Facile fabrication of super-hydrophobic and super-oleophilic Ota-PDA-PU sponge for efficient oil/water separation

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Received 6 October 2018; Accepted 15 April 2019

ABSTRACT

With the aggravation of environmental pollution caused by oil and chemical leakages, oil-water separation has attracted much attention from both academia and industry. In this paper, a cost effective immersion method based on the modification of polyurethane sponge has been developed in the application field of oil/water separation. Octadecanethio and polydopamine were used to grafted onto PU sponge which was roughened by etching method. The morphology, composition and surface properties of prepared Ota-PDA-PU sponges were characterized by various techniques. The characterization results of the modified sponge exhibited rough surface structure, excellent flexibility, and possessed super-hydrophobic characteristic with a high water contact angle (WAC) of 155 ± 1º. The as-prepared sponge displayed high absorption selectivity for different organic solvents and oils, the absorption capacity for sesame oil attained 40 times of its own weight. Meanwhile, the absorption selectivity has no decrease after 10 cycles of absorption-desorption process. More importantly, the as-prepared sponge could be used as a filter for oil-water separation.

Keywords: Oil/water separation; Super-hydrophobicity; Dopamine hydrochloride; Polyurethane sponge

1. Introduction

With the development of economy, the frequent occurrence of oil spillage and chemical leakage had a devastating effect on marine, which not only threaten each species along with the marine food chain, but affect human beings [1,2]. In other areas such as oil and gas industry, oil-water separation technology is also required. Therefore, remove organic pollutants from organic solvents/water mixtures urgently needs to be addressed. Traditionally, oil-water separation technologies include controlled burning [3,4], gravity separation [5], bioremediation [6], membrane separation [7-9] and using absorbent materials [10]. However, the majority of traditional technologies often suffered from problems of high cost, time-consuming, poor oil absorption capacity and tedious manual operation [11]. Recently, with the development of colloid and interface science and bionics, a variety of functional materials were fabricated, which possess simultaneous super-hydrophobicity and super-oleophility, through the rational control of surface structures and chemical compositions that offered a new idea for developing efficient oil-water separation material [12-13]. Compared to conventional separation technologies, the special wettability-controlled oil water separations show big advantages in both the separating speed and the efficiency of separation.

A commercial polyurethane (PU) sponge is a kind of cheap 3D porous material. 3D material is mainly used to absorb oil from water but not to continuously separate oil/water mixture. This absorbing method is appropriate for
leakage because the water quantity is much larger than oil in the sea. The porous micro structure of the PU sponge can provide a significantly large space for the storage of oils. Meanwhile, it possesses excellent flexibility, low density and easily scalable fabrication [14]. However, it is naturally hydrophilic that often absorbing both water and oils, which makes it not suitable for selectively removing oils from water. Up to now, many materials such as TiO₂ nanoparticles [15], r-GO [16–19], GO [20,21], Fe₃O₄ nanoparticles [22–24], nanocellulose [25] and MoS₂ [26] for practical applied to modify the PU sponges to increase the hydrophobicity of the modified PU sponge. Nevertheless, these methods in practical applications have limitations, because of high cost and complex preparation processes. For avoiding these problems, we tried to gain a PU sponge with great absorption capacity through a more facile and lower cost method.

In this study, we used a simple and cheap method to synthesize super-hydrophobic and super-oleophilic polyurethane sponge which was modified with polydopamine and octadecanethiol (Ota-PDA-PU sponge). Firstly, porous polyurethane sponge was employed to apply as a substrate, then the PU sponge was etched by chromic acid to attain rough surface. Finally, the sponge was modified by polydopamine and octadecanethiol. The as-prepared sponge displayed rough morphology, super-hydrophobicity and super-oleophily, and possessed high selectivity, splendid absorption capacities and outstanding recyclability for a variety of organic solvents and oils. Furthermore, the as-prepared sponge could be used as a filter for oil-water separation.

