Research Article

A Modified Porous Sponge with Selective Ability for Oil Removal from Oil-Water Mixtures

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As oil and chemical spills pose a significant threat to the water environment, the need to develop efficient sorbent materials to remove oil and organic pollutants from water has arisen. This study aimed to develop a simple modification scheme to impart oil and water selective absorption capacity to a common three-dimensional porous material. Commercially available polyurethane sponges were used as the base material, and vinyl silica aerogel particles were loaded onto the sponges using polydimethylsiloxane as an adhesion agent. As a result, the water contact angle of the modified sponge increased from 118° to 149.2°, and the water absorption decreased from 106.5 g/g to 0.2 g/g; it could absorb oil in oil-water mixtures without absorbing water and maintain an excellent level of selective absorption ability after 20 cycles. This modification scheme is easy to operate and robust and is a scheme of practical application.

1. Introduction

Water pollution caused by oil-spilling during oil extraction and transportation and toxic organic solvents cause huge economic losses and seriously damage the ecological environment every year [1, 2, 3]. Therefore, it is imperative to find a suitable method for removing oil contaminants from water. The commonly used separation methods include gravity separation, centrifugation, flotation, membrane separation, absorption, advanced oxidation, and biological methods [4, 5, 6]. Among the various treatment methods, absorption using porous materials as absorbent has a wide application prospect, which is low cost, easy to operate, wide application, and eco-friendly [7]. Traditional absorbent materials for oil and chemicals can be classified into three main kinds: inorganic minerals [8], polymers [9], and natural organic absorbent materials [10, 11]. These materials are widely available and inexpensive, but many of them do not have the selectivity of absorption, which results in low absorption efficiency [12, 13, 14, 15]. In recent years, many new absorbent materials have been developed by researchers, such as porous aerogel [16, 17], PLA foam [18], and different types of carbon-based oil absorbent materials [19, 20]. However, they are too complicated to be manufactured, unable to be continuously absorbed, difficult to be recycled, and produce secondary pollution. These problems have driven researchers to search for more ideal materials for oil absorption.

The sponge is a low-cost, three-dimensional material with a high porosity structure and a large specific surface area and is able to remove the absorbed liquid by squeezing, making it a more desirable material for oil absorption. However, commercial sponges, including polyurethane sponges and melamine sponges, are not selective for oil and water, limiting their application in oil absorption. Therefore, surface modification of commercial sponges, using various techniques to control surface roughness and reduce surface energy to improve oil absorption, is an important research direction. For example, Lei and Zheng modified natural cellulose nanocrystals on carbonaceous melamine sponges by a simple dip-coating method and showed good oil and water selectivity with a maximum oil absorption capacity of 201 g/g or 94% of its volume [21]. Chen used chemical vapor deposition to polymerize polypyrrole onto the surface of the original melamine sponge. In situ reduction to form silver nanoparticles distributed on the outer surface of polypyrrole and finally dipped into an ethanol
solution of dodecafluoroheptyl-propyl-trimethoxysilane to obtain a superhydrophobic sponge with good oil absorption capacity, which reached absorption equilibrium within 1 min and had an absorption capacity of nearly 100 g/g for dichloromethane [22]. Jansz and Goharshadi used 2-aminophenol or ortho-aminophenol as surface energy reducers and binding agents for the in situ reductions of graphene-modified polyurethane sponges, which were superhydrophobic with contact angles up to 179° and excellent absorption capacity for nine organic solvents and four oils [23]. However, there are some problems with these solutions. For example, the sponge surface-attached particles fall off during usage, and the preparation process is complex and requires strict criteria.

In this study, a simple modification scheme for hydrophobic modification of ordinary three-dimensional porous sponges was proposed. Hydrophobic vinyl-modified silica aerogel particles were first prepared using an atmospheric pressure drying method, as shown in Figure 1. The sponge was then immersed in a polydimethylsiloxane (PDMS) solution, and hydrophobic aerogel particles were added after the sponge skeleton had made sufficient contact with the solution. After the three had been thoroughly mixed, the sponge was removed, the solvent was dried at 60°C, and the PDMS was cross-linked and cured. According to the adsorption theory in the bonding mechanism, intermolecular forces and hydrogen bonds were formed between the PDMS molecules and the sponge, and the PDMS cross-linked and cured to form a thin film that tightly wrapped around the sponge skeleton. During the curing process, some of the vinyl on the surface of the hydrophobic aerogel particles and the silicon hydride groups in the curing agent underwent a silylation reaction, formed Si-C bonds [24, 25], so that the aerogel particles bonded firmly to the PDMS film and formed a rough structure on the surface of the sponge, as shown in Figure 2.

