, when the water contact angles of the material are above a critical angle of 150°, the material can be considered as a superhydrophobic material. Thereby, the Fe₃O₄/OA MPs we prepared possess the characteristic of superhydrophobicity. That means the Fe₃O₄/OA MPs with a superhydrophobic surface can be obtained by the simple OA coating method. Figure 6c shows the shape of the oil droplet on the Fe₃O₄/OA MPs bed. According to our observations, the oil droplet can merge with the bed of Fe₃O₄/OA MPs quickly and cannot maintain the shape of the droplets. In addition, it can be seen from Figure 6d that the left contact angle of lubricant oil is 24.89°, and the right contact angle is 24.70°. It demonstrates that Fe₃O₄/OA MPs are superoleophilic. The results shown in Figure 6 illustrate that Fe₃O₄/OA MPs exhibit superhydrophobicity and superoleophilicity, making it possible to remove oil slick on the water surface selectively.

2.5. Sedimentation Stability Analysis. As shown in Figure 7, when the magnet contacts the bottle wall, a fraction of MRF in the bottle is attracted and shows a good magnetic response as the magnet moves.

As a magnetic suspension, the sedimentation stability of MRF was also investigated. The particle migration velocity of MRF was calculated by eq 2.

\[
V = \frac{1}{18} \times 1 \times \frac{g \times d^2}{\nu} \times \frac{1 - \varphi}{1 + \frac{4.6\varphi}{(1 - \varphi)^2}}
\]

where \( V \) is the particle migration velocity, \( \rho_p \) is the particle density, \( \rho_l \) is the liquid density, \( \nu \) is the kinematic viscosity of the liquid, \( g \) is the gravity constant, \( d \) represents the particle diameter, and \( \varphi \) is the volume fraction of MRF.

The value of the particle migration velocity can be used to evaluate the sedimentation stability of MRF. The kinematic viscosity of the MRF measured by the rheometer is 274.3 mPa·s. Besides, it was found that the particle–fluid density mismatch will affect the particle migration velocity. The
density of Fe3O4/OA MPs and Fe3O4 microspheres are 5.785 and 8.125 g·cm⁻³, respectively. The lower density indicates that the particle–fluid density mismatch of Fe3O4/OA MPs is smaller than that of Fe3O4 microspheres, suggesting that the prepared MRF has good sedimentation stability.

2.6. Oil Removal Efficiency Study. In order to investigate the oil removal capacity of the MRF, the weight was measured to determine the efficiency of oil removal. As shown in Figure 8, the detailed experimental steps are as follows: first, 200 mL of fresh water was added to a 500 mL beaker, creating a water environment. In the next step, 2 g of lubricant oil was dropped into the middle of the water surface in the beaker to form oil slick (Figure 8a). The red dye (Sudan III) was used to label lubricant oil to observe the diffusion of oil on the water surface clearly and to confirm the position and shape of the oil slick. Then, a certain amount of MRF was added into the oil slick. It was found that when brought into contact with the oil slick, the MRF diffused in the oil phase and wrapped up the oil within a few seconds. Finally, oil–MRF mixtures floated on the water surface (Figure 8b). As expected, the MRF completely repelled water and exhibited the property of hydrophobicity. Then, the oil–MRF mixture can be moved by the magnet easily (Figure 8c), and it can be seen that most of the mixture was moved (Figure 8d). There still exists a small amount of oil on the water surface.

MRF can effectively remove oil slick on the water surface, which is mainly contributed by London dispersive forces. The London dispersive forces between the hydrophobic part of oil molecules and the carrier fluid are much stronger, whereas the interactions between the oil molecules and water molecules are much weaker. Therefore, the oil slick moves with the MRF because of the London dispersive forces.