2. Experimental

2.1 Materials

All chemical reagents were of analytical grade level and used without further purification. The deionized water was used to prepare all solutions. PU sponges were purchased from Alibaba Enterprise. Xylene was supplied from Shandong Xiya Reagent. Tetrachloromethane was obtained from Sinopharm Chemical reagent Co., Ltd. n-Hexane was purchased from Shanghai Titan Scientific Co., Ltd. Dopamine and octadecanethiol were supplied by Shanghai Aladdin Bo-chem technology Co., Ltd. Potassium dichromate was obtained from Tianjin Fengchuan chemical Co., Ltd. Kerosene, diesel oil, lubricating oil and sesame oil were purchased from nearby stores.

2.2 Fabrication of super-hydrophobic Ota-PDA-PU sponge

Super-hydrophobic Ota-PDA-PU sponge with oil/water separation was fabricated through the following procedure. Firstly, PU sponge was cut into cubes and ultrasonically treated with ethanol and deionized water for 30 min and dried at 60°C. Secondly, the cleaned PU sponge was etched with chromic acid solution for 1 min at room temperature. After etching, the PU sponge was rinsed sufficiently with deionized water, and then dried in the oven at 60°C. Thirdly, this PU sponge with rough structures was immersed into a dopamine-10 mM Tris (hydroxymethyl) aminomethane hydrochloride solution with concentration of 2 g/L for 24 h, and the temperature was maintained at 45°C. Afterwards, the PU sponge was removed, thoroughly rinsed with water, and then dried in an oven at 60°C. The sample was then placed in a 50 mM octadecanethiol solution for 24 h. Subsequently, the PU sponge was removed, thoroughly rinsed with ethanol and water, and then dried in oven.

2.3 Oil absorption of the Ota-PDA-PU sponge

The absorption capacities (Q) of the Ota-PDA-PU sponge for six types of oils and organic solvents (lubricating oil, diesel oil, sesame oil, xylene, kerosene and n-Hexane) were tested. All tests were performed at room temperature. A block of the Ota-PDA-PU sponge was put into a 200 mL glass beakers filled with enough oil for 5 min. Then the soaked Ota-PDA-PU sponge was taken out and recorded the weight. The Q value was calculated with the equation:

\[
Q = \frac{M_1 - M_0}{M_0}
\]

where \(M_0\) and \(M_1\) are the weights of the sponge before and after the absorption of oil.

2.4 Oil-water separation of the Ota-PDA-PU sponge

The oil-water separation processes were performed in a simple self-made equipment as shown in Fig. 8. Ota-PDA-PU sponge was settled between two glass vessels and 10 mL water (dyed with methylene blue) was poured into the upper tube. Then, pouring 10 mL tetrachloromethane (dyed with Sudan II) into the upper tube.

2.5 Characterization

X-ray photo electron spectroscopy (XPS, PHI Quantera SXM, ULVAC-PHI, Japan) measured the surface chemical composition of samples. The morphology of the samples was examined by scanning electron microscopy (SEM) using a TESCAN MIRA3 LMU microscope. The flexibility and compressibility was investigated by 810 material test system (MTS). The water contact angles (WCAs) and oil contact angles (OCAs) were measured by the instrument (JC2000D1, Power each. Co. Ltd) at room temperature. WCAs on all samples were measured for three times and average value taken.

3. Results and discussion

3.1 Morphology of material

It is well known that the surface morphology is significance to the wettability of as-prepared material. So scanning electron microscopy (SEM) was used to investigate the surface morphologies of the sponges before and after the hydrophobic modification. Figs. 1a, b and c display the original sponge, which suggested that the original sponge possessed inherent three-dimensional porous network
structure (pore size of the original sponge is 100–200 μm, and the average diameter of skeleton is about 10 μm), and the skeleton is smooth and flat. The highly porous structure dramatically introduced enough space to store the absorbed oils. The morphology of sponge after the hydrophobic modification is shown in Figs. 1d, e and f, it can be seen that three-dimensional porous network structure have been reserved in Ota-PDA-PU sponge after modification. Interestingly, the skeleton of Ota-PDA-PU sponge became rough coated by a thin coating with numbers of particles. The particles may be caused by the aggregation of PDA on the surface of PU sponge. Together with the etching by chromic acid, these particles enhance the surface roughness. The purpose of enhance surface roughness is to enhance this special wettability based on Wenzel model but not to endow the sponge with special wettability.

