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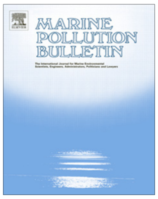

Highly recyclable superhydrophobic sponge suitable for the selective sorption of high viscosity oil from water

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ABSTRACT

Inspired by the adhesion of marine mussels, a kind of superhydrophobic oil sorbent was successfully fabricated by robustly immobilizing the micro/nanostructure layer onto the sponge skeleton. The as-prepared sponges possess excellent hydrophobicity with the water contact angle of 154°, which enables the sponge to selectively absorb various oils floating on water surface. The oil sorption capacities of as-prepared sponge for a series of oils can reach 18.3–46.8 g/g. The absorbed oil can be recovered by mechanical squeezing and the resulting sponge can be recycled more than 70 cycles while still keeping high oil sorption capability. More importantly, the obtained sponge has excellent affinity to the high viscosity oils. Therefore, the as-prepared sponge might find practical applications in the large-scale removal of oils especially high viscosity oils from water surface.

1. Introduction

Unintentional discharge of oil in daily life and frequent oil spill accidents in the oil exploration, transportation and processing of oil have caused severe damage to the ecosystems of freshwater and ocean (Al-Majed et al., 2012; Wu et al., 2014). As a result, many technologies including skimmers (Broje and Keller, 2007), dispersants (Kujawinski et al., 2011), oil-absorbing materials (Zhang et al., 2013), and in situ burning (Aurell and Gullett, 2010) have been developed to solve the problem. Oil-absorbing materials are generally considered as one of most effective choices for the cleanup and collection of spilled oil. Up to date, a variety of materials including kapok fiber (Dong et al., 2015), aerogel (Hayase et al., 2013), sponges (Ge et al., 2014), electrospun fibers (Lin et al., 2012), and calcium carbonate (Arbatan et al., 2011) have been prepared for separating oils from water. However, a large numbers of oil-absorbing materials have many disadvantages, such as high cost, low oil sorption capacity, poor hydrophobicity, complicated fabrication procedures and poor durability as well as recyclability. Despite this, the oil sorbent based on sponge with special 3D porous structure demonstrates great application prospect due to their high uptake capacity, low price, and excellent flexibility. Recently, there is a growing attention about the fabrication of superhydrophobic sponges for the cleanup of oil by various methods (Sun et al., 2013; Zhu et al., 2013; Nguyen et al., 2012; Gao et al., 2014; Chen and Pan, 2013). However, owing to the weak adhesion between micro/nanostructured layer and sponge skeletons, the hydrophobic layer is easily detached from the skeletons of sponges in repeated use processes, which limits its practical applications. Therefore, it is indispensable to fabricate robust and highly efficient superhydrophobic sponges by facile and simple strategies for addressing the global-scale environment challenges.

As well-known, by means of Mytilus edulis foot protein, marine mussels can adhere to all types of surface of substrates with high binding strength. As a molecular structural mimic of Mytilus edulis foot protein 5 (Mefp-5), dopamine, containing catechol and amine functional groups, can form strong covalent and noncovalent interfacial interactions with all types of substances through self-polymerization (Hong et al., 2012; Josep et al., 2013). The research results have been widely applied in many fields like surface coating (Yu et al., 2013), immobilization of biomolecules (Lee et al., 2009), and biomedicine (Losic et al., 2010). Recently, dopamine has been used in the preparation of oil/water separation materials, and the formed polydopamine layer offers an excellent platform for the fitting of functional groups and immobilization of nanoparticles (Zhu and Pan, 2014). A kind of mesh for separating oil/water mixture has been successfully prepared by combining mussel-inspired chemistry and Michael addition reaction (Cao et al., 2013). Superhydrophobic melamine sponge with excellent flame retardancy was also prepared through the deposition of polydopamine films and modification of 1H,1H,2H,2H-perfluorod

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ecanethiol (Ruan et al., 2014). Therefore, mussel-inspired chemistry may provide a great opportunity for developing robust, efficient, and reusable oil-absorbing materials under mild conditions.

Here, silica nanoparticles were immobilized onto the skeleton of polyurethane sponges via strong covalent and noncovalent interactions derived from the self-polymerization of dopamine. To our knowledge, there is no information known about the combined use of polydopamine and silica nanoparticles in fabricating superhydrophobic sponge with stable micro/nanostructured layer for selective sorption of oil from water surface. The as-prepared sponges exhibit high oil sorption capacity, excellent selective sorption for oil from water surface, quick oil sorption rate for high viscosity oils, and excellent chemical durability. More interesting, the as-prepared sponges can be recycled more than 70 times. Moreover, the facile approach can be easily put into large-scale production. Therefore, the as-prepared sponge has bright application prospect in the cleanup of spilled oils with high viscosity from water.

