Surface infiltration study of palmitic acid modification for oil-water separation

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Abstract. Removal of oil and organic pollutants from water is desired due to the frequent oil spill accidents and increase of industrial oily wastewater. The development of absorbent materials with high absorption capacity for separation and removal of oils from water should be of great importance to address environmental issues. In this paper, we reported a simple method to hydrophobic surface modification, which fabricated by palmitic acid solution-immersion processes, as well as their excellent adsorption performance for oils and organic solvents. The hydrophobicity, oil-absorption capacity and selectivity of the as-prepared sponges were evaluated. The results show that the sponges fast and selectively absorbed various kinds of oils up to above 33 times their weight. These sponges have great potentials for large-scale removal of oil or organic solvents spills from water.

1. Introduction

As one of the most important and non-renewable energy sources, oil is usually reported by spillage during exploitation and transport, this spillage always damages the coastal environment and marine ecosystems. To avoid such environmental disasters, the cleanup or collection of the spilled crude oil from water surfaces is essential.

Currently, the conventional methods used to solve these problems include oil containment booms, oil skimmer vessels, combustion, and physical absorption by porous materials[1-2]. Among these methods, absorption by porous material is considered as a simple, fast and efficient one, and they have attracted broad attention, such as zeolites, activated carbon, and sponges[3]. Although widely applied in practical applications, these absorbent materials still have limitations because they absorb not only oils but also water, which reduces the separation selectivity and efficiency.

Due to the oil-water separation is an interfacial phenomenon, using special wettability to design novel membranes is a facile and effective way[4-5]. The surfaces with hydrophobic and oleophilic properties have attracted considerable interest in the field of the spilled crude oil from water because they only absorb oil while repelling water completely, which exhibiting high oil water separation efficiency and selectivity. It is of great significance to develop hydrophobic interfaces for oil-water separation in a simple, economical and scalable approach.

A polyurethane sponge is a kind of porous and hydrophilic polymer that has characteristics of high porosity, low density, good elasticity, and easily scalable fabrication, which provides high absorption ability, durability and floating on the water, along with the deficiencies of original hydrophily.
Therefore, it is essential to change the hydrophilicity of sponges to hydrophobicity and oleophilicity for oil-water separation. In this study, we prepare a modified polyurethane sponge through a simple method that did not require intricate equipment or synthesis processes to fabricate high oil-absorption ability materials based on hydrophobic and oleophilic polyurethane sponges. We anchored hydrophobic Long chain alkane coatings onto the frames of the sponges by palmitic acid modification to change their wettability. The modified sponges showed hydrophobic and outstanding capacities with a high oil absorption capacity. Moreover, the absorbed oil could be removed and collected just by simple squeezing, and then, the sponges could be used recycling. This work provides an effective strategy for the cleanup of oil spillage and chemical leakage on the water surface.

2. Experimental

2.1. Materials
Polyurethane sponges (60 pores per linear inch) were obtained from a local store. Chromium trioxide, concentrated sulfuric acid, ethanol, acetone, and palmitic acid were purchased from Sinopharm Chemical Reagent Co., Ltd. Diesel oil was obtained from China National Petroleum Corporation. All chemicals were analytical-grade and used without further purification.

2.2. Preparation of hydrophobic sponges
The original polyurethane sponges were cleaned ultrasonically with acetone and distilled water for 3 h successively to remove possible impurities. Then, the sponges were etched in \( \text{CrO}_3 \) (100 g L\(^{-1}\)) and \( \text{H}_2\text{SO}_4 \) (100 g L\(^{-1}\)) mixed solution for 30 s. After being washed with distilled water and dried in vacuum, the sponges were immersed in an ethanol solution of palmitic acid for 12 h. The obtained sponges were dried at ambient temperature for 8 h to allow the ethanol to evaporate completely. By these processes, the surfaces of polyurethane sponges were coated with low-surface-energy long chain alkane layers to obtain hydrophobic surfaces.

2.3. Hydrophobicity and oil-water separation performance

2.3.1. Contact angle
The contact angles (CA) of sponges were measured by DSA 25 (KRÜSS, Germany) apparatus at ambient temperature. The volume of the individual water droplets in all measurements was 5 μL. The average value of five measurements acquired at different positions on the same sample was adopted.

2.3.2. Oil-water separation
The removal of oils from the water surface was carried out by dipping the sponges into oil water mixtures. The oil-absorption capacity \( k \) of the sponges was determined by weight measurements, which calculated using the equation:

\[
k = \frac{m_2 - m_1}{m_1}
\]

where, \( m_1 \) and \( m_2 \) were the weight of sponge before and after oil absorbance, respectively. In a typical adsorption experiment, the sponge sample was put into the mixture and suspended for 1 minute to reach the adsorption equilibrium. All adsorption experiments were conducted three times and an average value was reported.

3. Results and discussion

3.1. Contact angle
The hydrophobicity of the sponges was evaluated by the measurement of the contact angles. The contact angles of the unmodified and modified polyurethane sponges are shown in Figure 1. As shown in Figure 1(a), the water contact angle of the unmodified sponge was about 68°, it showed that the
intrinsic sponge was hydrophilicity. However, as shown in Figure 1(b), the water contact angle of the sponge was enlarged to 139° after modification by palmitic acid. The change of hydrophilicity and hydrophobicity were attributed to the modification by palmitic acid that the hydrophobic group of long-chain alkanes anchored onto the structure and surface of the sponge. As shown in Figure 1(b), although the sponge was abundant protruding structures on the surface, the water droplet still appears spherical on the sponge surface rather than penetrating into the sponge or spreading over the surface.

![Figure 1](image1.png)

Figure 1. (a) Water contact angle image of the unmodified sponge, (b) Water contact angle image of the modified sponge

3.2. Oil-water separation

The modified sponges had hydrophobic properties and could be used in efficient oil-water separation. Figure 2 showed that the process in oil-water separation and oil collection of sponges. The orange-dyed diesel oil was spread on the surface of the water to form an oil-water mixture. The as-prepared sponge was immersed in the oil-water mixture, and it can be found that the diesel oil was quickly absorbed in few seconds. Because the modified sponge had good elasticity, the oil can be quickly collected and separated from water by repeatedly absorption and squeezing processes.

![Figure 2](image2.png)

Figure 2. Illustration for the removal and collection of oils from the water surface by modified polyurethane sponges

Figure 3 showed the oil absorption capacity \( k \) of the modified sponges with different concentrations of palmitic acid. When the concentration of palmitic acid was at a suitable concentration of 0.02-0.08 mol/L, the oil absorption capacity of the modified sponge to the diesel oil could reach about 33 times of its own weight. It can be seen that the oil absorption value of the 0.16 mol/L palmitic acid modified
sponge was significantly decreased because the concentration of palmitic acid was too high, which blocked many internal passages of the sponge, thereby affecting the absorption effect of the sponge.

![Figure 3. The oil absorption capacity of unmodified and modified sponges for oil](image)

4. Conclusions
In this study, we reported the easy removal and collection of oil from a water surface by hydrophobic sponges. The hydrophobic sponges were prepared by simple solution immersion process, which had the advantages of low cost, easy availability, and easy expansion of fabrication. By dipping the sponges into the oil-water mixture, the sponge can quickly and selectively remove oil from the surface of the water, and the sponge had an oil absorption capacity of up to about 33 times its weight. Therefore, the sponges could be used for promising alternatives to conventional absorbent material in the large-scale removal of oil spill from water surfaces.

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