3.2. Chemical composition of sponge

XPS measurement was employed to investigate the elemental composition of the PU sponge and the Ota-PDA-PU sponge. As shown in Fig. 2a, only C, O and N were detected in the PU sponge, after hydrophobic modification, new peak with binding energy of 164.17 eV appeared in the sample, which were attributed to the binding energy of S2p. Further information about the chemical composition of the surfaces could be obtained by analyzing the high-resolution S2p spectrum and N1s spectrum, as shown in Figs. 2b and c. The S2p peak could be deconvoluted into four peaks at 162.0, 163.0, 163.7 and 164.7 eV [27–29]. Of these, 162.0 and 163.0 eV could be assigned to the binding energy of S2p 3/2 and S2p 1/2 of octadecanethiol, and 163.7 and 164.7 eV could be attributed to the binding energy of S2p 3/2 and S2p 1/2 of C=C-S, respectively. The N1s peak could be deconvoluted into four peaks at 398.2, 399.2, 404.0 and 401.5 eV [30], which were attributed to the C=N, N-H, –NH 2 and hydrogen bond. These results indicated that the octadecanethiol are chemically bound on the surface of PDA-PU sponge through the michael addition reaction [31]. Because the low surface energy of PU sponge surface modified by octadecanethiol, Ota-PDA-PU sponge attains special wettability of hydrophobicity and oleophilicity.

3.3. Mechanical property of the Ota-PDA-PU sponge

Flexibility and compressibility are strongly required for the reuse of sponge and the recovery of oil and organic reagents. So the flexibility and compressibility of Ota-PDA-PU sponge was investigated by a uniaxial compression and rebound tests with different set strains (20–80%). As shown in Fig. 3, the sponge displays nearly reproducible results which the sponge could completely recover its original shape after compression at different set strains. Under moderate-strain compression (ε = 20 to 60%), all the unloading curves are above the line y = 0 while returning to the original state, indicating a complete volume recovery without any plastic deformation. With a larger strain compression of 80%, it only shows a small plastic deformation of less than 10%. It was suggested that the process of chromic acid etching did not destroy the flexibility and compressibility of sponge, and the Ota-PDA-PU sponge was suitable to use as a recycle-absorbent for oil and organic solvents by manual squeezing.

3.4. Wetting behavior

It is believed that the modification by octadecanethiol and rough surface caused by the PDA particles result in the super-hydrophobicity and super-oleophilicity of Ota-PDA-PU sponge. In order to exhibit super-hydrophobicity and super-oleophilicity of Ota-PDA-PU sponge, the wetting behavior of water and oil on the surface of Ota-PDA-PU sponge was studied, and the results are displayed in Fig. 4. As shown in Fig. 4a, a water droplet maintained nearly a spherical shape with a high WAC of 155 ± 1º (as shown in Fig. 4b) when it was placed on the sponge surface, similar to it on a lotus leaf surface. On the contrary, when a kerosene droplet was dropped on the surface of Ota-PDA-PU sponge, it quickly spread
over the surface and was instantaneously sucked by Ota-PDA-PU sponge with an OAC of 0° (as shown in Fig. 4c), which suggested the hydrophobic and oleophilic property of Ota-PDA-PU sponge. Moreover, it can be seen that the Ota-PDA-PU sponge surface looked like a clear silver mirror when the sponge was immersed into the water by outside force (Fig. 4c), which was ascribed to the sponge was wrapped with a layer of air bubble and established a composite solid-liquid-air interface which was referred to so-called non-wetting Cassie-Baxter surfaces [32]. After the external force was released, the sponge immediately floated on the water surface, and no water was found in the sponge surface, exhibiting excellent water proofing property.