As a result, the wettability of the polyurethane sponge changed from amphiphilic to hydrophobic, and the water absorption dropped significantly from 106 g/g to 0.2 g/g. It could be immersed in oil-water mixtures to absorb the oil but not the water and could be squeezed to recover more than 85% of the absorbed oil, as the process shown in Figure 3 and the video https://drive.google.com/file/d/152LuHaAY6KQjSU2fhv_ej2y4nTulzAN8/view?usp=sharing. No particle shedding occurred after 10 dip-squeeze cycles, and the selectivity remained constant. Moreover, the effect was stable and almost independent of the external environment when placed in different temperatures and solutions for 4 hours to simulate various usage conditions.

2. Experimental

2.1. Materials. Vinyletrimethoxysilane (VTES), hydrochloric acid, ammonia, ethanol, hexane, toluene, xylene, dichloroethylene, and acetone were supplied by Aladdin (China), and polydimethylsiloxane (PDMS, Sylgard 184) was purchased from Dow Corning (China). Gasoline, olive oil, and polyurethane sponge were purchased from local gas stations and supermarkets.

2.2. Preparation. The hydrophobic vinyl silica aerogel particles and aerogel particles/PDMS@PU sponge were prepared in this work.

2.2.1. Preparation of Vinyl Silica Aerogel Particles. At room temperature, a certain amount of ethanol and vinyletrimethoxysilane (1:8 ratio of VTM to EtOH) was added to a beaker. The hydrolisis process was completed after starting stirring and adding 0.1 mol/L hydrochloric acid solution dropwise to pH = 3 and continuing stirring for 2 h. After that, 1 mol/L ammonia solution was added drop by drop and stirred vigorously until pH = 9, then the beaker was sealed, and the gel was carried out at 50°C. After the gel formed, the beaker was sealed with an appropriate amount of ethanol and aged at 60°C for 24 h. Finally, the gel was dried under normal pressure at 60°C and 80°C for 24 h. The aerogel solid was obtained and then ground and sieved through 400 mesh.

2.2.2. Preparation of Hydrophobically Modified Sponge Samples. 1 g of PDMS prepolymer and 0.1 g of curing agent (Sylgard 184, Dow Corning Corporation) were mixed with 20 ml of hexane to make a solution. Then, the polyurethane sponge was cut into small pieces and stirred for 10 min. 0.5 g of aerogel particles were added into 30 ml of hexane, ultrasonicated and dispersed for 1 h to form a suspension, and then slowly poured into the PDMS solution and stirred for 10 min, after which the sponge was taken out and cured at 60°C for 3 h. The sponge was ultrasonicated for 5 min to remove the loosely loaded aerogel and then dried. The modification was completed.

2.3. Characterization. The microstructures of the vinyl silica aerogels and superhydrophobic modified sponges were
Figure 2: The vinyl modified silica aerogel particles were bonded to the sponge skeleton surface using PDMS.

Figure 3: Modified sponges selectively absorbed and recovered oil from oil-water mixtures by immersion-extrusion.
characterized by scanning electron microscopy (SEM, JSM-7001F, Japan); the specimens for SEM observation were coated with Pt to reduce the charging effect. The thermal effects of the materials were tested by differential scanning calorimetry and thermogravimetry (TG-DSC, Jupiter STA449 F3, Germany). The chemical structure of the materials was studied using Fourier transform infrared spectroscopy (FTIR, Nicolet NEXUS 470, USA). The material wettability was characterized by measuring the water contact angle and the rolling angle on the surface of the material. The volume of the water droplets was 3 μl for the water contact angle and 10 μl for the rolling angle (CA, Dataphysics OCA20, Germany). The analysis of the specific surface area and pore size of samples used a specific surface area analyzer (SSA, Micromeritics ASAP2460, USA). The density was calculated using the ratio of mass and volume, where mass was determined by an electronic balance and volume was determined by the drainage method.

2.3.1. Physical Properties of Aerogel. Calculate the density of the aerogel using the formula given below:

$$\rho = \frac{m}{v},$$

Where $m$ is the mass of aerogel and $v$ is the volume of aerogel.

2.3.2. Oil and Solvent Absorption Test. The sponge was weighed and immersed in the liquid to be measured and repeatedly squeezed several times to fill the sponge with liquid. It was taken out after 1 minute and quickly weighed again. The absorption capacity of the sponge $w$ is defined as

$$w = \frac{m_1 - m_0}{m_0},$$
where $m_0$ is the initial mass of the sponge and $m_1$ is the mass of the absorbed sponge that has reached the saturation.

2.3.3. The Ability to Select oil and Water. Different proportions of oil-water mixtures were prepared for the selectivity test. The sponge was placed in a beaker with different proportions of the oil-water mixture and treated with ultrasound for 5 minutes. Took the sponge out of the beaker, measured the volume of oil and water absorbed by the sponge separately and calculated the mass of oil and water absorbed by the sponge from the density. The oil-water selective ability of the sponge is calculated using the following equation:

$$ S = \frac{m_{\text{oil}}}{m_{\text{oil}} + m_{\text{water}}} \times 100\% , \quad (3) $$

where $m_{\text{oil}}$ is the mass of oil or organic solvent absorbed by the sponge and $m_{\text{water}}$ is the mass of water absorbed by the sponge.