Figure 9 shows the oil removal efficiency of MRF in different types of water surfaces and demonstrates that MRF has excellent oil removal capacity. It can be found that on different types of water surfaces, the oil removal efficiency of the MRF is proportional to the mass of the MRF added in. After adding 0.5 g of MRF to the oil slick in the fresh water, the oil removal efficiency reached at 82.93%, indicating that a small amount of MRF already has good oil removal performance. Moreover,
Fe₃O₄/OA MPs have good reusability. The excellent surface selectivity and to realize the oil surface. MRF can be used to recover oil slick on the water material was prepared for oil paramagnetism, thermal stability, and has been introduced into superhydrophobicity, superlipophilicity, unsinkability, super-oil reusability of Fe₃O₄/OA MPs will play an important role in the removal of oil slick on the water surface.

In summary, Fe₃O₄/OA magnetic nanoparticles (MPs) were synthesized by the chemical coprecipitation method, which were coated with an oleic acid bilayer. Fe₃O₄/OA MPs has superhydrophobicity, superlipophilicity, unsinkability, super-paramagnetism, thermal stability, and has been introduced into the preparation of oil-based MRF. In this study, an improved material was prepared for oil-water separation on the water surface. MRF can be used to recover oil slick on the water surface selectively and to realize the oil-water separation under the guidance of the magnet quickly and efficiently. The oil-water separation. The efficiency of oil removal from different water surfaces only results in slight changes. The oil removal efficiency remains above 93%, which indicates that Fe₃O₄/OA MPs have good reusability. The excellent reusability of Fe₃O₄/OA MPs will play an important role in the removal of oil slick on the water surface.

3. CONCLUSIONS

In summary, Fe₃O₄/OA magnetic nanoparticles (MPs) were synthesized by the chemical coprecipitation method, which were coated with an oleic acid bilayer. Fe₃O₄/OA MPs has superhydrophobicity, superlipophilicity, unsinkability, super-paramagnetism, thermal stability, and has been introduced into the preparation of oil-based MRF. In this study, an improved material was prepared for oil-water separation on the water surface. MRF can be used to recover oil slick on the water surface selectively and to realize the oil-water separation under the guidance of the magnet quickly and efficiently. The oil removal efficiencies of the MRF in salt water, fresh water, and deionized water were 92.71, 94.39, and 93.63%, respectively. It is worth noting that the efficiency of oil removal is still above 93% after five oil-water separation cycles, which indicates that Fe₃O₄/OA MPts have excellent reusability. Therefore, we believe that MRF will contribute to the removal of oil slick on the water surface in the future.

4. EXPERIMENTAL SECTION

4.1. Materials. All the chemicals were of analytical grade and can be used without further treatment. Ferric chloride hexahydrate (FeCl₃·6H₂O) and ferrous chloride tetrahydrate (FeCl₂·4H₂O) were from Shanghai Runjie Chemical Products Co., Ltd., Shanghai, China. Ammonia (NH₃·H₂O) and oleic acid (C₁₈H₃₄O₂) were purchased from Shanghai Lingfeng Fine Chemicals Co., Ltd., Shanghai, China. Anhydrous ethanol (C₂H₆O) was obtained from Wuxi Yasheng Chemical Co., Ltd., Wuxi, China. Sodium chloride (NaCl) was received from Xilong Science Co., Ltd., Shantou, China. The lubricant oil (SUPER 1300 C 15 W-40) used as carrier fluid was purchased from Exxon Mobil Corporation, Tianjin, China. Deionized water was received from Wahaha Group, Hangzhou, China. All solutions were prepared with deionized water.