2. Experimental

2.1. Materials

Polyurethane sponge was purchased from market, Yinchuan, China. Dopamine hydrochloride (chemically pure) and Tris(hydroxymethyl)aminomethane (Tris–HCl, chemically pure) were received from Nanjin Aoduo Biotechnology Co. Ltd., China. Dodecyltrimethoxysilane (DTMS, chemically pure) was provided by Nanjin Chengong Organosilicon Co. Ltd, China. Tetraethylorthosilicate (TEOS, chemically pure), $NH_3{\cdot}H_2O$, paraffin oil, *n*-hexane, chloroform, and toluene (analytical grade) were supplied by Ningxia Yaoyi Chemical Reagent Co. Ltd., China. Crude oil was supplied by PetroChina Baota Petrochemical Company, China. Linseed oil came from market, Yinchuan, China. The physical properties of six kinds of oils are shown in Table 1.

Table 1
Characteristics of investigated oils at room temperature.

Oils	Viscosity (mm^2/s)	Density (g/mL)
n-hexane	0.44	0.69
Toluene	0.68	0.87
Chloroform	0.38	1.5
Linseed oil	62.6	0.91
Paraffin oil	48.6	0.92
Crude oil	88.5	0.85

2.2. Preparation of superhydrophobic sponge

Before use, polyurethane sponge was ultrasonically cleaned in ethanol. In a typical experiment, 0.63 g silica nanoparticles and 0.5 mg of dopamine hydrochloride were added into 250 mL of Tris–HCl solution to treat for 5 min under ultrasonic. The sponge was immersed into the dispersions and stirred for 16 h at room temperature. Then, the nanoparticles-loaded sponge was modified in DTMS solution, and then dried in an oven at 80 °C to constant weight. Preparation of silica nanoparticles is as follows: 6 mL of TEOS and 5 mL of $NH_3{\cdot}H_2O$ were added into 100 mL of ethanol to stir for 6 h at room temperature, and then the obtained nanoparticles were collected and dried for use.

2.3. Measurements of oil sorption capacity

In oil medium without water: the dried sample was immersed into different oils for a certain time until saturation, and then the oil-saturated sample was taken out from the oil and drained for 15 s. The oil sorption capacity of the sample was determined by weighing the samples before and after the sorption, and calculated by the following formula:

$$Q = (W_t - W_i)/W_i$$

where Q is the oil sorption capacity of the sorbents calculated as grams of oil per gram of sample, W_t is the weight of sorbent with oil (g), W_i is the initial weight of sorbents (g).

In oil from water: The oil was mixed with 50 mL of water in a 100 mL beaker, and the formed oil layer will float to the surface of the water except for chloroform. Then, the as-prepared sponge was left in the oil on water surface for 30 s min at room temperature. After that, the sorbent was removed from the beaker using tweezer and weighed. For chloroform, the sample was immersed into the bottom of beak to absorb chloroform by external force, and then the chloroform-loaded sponge was removed using tweezer. The oil sorption capacity of the as-prepared sponge for the oils from water was also calculated according to the above formula.

2.4. Characterizations

The micrographs of samples were examined using SEM (JSM-5600LV, JEOL). Before SEM observation, all samples were fixed on aluminum stubs and coated with gold. The surface wettability of water on the surface of sponge was observed with a digital SLR camera after the water was dripped on the surface of sponge from a syringe (1 mL). Contact angle measurements were carried out using a Krüss DSA 100 (Krüss Company, Ltd., Germany) apparatus at ambient temperature, and the volumes of probing liquids in the measurements were approximately 5 μL.

3. Results and discussion

3.1. Fabrication of superhydrophobic sponge and its morphology analysis

The fabrication procedure of superhydrophobic sponge with excellent robustness is displayed in Fig. 1. The pristine sponge is added into the Tris–HCl buffer solution containing dopamine and silica nanoparticles to react a certain time, then the nanoparticles-adhered sponge is transferred into the solution of organosilane to modify for a certain time, superhydrophobic sponge will be obtained after the drying. The nanoparticles will strongly adhered to the skeleton of sponge under the covalent and noncovalent interactions between the nanoparticles and the sponge surface derived from self-polymerization of dopamine. In order to reveal the hydrophobic property of the as-prepared sponge, the surface wettability of water on the surface of pristine and treated sponge is observed, as shown in Fig. 2. The water droplet cannot stay on the surface of pristine sponge but sinks quickly into the sponge to form a large spreading radius on the surface (Fig. 2(a)). In contrast, the as-prepared sponge reveals excellent hydrophobic property with the water contact angle of 154° (Fig. 2(b)). When spraying the water onto the as-prepared sponge, the water droplet is quickly spread out over the entire surface of pristine sponge (Fig. 2(a)), while a nearly sphere-like water droplet forms immediately to roll down the sponge surface (Fig. 2(b1)). These results mean that the hydrophobic property of pristine sponge was significantly improved by the facile surface treatment. To confirm the formation of micro/nanostructure on the skeleton of sponge, SEM analyses were conducted to observe the morphology of pristine and the as-prepared sponge. The SEM images reveal that pristine sponge exhibits a smooth surface inside 3D porous structure, while a large number of nanoparticles are uniformly immobilized onto the skeleton of sponge after the treatment

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