Preparation of Superhydrophobic Magnetic Polyurethane Sponge for Removing Oil Pollutants from Water

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Abstract: The superhydrophobic magnetic sponge were prepared by Fe3O4 nanoparticles and stearic acid which were coated on the surface of polyurethane sponge. The preparation process of the superhydrophobic materials are prepared under mild, low-cost and environment-friendly conditions. Pieces of PU sponges were decorated immersed in a ethanol solution which uniform suspension Fe3O4 nanoparticles ethanol by ultrasonication, and the obtained PU sponges were modified with stearic acid. The Fe3O4 and stearic acid were coated onto the skeleton surface of the sponge, which make the as-prepared sponge possess magnetic and hierarchically microstructure. The high elasticity sponge can through the simple squeeze realize oil recovery. After 5 cycles, the as-prepared sponge retains excellent absorption properties. The superhydrophobic magnetic polyurethane sponge has great potential in industrial oil separation and oil spill recovery in future.

1. Introduction
With the acceleration of urbanization and industrialization in recent years, the problem of oil pollution and oil spill is becoming more and more serious, which can cause great harm to human health, water environment and ecological balance [1]. Water pollution has become one of the most urgent and urgent environmental problems in the world. Because of the characteristics of selective oil absorption capacity, strong oil absorption capacity and rapid recovery and utilization, the research on the structure of 3D network superhydrophobic materials is developing rapidly. [2-4]. Recently, magnetic polyurethane sponge[5-7] has been applied in the field of oil-water mixture separation, as it has a good magnetic response capacity convenient for the magnetic driving and recycling of material, a developed 3D network structure easy to store oil, and high resilience conducive to the recycling of oil by squeezing. However, reports of superhydrophobic magnetic sponges are generally unsatisfactory because of their poor performance in oil absorption and recovery. In addition, in the preparation process, expensive low surface energy materials are used for surface modification, which is complex and expensive. Therefore, the development of a magnetically driven superhydrophobic polyurethane sponge is a simple preparation, low cost, special ability of oil and water separation and environmental friendliness. Stearic acid is a kind of saturated fatty acid, which is also an ecological friendly material.
It is non-toxic, cheap, insoluble in water, and has a high melting point. As a candidate for green materials, stearic acid has been used to prepare superhydrophobic materials. As a candidate of green material, stearic acid has been used in the preparation of super-hydrophobic material [8,9], but has not been reported to be used as a surface modifier in the preparation of magnetic driven superhydrophobic polyurethane sponge.

Current work reports the preparation of magnetic driven superhydrophobic polyurethane sponge, which is to fix Fe$_3$O$_4$ nanoparticles and stearic acid on the surface of a polyurethane sponge framework in two steps, thus forming the microstructure of evenly distributed micro-nano coatings on the sponge framework. The optimum preparation conditions were selected by characterized of the water contact angle and Scanning electron microscope. By driving and recycling oil simply with magnets, the as-prepared sponge exhibits extremely high absorptive capacities and excellent absorptive selectivity in the separation of oil/water mixtures. It is exciting that the as-prepared sponge shows recyclability in the separation of oil/water mixtures. So the superhydrophobic polyurethane sponge can be applied extensively in in future industrial oil separation and oil spill recovery.

2. Experimental section

2.1 Materials
Commerical PU sponges were bought directly from market, Yan’an, China. Fe$_3$O$_4$ nanoparticals, Stearic acid, ethanol, n-Hexane, toluene, chloroform and Oil Red O were purchased from Shanghai Aladdin Reagent Co., Ltd.

2.2 Preparation of Superhydrophobic Spone
The pristine PU sponge was cut into pieces of 2×2×1cm size, which was washed respectively in ethanol for 30 min with ultrasonically, and dried at 80°C for 2h. Several pieces of clean spones were immersed in a uniform suspension contains 100mg Fe$_3$O$_4$ nanoparticles and 50mL ethanol by ultrasonication for 30min, and fully dried. Then, the obtained PU sponges were dipped into stearic acid solution(2wt.%) overnight at room temperature. Finally, the sponges were heat-treated at 80°C for 6h to obtain the superhydrophobic polyurethane sponge(Fig.1).

2.3 Characterizations
Scanning electron microscope (SEM, JSM-6390A, JEOL, Japan) was applied to characterize the microstructures of cellulose sponges. X-ray diffraction (XRD, XRD-7000, SHIMADZU, Japan) was carried out at a scan rate of 2° min$^{-1}$ in the 2θ range of 20°-80°. The Fourier transform infrared
spectroscopy (FTIR, TENSOR II, BRUKER, Germany) in a range of 400–4000 cm⁻¹. Water/oil contact angle measurements (CA, DMo-501, KYOWA, Japan), using 4 μL water droplet at an ambient temperature. Thermo gravimetric analysis (TGA, STA449F3, NETZSCH, Germany) was characterized the thermal stability of sponges.