4.2. Preparation of Magnetorheological Fluid. Fe₃O₄/OA magnetic nanoparticles (MPs) were synthesized by the chemical coprecipitation method. The detailed processes for the synthesis of Fe₃O₄/OA core-shell MPs are as follows: 21.6 g of FeCl₃·6H₂O and 8.1 g of FeCl₂·4H₂O were mixed in 300 mL of deionized water. The solution was stirred for 30 min to form a homogenous mixture in a closed condition. Then, 50 mL of NH₃·H₂O and 2 mL of oleic acid (OA) were slowly added into the Fe₃⁺/Fe²⁺ mixture by water bath heating at 80 °C. Notably, it is important to control the titration rate of NH₃·H₂O and OA. NH₃·H₂O and OA were added into the Fe₃⁺/Fe²⁺ mixture at a rate of four drops (about 0.43 mL/drop) of NH₃·H₂O and one drop (about 0.01 mL/drop) of OA until 20 mL of NH₃·H₂O was added in. Afterward, the titration rate of NH₃·H₂O and OA was changed to two drops of NH₃·H₂O and one drop of OA until the remaining OA was added in. When 50 mL of NH₃·H₂O was added in, the pH of the mixture was measured to be 9. Finally, the mixture was stirred for 30 min until the color of the mixture turned to brilliant black, which means that Fe₃O₄/OA MPs were obtained.

The wet precipitate of Fe₃O₄/OA MPs was collected by placing a magnet on the bottom of the beaker. Furthermore, the wet precipitate was further washed for three times with deionized water and for two times with anhydrous ethanol to eliminate impurities. Five vol % of oil-based magnetorheological fluid (MRF) was obtained by mixing wet precipitate and carrier fluid (lubricant oil) in a ratio of 1:7. The Fe₃O₄/OA MPs were dispersed in carrier fluid to form a stable suspension by ultrasonic treatment for 30 min.

4.3. Characterization. Contact angles (CAs) are measured by a contact angle measurement instrument (Automatic Contact Angle Meter Model, JCY, CHN). For measurements, a droplet (5 μL) of deionized water or lubricant oil was used as an indicator at room temperature. The X-ray diffractometer (XRD, Bruker D8 Advance) with Cu Kα radiation was used to analyze the crystal lattice structure of the Fe₃O₄/OA MPs phase, and the scanning angle ranged from 20 to 90° of 2θ. The microstructure of Fe₃O₄/OA MPs was observed by scanning electron microscopy (SEM, SU 8200, JPN). At 100 kV, the...
transmission electron microscopy (TEM, JEM-1011, JPN) was used to evaluate the coating of OA on the surfaces of Fe₃O₄ microspheres. Using N₂ gas protection, the thermal stability was investigated by using a thermogravimetric analyzer (TGA, STA3449F5 Jupiter, DEU) at a heating rate of 10 °C/min in a range from 20 to 800 °C. The magnetic properties of Fe₃O₄/OA MPs were measured by the vibrating sample magnetometer (VSM, SQUID-MPMS3, USA). The viscosity of the oil-based MRF was measured by a rheometer (Anton Paar MCR 72, AUT).

4.4. Oil Removal Experiments. The oil removal capacity of the oil-based MRF can be determined by weight measurements.35,36 First, oil was poured on the surface of water contained in a beaker. Then, the MRF was added to the oil slick surface. Then, the MRF spread and mixed with oil quickly. The final step was to separate the oil–MRF mixture from the water surface by a magnet. The oil removal rate of the MRF can be calculated according to eq 3.

\[ K = \frac{M_2 - M_1}{M_1} \]

where \( K \) is the oil removal rate, \( M_2 \) and \( M_1 \) are the total masses of oil, water, MRF, and beaker before and after oil removal, respectively. \( M_1 \) is the mass of oil slick added into the beaker. The weight of the oil removed was calculated from the difference between \( M_2 \) and \( M_1 \).

Most of the contaminated oil in the oil–MRF mixture was separated by a high-speed centrifuge. After separating, the wet precipitate of Fe₃O₄/OA MPs was washed in anhydrous water contained in a beaker. Then, the MRF was added to the oil slick surface. Then, the MRF spread and mixed with oil quickly. The final step was to separate the oil–MRF mixture from the water surface by a magnet. The oil removal rate of the MRF can be calculated according to eq 3.

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### Notes

The authors declare no competing financial interest.

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