3. Results and Discussion

3.1. Characterization of Vinyl Silica Aerogel

3.1.1. FTIR and TGA Analysis. Figure 4(a) shows the infrared spectra of vinyl silica aerogels. The absorption peaks at 1128 cm$^{-1}$ and 1025 cm$^{-1}$ are the asymmetric stretching vibration and bending vibration peaks of Si-O-Si. The absorption peak at 3440 cm$^{-1}$ is the asymmetric stretching vibration peak of Si-OH, indicating that there is still unreacted -OH in the aerogel system, and its presence has a great influence on the hydrophobicity of the aerogel. 1278 cm$^{-1}$ and 784 cm$^{-1}$ are the vibrational absorption peaks of Si-C, the absorption peak at 1630 cm$^{-1}$ is the stretching vibration peak of C=C, and the absorption peaks at 2978 cm$^{-1}$ and 1411 cm$^{-1}$ are caused by the C-H stretching vibration and in-plane bending vibration within -C=C-, which proves that vinyl exists in the aerogel system [26].

The thermal behavior of the aerogel in the air was analyzed using TGA, and the results are shown in Figure 4(b). The aerogel particles have two heat absorption peaks at 298°C and 461.3°C. The heat absorption peak at 298°C is due to the dehydration condensation reaction between the hydroxyl groups, which indicates that the aerogel has a certain amount of hydroxyl groups. The pyrolysis of vinyl siloxane causes the heat absorption peak at 461.3°C. The weight loss of the vinyl silica aerogel particles occurs mainly in three stages: (1) Below 100°C, the weight loss is not obvious because the surface was hydrophobic and less water was adsorbed; (2) the weight drops rapidly at 298°C, which is
caused by the dehydration condensation of the hydroxyl groups; and (3) from 298°C to 800°C, more weight is lost due to the pyrolysis of the vinyl groups. The total weight loss is 16.53%.

3.1.2. Pore Structure of Vinyl Silica Aerogel. The \( \text{N}_2 \) adsorption-desorption isothermal curve in Figure 4(c) shows a typical type IV pore structure and an H3 hysteresis loop, indicating that the aerogel has typical open cylindrical pores. As shown in Figure 4(d), the pore size is mainly distributed between 1 and 20 nm, and also a small amount distributed between 20 and 100 nm. The specific surface area calculated by the BET method is 612 m\(^2\)/g. The overall structural density of the aerogel is about 0.05 g/cm\(^3\) measured by using the specific gravity method.

3.2. Properties of the Modified Sponges

3.2.1. Wettability of the Modified Sponge. The wettability of the sponge plays a crucial role in whether the sample can selectively absorb oil from the oil-water mixture and indicate the modified effect. Figure 5 compared the water contact angle of the original sponge, the sponge after immersion in PDMS solution, and the sponge after loading with hydrophobic aerogel particles. Because the sponge had a porous structure, the air enclosed beneath the water droplets resulted in a strong hydrophobicity with a water contact angle of 118.0 ± 1.2°, but the water droplets quickly penetrated the unmodified sponge, and the sponge was unable to separate the oil-water mixture. Because PDMS is hydrophobic, the water contact angle of the sponge raised to 130.7 ± 1.5° after immersion in the PDMS solution, but the rolling angle was more than 90°. With the loading of hydrophobic aerogel particles, a significant increase in the water contact angle of the sponge was observed. The introduction of hydrophobic aerogel particles had two effects: an increase in surface roughness and a reduction in surface energy, both of which increase the hydrophobicity of the sponge significantly. The water contact angle of the modified sponge was 149.2 ± 2.7°, the rolling angle was 27.8 ± 2.3°, while the oil droplets completely penetrated the pores as shown in Figure 5(d), indicating that the modified sponge was oleophilic and hydrophobic.

3.2.2. Microstructure of the Modified Sponge. The surface morphology of the sponge was observed using scanning electron microscopy, as shown in Figure 6. The pore size of the sponge was about 100-300 µm, and this porous structure was the reason for the high absorption capacity. The sponge skeleton was covered with aerogel particles to form a raised structure, which helped to improve the hydrophobicity of the sponge. This modification method impacted less on the pore structure of the sponge. It did not seal the pores so that no significant reduction in the absorption of the modified sponge took place, and it was able to increase the hydrophobicity significantly, making the sponge wettability changed from amphiphilic to oleophilic and hydrophobic and able to absorb oil from oil-water mixtures.