3. Results and discussion
The pristine sponge in different ratio showed a smooth surface under the scanning electron microscope amplification (Fig.2 (a)). On the contrary, surface of the as-prepared sponge with uniformly distributed micro/nano structure (Fig.2(b)) under the scanning electron microscope amplification, it is because this kind of structure that prompted the sponge has excellent superhydrophobic/superhydrophilic. Fig.2(c) shows that the sponge skeleton was only coated by the stearic acid observation in scanning electron micrograph, and there are not enough roughness on the surface of sponge, so the superhydrophobicity is not well. Fig.2(d) shows the sponge skeleton only under the Fe₃O₄ nanoparticles coating of scanning electron microscopy, it can be seen that Fe₃O₄ nanoparticles were scattered unevenly only coating on the surface of sponge, did not constitute a hierarchical micro/nano structure. Therefore, the micro/nano structure of Fe₃O₄ and stearic acid layer as superhydrophobic sponge is ideal.

In this study, the concentration of stearic acid was 0.5%, 1%, 2%, 3% and 4% to preparation the superhydrophobic sponge. The results showed that the concentration of stearic acid had a great influence on the water contact angle of the sponge surface. Among them, the water contact angle of the as-prepared sponge with a stearic acid concentration of 2% was up to 158° (Fig.4). The main reason was that the microstructure of stearic acid at different concentrations was different on the surface of sponge skeleton. Fig.3 shows that the stearic acid concentration of 0.5% and 4% superhydrophobic material skeleton surface scanning electron microscopy, Fig.3(a) shows that the skeleton surface has certain roughness, but its micro-nano grading structure is not obvious. Fig.3(b) shows that the micro-nano scale structure of the skeleton surface is dispersed and uneven, and the concentration of stearic acid is too high, leading to the blockage of some spongy skeleton pores. Therefore, the superhydrophobic sponge composite material with high water contact Angle can be prepared by choosing the concentration of stearic acid solution in the material preparation as 2%.

Fig.2. SEM images of the sponges:(a) pristine sponge,(b) as-prepared sponge,(c) stearic acid sponge, and (d) Fe₃O₄ sponge.

Fig.3. SEM images of the as-prepared sponge by different concentration of stearic acid:(a) The stearic acid concentration is 0.5%, and(b) The stearic acid concentration is 4%.
Fig. 4. The effect on value of water contact angle on the as-prepared sponge with different concentration of stearic acid.

The hydrophobicity of the as-prepared was further investigated. Fig. 5(a) shows that the water and oils or organic solvents (dyed with Oil Red O) droplets on the as-prepared sponge surface. It was absorbed quickly when the oils or organic solvents droplets dripped on the as-prepared sponge. Instead, water droplets keep the spherical shape. Notably, the hydrophobic properties were still maintained excellently by the section of the as-prepared sponge inside(Fig.5(b)). The surface wettability of the as-prepared sponge by the water contact angle measurements on a date physics instrument (CA, DMo-501, KYOWA, Japan). A water droplet (4μL) was deposited on the surface of the as-prepared sponge at ambient temperature. The water contact angle of 158°, as shown in Fig.5(c). These results indicate that the as-prepared sponge exhibited excellent superhydrophobicity and superoleophilicity.

Fig. 5. Images of (a) the water and oil or (dyed with Oil Red O) droplets on the as-prepared sponge surface, (b) the water droplets on the surface of intersected superhydrophobic sponge, (c) the pristine sponge (white) and as-prepared sponge (black) after being placed on water.

The FTIR spectra of the as-prepared sponge, pristine sponge, and stearic acid are shown in Fig.6(a). For the pristine sponge, the peak at 3290 cm⁻¹ is attributed to the stretching vibration of N-H. The peak at 2971 cm⁻¹ is assigned to the C-H stretching of -CH₃ and -CH₂, and the peak at 2275 cm⁻¹ is due to the asymmetric stretching of -NCO. The peaks at 1721, 1620, and 1098 cm⁻¹ are associated with C=O stretching in the amide, urea and ether groups respectively, and the peak at 1533 cm⁻¹ is attributed to the amide II band[10]. For the stearic acid, the strong absorption peaks at 1703 and 1463 cm⁻¹ is due to the C=O stretching vibration and the symmetric bending of -CH₂-[11]. For the as-prepared sponge, the peak at 553 cm⁻¹ is stretching vibration of Fe-O. The peaks at 2914, 2848, and 1463 cm⁻¹ are corresponds to symmetric, asymmetric stretching vibration, and symmetric bending of -CH₂- groups, respectively[12]. These absorption peaks were significantly higher than the pristine sponge make us conclude that the Fe₂O₃ and stearic acid were coated onto the skeleton surface of the sponge, which make the as-prepared sponge possess magnetic and superhydrophobic properties.
Fig. 6. (a) FTIR spectra of the as-prepared sponge, pristine sponge, stearic acid sponge, Fe$_3$O$_4$ sponge, and Fe$_3$O$_4$. (b) Stress-strain curves of the as-prepared sponge, pristine sponge, stearic acid sponge, and Fe$_3$O$_4$ sponge.

