Recyclable Magnetically Driven Superhydrophobic Polyurethane Sponge for highly efficient Oil/Water mixtures and emulsions separation

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ABSTRACT: Magnetically driven superhydrophobic materials were coated on the surface of polyurethane sponges by Fe₃O₄ nanoparticles and stearic acid. The as-prepared sponge was characterized by scanning electron microscope, fourier transform infrared spectroscopy and other analytical techniques. The surface wettability of the as-prepared sponge, the separation capacity of oil/water mixtures and emulsions, the sorption kinetics of different types of oil, and the recyclability of the materials were studied. 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 water contact angle reach up to 158° on the surface of the superhydrophobic sponge. The materials also shows highly efficient oil/water mixtures and emulsions separation. Moreover, the oil separation capacities still keep a high value after 50 cycles of squeezing the saturated absorbed as-prepared sponge. All of these satisfactory properties made the as-prepared sponge as an ideal absorbents for oil/water mixtures and emulsions separation in the 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. 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 highly efficient oil/water mixtures and emulsions separation. So the superhydrophobic polyurethane sponge can be applied extensively in future industrial oil separation and oil spill recovery.

2. Experimental section

2.1 Materials

Commercial PU sponges were bought directly from market, Yan’an, China. Fe$_3$O$_4$ nanoparticles, Stearic acid, ethanol, n-Hexane, toluene, chloroform, Span80, and Oil Red O were purchased from Shanghai Aladdin Reagent Co., Ltd. Diesel, and Crude oil were supplied by Sinopec, Yan’an, China. Peanut oil was provided by supermarket, Yan’an, China.

2.2 Preparation of Superhydrophobic Sponge

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 sponges 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, the sample was sprayed with gold before the SEM morphology investigation. Water/oil contact angle measurements (CA, DMo-501, KYOWA, Japan), using 4 μL water droplet at an ambient temperature.

3. RESULTS AND DISCUSSION

3.1 Surface Wettability of Superhydrophobic Sponge
The hydrophobicity of the as-prepared was further investigated. Fig.2(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.2(b)). When the pristine and as-prepared sponge were put on the water surface, the pristine sponge sank beneath the water surface, on the contrary the as-prepared sponge floats on the water surface, as shown in Fig.2(c). The as-prepared sponge was completely immersed in a water by an external force, a typical silver-mirror-like surface was shown in Fig.2(d), which result from the interfacial interference between water and air trapped inside the pores [10,11].

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 an ambient temperature. The water contact angle of 158°, as shown in Fig.2(e). These results indicate that the as-prepared sponge exhibited excellent superhydrophobicity and superoleophilicity.
Fig. 2. Images of (a) the water contact angle in air, (b) the water and oil (dyed with Oil Red O) droplets on the as-prepared sponge surface, (c) the water droplets on the surface of intersected superhydrophobic sponge, (d) the as-prepared sponge was completely immersed in water by an external force, (e) the pristine sponge (white) and as-prepared sponge (black) after being placed on water.

Fig. 3. SEM images of the sponges: (a) pristine sponge, (b) as-prepared sponge

Fig. 3 shows SEM images of the sample. Scanning electron microscope (SEM, JSM-6390A, JEOL, Japan) was applied to characterize the microstructures of the pristine sponge and as-prepared sponge. The pristine sponge contained highly 3D network structure of pores and quite smooth surface (Fig. 3(a)(b)). A 3D hierarchical structure with surface of the as-prepared sponge was observed (Fig. 3(c)), and the hierarchical structure under higher magnification exhibited a homogeneous distribution (Fig. 3(d)). The unique microstructure of the as-prepared sponge surface make it shows superhydrophobicity.
3.2 Oil/Water Separation Performance

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.4). A piece of the as-prepared sponge followed by the magnetic collection contacts with toluene layer on water surface and chloroform droplet underwater, 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.5. (a) Absorption kinetic curves of the as-prepared sponge for water and a range of oils or organic solvents (20°C). (b) Recyclability of the as-prepared sponge for absorption of n-hexane.

The as-prepared sponge exhibited excellent sorption capacities of oils or organic solvents. The absorption capacity (k) can be defined as the weight-gain ratio of the sponge, which is calculated according to the following equation [12,13]: \( k = (M_2-M_1)/M_1 \), where \( M_1 \) and \( M_2 \) are the weight of the as-prepared sponge before and after absorption of oil or organic solvents, respectively. The sorption kinetics of toluene, diesel, and crude oil using the as-prepared sponge shown in Fig.5(a), Obviously, the sorption rate for toluene (viscosity: 0.69mm²/s) is quicker than diesel (viscosity: 4.65mm²/s) and crude oil (viscosity: 20.66mm²/s), implying that the oil sorption rate has important relationship with the viscosity of oils [14-16].

The absorption capacities are higher than those of other reported superhydrophobic magnetic sponges [17-20]. In addition, the oil separation capacities still keep a high value after 50 cycles of squeezing the saturated absorbed as-prepared sponge (Fig.5(b)). This result showed that the
as-prepared sponge not only has high oil/water separation efficiency but also the excellent recyclability.

![Image](image_url)

**Fig. 6.** (a) Images of the n-hexane-in-water emulsion before(left) and after(right) separation. (b) UV–vis spectroscopy absorption data for water reference, separated water and the n-hexane-in-water emulsion.

In order to further research the oil/water separation capacity of the as-prepared sponge, we prepared surfactant-stabilized n-hexane-in-water emulsion (3/100 v/v) with the addition of 0.1 wt% Span80 under high stirring for 2h [21]. The n-hexane-in-water emulsion before(left) and after(right) separation by the as-prepared sponge shown in Fig.6(a). Before the separation, the oil - water mixture appears emulsion solution. After separation, it became transparent. As shown in Fig.6(b) the separated water and reference water absorption curve are very close, but the n-hexane-in-water emulsion had an obvious typical peak of absorption at about 208 nm. The results show that the excellent separation capability of n-hexane-in-water emulsion by the as-prepared sponge.

4. Conclusions

The magnetically driven superhydrophobic polyurethane sponge consists of two steps, the preparation conditions are mild and low-cost. The as-prepared sponge exhibited excellent absorption capacities for various of oils and organic solvents. Moreover, the oil separation capacities still keep a high value after 50 cycles of squeezing the saturated absorbed as-prepared sponge. More important, the sponge exhibits excellent separation performance in the separation of emulsified oil in water. All of these satisfactory properties made the as-prepared sponge as an ideal absorbents for oil and organic solvents contaminants from water.

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