3.2.3. Absorption Capacity of Modified Sponges. In order to evaluate the modification effect on the absorption capacity of the sponge, the absorption amounts of different oils and water were tested before and after the modification of the sponge, as shown in Figure 7. The modification had a little
effect on the oil absorption capacity of the sponge. This result also verified that the aerogel particles shown in the SEM pictures did not block the pores of the sponge but only attached to the sponge skeleton and occupied a small amount of the internal space of the sponge. However, the water absorption of the modified sponge occurred a significant decrease from 106.5 g/g to 0.2 g/g, which proved that the hydrophobic modification of the sponge was very effective, and the modified sponge had a strong oil-water selective property.

3.2.4. Oil and Water Selective Absorption Ability of the Modified Sponge. In order to verify the effect of sponge modification, the sponges before and after modification were put into simulated real wastewater to be tested. The amounts of oil and water absorbed by the sponge in different types and proportions (5%, 25%, and 50%) of the oil-water mixture were measured, respectively, and the oil-water selectivity is calculated by Equation (3), and the results are shown in Figure 8 and Table 1. The proportion of oil in the liquid absorbed by the original sponge was basically equal to the tested proportion and did not have oil-water selectivity. The oil content in the liquid absorbed by the modified sponge was close to 100%, which proved that the hydrophobic modification of the sponge was very effective, and the selectivity of the modified sponge was greatly improved, and it could accurately separate oil from the oil-water mixture, which provided high application value.

3.2.5. Stability of the Modified Sponge. The absorbent material is required to tolerate different temperatures and acidity in practical use. In order to test the stability of the modified sponge, it was placed in different pH liquids and different temperature environments, and the contact angle was measured after 4 hours, and the results are shown in Figure 9. The contact angle of the modified sponge almost did not change after the different environments tested, indicating that this modified sponge had good tolerance to different use environments and could keep hydrophobicity unchanged.

It was also required for the modified sponge that the aerogel particles on the sponge skeleton did not fall off and maintain hydrophobicity and good selectivity after several absorption-squeeze desorption cycles. In order to study the

Table 1: Selectivity of the modified sponges.

<table>
<thead>
<tr>
<th>Oil-water mixture</th>
<th>5% oil content</th>
<th>25% oil content</th>
<th>50% oil content</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xylene-water mixture</td>
<td>99.8</td>
<td>99.4</td>
<td>99.5</td>
</tr>
<tr>
<td>Hexane-water mixture</td>
<td>99.7</td>
<td>99.9</td>
<td>99.6</td>
</tr>
<tr>
<td>Dichloroethane-water</td>
<td>99.0</td>
<td>99.8</td>
<td>99.3</td>
</tr>
<tr>
<td>Toluene-water mixture</td>
<td>99.1</td>
<td>99.5</td>
<td>99.7</td>
</tr>
<tr>
<td>Gasoline-water mixture</td>
<td>99.5</td>
<td>99.7</td>
<td>99.7</td>
</tr>
<tr>
<td>Olive oil-water mixture</td>
<td>99.7</td>
<td>99.2</td>
<td>99.4</td>
</tr>
</tbody>
</table>

*Selectivity was calculated using the following equation: $s = \frac{m_{oil}}{m_{oil} + m_{water}} \times 100\%$. 

Figure 8: The absorption capacity of the sponge in the oil/water binary system before and after modification.
durability of the modified sponge, a mixture of 25% toluene and water was selected to simulate wastewater for the absorption-extrusion desorption cycle, and the selectivity of the modified sponge was calculated. The contact angle was measured every 10 cycles, and the results are shown in Figure 10. After 50 cycles, the selectivity dropped to 87.3%, and the contact angle became 132.2°, which was still a relatively high selectivity. This environmental tolerance and durability were due to the stability and flexibility of PDMS, which maintained robustness in different environments and held the aerogel particles in the sponge skeleton after multiple compressions to maintain the modification effect.

4. Conclusion

We report a simple and durable sponge modification scheme that could reduce the surface energy of the sponge and provide a rough structure by firmly adhering hydrophobic vinyl silica aerogel particles to the sponge skeleton with PDMS. This scheme could vastly improve the hydrophobic properties of the sponge and could change the wettability of the sponge from amphiphilic to hydrophobic. The modified sponge could absorb oil from the oil-water mixture without absorbing water. The modification did not block the pores of the sponge and occupied only a small amount of internal space, so the absorption amount of the modified sponge changed slightly. The water contact angle of the modified sponge was almost unchanged after 4 hours of simulating various environments. After 50 cycles, the water contact angle of the modified sponge decreased from 149.2° to 132.2°, which was still hydrophobic, and the selectivity decreased to 87.3%, which could maintain a certain oil-water selectivity. It was expected that this would be a promising solution for the hydrophobic modification of sponge in applying oil-water separation.

Data Availability

All data included in this study are available upon request by contact with the corresponding author.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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