Stress-strain curves of the pristine sponge and as-prepared sponge which were compressed (the rate of compression is 10 mm/min) to 75% of the original thickness at room temperature. As shown in Fig. 6(b) the elastic properties of the two kinds of sponge have a small difference. Therefore, the superhydrophobic layer does not damage the elastic characteristics of the sponge, and the as-prepared sponge still has excellent elastic properties.

Fig. 7. (a) XRD patterns of the Fe$_3$O$_4$, Fe$_3$O$_4$ sponge, and as-prepared sponge. (b) TGA of the as-prepared sponge, pristine sponge, stearic acid sponge, and Fe$_3$O$_4$ sponge.

The XRD diffraction patterns of the Fe$_3$O$_4$, Fe$_3$O$_4$ sponge, and as-prepared sponge were shown in Fig. 7(a). There are the same characteristic peaks and positions between the as-prepared sponge and Fe$_3$O$_4$ nanoparticles. This indicated that Fe$_3$O$_4$ nanoparticles were successfully deposited on the skeleton surface of the sponge, resulting in a certain magnetism of the as-prepared sponge[13]. The curves of as-prepared sponge displayed a pronounced peak center at about 21°, assigning for the reflection of stearic acid (JCPDS card No. 38-1923) crystal diffraction plane.

Thermo gravimetric analysis is used to study thermal stability and composition of materials. The TGA curves of the pristine and as-prepared sponge are shown in Figure 7(b). From the curve a of TGA, we can see that the temperature under 200 °C, a slight of mass loss at about 2% of the as-prepared sponge, pristine sponge, and Fe$_3$O$_4$ sponge at the same time stearic acid sponge loss of 20%, this is due to meet on the sponge stearic acid has a relatively low thermal stability, losses to the quality of the sponge faster. After introducing the Fe$_3$O$_4$ nanoparticles on the sponge, the mass of the as-prepared sponge decomposition rate is reduced. This is mainly because the Fe$_3$O$_4$ nanoparticles has strong heat resistant performance, so as to offset the quality loss caused by stearic acid decomposition. The experimental results show that the Fe$_3$O$_4$ nanoparticles is not only beneficial to the construction of microstructure, but also improves the thermal stability of the sponge.
Fig. 8. Images of processes for the selective sorption of (a) toluene (dyed with Oil Red O) and (b) chloroform (dyed with Oil Red O) from water by a piece of as-prepared sponge.

In order to deeply investigate the abilities of oil/water mixture of the as-prepared sponge, two models were established by different densities (toluene and chloroform) of oils or organic solvents which dyed with Oil Red O (Fig. 8). A piece of the as-prepared sponge (Fig. 8(a) followed by the magnetic collection) contacts with toluene layer on water surface and chloroform droplet underwater (Fig. 8(b)), the toluene and chloroform can be completely separated rapidly from water. On the basis of the as-prepared sponge superhydrophobic/superoleophilic properties and 3D structure with interconnected pores.

Fig. 9. Recyclability of the as-prepared sponge for absorption of n-hexane.

In order to investigate the repeatability of the as-prepared sponge, we adopted the method of absorbing-squeezing and absorption of oil to study the recycling performance of the materials. Because of the superhydrophobic sponge has special micro/nano structure, its performance of the superhydrophobic/superoleophilicity. The three-dimensional network structure of the as-prepared sponge to provide storage space to absorb the oil. The high elasticity sponge can through the simple squeeze realize oil recovery. After 5 cycles, the as-prepared sponge retains excellent absorption properties (Fig. 9). This material has great potential in future industrial oil separation and oil spill recovery.

4. CONCLUSIONS

The magnetically driven superhydrophobic polyurethane sponge consists of two steps. The as-prepared sponge is prepared under mild, low-cost and environment-friendly conditions. The water contact Angle of the as-prepared sponge with a stearic acid concentration of 2% was up to 158 degrees. Moreover, the oil separation capacities still keep a high value after 5 cycles of squeezing the saturated
absorbed as-prepared sponge. It is magnetic responsive, so can be coupled with external magnetic fields for the magnetic driven selective separation of oil/water mixtures. All of these satisfactory properties made the as-prepared sponge as an ideal absorbents for oil-water mixture separation and oil spillage cleanup.

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