The super-hydrophobicity and super-olephilicity of Ota-PDA-PU sponge was further investigated via a contact process, and the result is shown in Fig. 5. Firstly, the super-hydrophobicity of Ota-PDA-PU sponge was examined, the water droplet (2 uL) was trapped on the needle tip of a micro-syringe and forced to be in contact with the Ota-PDA-PU sponge surface, and it is hardly pushed into the sample even when the water droplet was squeezed. In addition, when the water droplet remove upward, water droplet can overcome the adhesion force with the Ota-PDA-PU sponge surface and detach from sponge surface (as shown in Fig. 5a), suggesting splendid hydrophobicity of the Ota-PDA-PU sponge. More interesting, when oil droplet contacted with the Ota-PDA-PU sponge, it spread and was absorbed with 1 s, making it impossible to get a reliable contact angle value (as shown in Fig. 5b), suggesting excellent olephilicity of the Ota-PDA-PU sponge.

3.5. Absorption behavior of Ota-PDA-PU sponge to organic liquids

As mentioned above, Ota-PDA-PU sponge possesses simultaneous super-hydrophobicity and super-olephilicity, which would endow Ota-PDA-PU sponge with remarkable separation property for removing oils from water. The separation property was investigated by two types of organic reagents with different densities, tetrachloromethane and kerosene. As shown in Fig. 6, a piece of Ota-PDA-PU sponge was forced to contact a drop of tetrachloromethane (dyed with Sudan II) under the water and a layer of kerosene (dyed with Sudan II) upon the water, it could absorbed tetrachloromethane and kerosene and repelled the water within a few seconds. Such fast absorption was attributed to the combination of high porosity, oleophilic nature, and capillary action in the material. Additionally, the absorption capacity of Ota-PDA-PU sponge was also investigated by a
series of oils and organic reagents, including n-hexane, xylene, kerosene, diesel oil, lubricating oil and sesame oil. The results are exhibited in Fig. 7a, Ota-PDA-PU sponge displayed excellent absorption capacity toward all those reagents, ranging from 24.5 to 39.2 times of its own weight. It was mostly ascribed to the strong capillary effect of the super-hydrophobic and super-oleophilic Ota-PDA-PU sponge, which was possessed with high porosity, small hole size, rough surface and low surface energy. Obviously, those experiments clearly suggested that the absorption capacity of the sponge was mainly determined by the densities and viscosities of reagents.

Fig. 7b shows the recyclability of Ota-PDA-PU sponge for removal of n-hexane, xylene, kerosene, diesel oil, lubricating oil and sesame oil. It can be seen that no obvious change was found after 10 cycles, indicated the sponge has excellent recycling performance.

3.6 Oil-water separation properties

Depending on the porosity, super-hydrophobicity and super-oleophilicity of Ota-PDA-PU sponge, the application of Ota-PDA-PU sponge in the field of oil-water separation was tested. As shown in Fig. 8, the water cannot go through the sponge under the force of gravity and tetrachloromethane quickly permeated through water and the sponge and dropped into the beaker due to the super-oleophilicity. The mechanism for the excellent oil-water separation properties of Ota-PDA-PU sponge was owed to the following reasons: Oily liquid was driven through the open pores of the sponge into its bulk in the presence of a capillary force, while water was completely excluded by the super-hydrophobic surface, resulting in separating oils from water with high efficiency.

4. Conclusion

In summary, this work provided a facile and cheap approach to fabricate super-hydrophobic and super-oleophilic Ota-PDA-PU sponge for oil-water separation.
Ota-PDA-PU sponge displayed rough morphology and excellent flexibility. More interesting, water droplet was able to maintain nearly a spherical shape on the Ota-PDA-PU sponge with a WAC of $155^\circ \pm 1^\circ$, and oils could penetrate the Ota-PDA-PU sponge with an OAC of $0^\circ$. What was more, the Ota-PDA-PU sponge possessed splendid absorption capacity up to 40 times of its own weight. Furthermore, the Ota-PDA-PU sponge exhibited excellent selectivity and outstanding recyclability for a variety of organic solvents and oils. More importantly, the as-prepared sponge could...
be used as a filter for continuous oil-water separation. Because of the inexpensive materials, facile synthesis processes, excellent performance and outstanding recyclability, the Qta-PDA-PL sponge will be a promising candidate for practical oil-water separation application.

Acknowledgments

The authors would like to thank the National Natural Science Foundation of China (21776319), Key Laboratory of Hunan Province for Water Environment and Agriculture Product Safety (2018TP1003).

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