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Oil sorbents with high sorption capacity, oil/water selectivity and reusability for oil spill cleanup

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ABSTRACT

A sorbent for oil spill cleanup was prepared through a novel strategy by treating polyurethane sponges with silica sol and gasoline successively. The oil sorption capacity, oil/water selectivity, reusability and sorption mechanism of prepared sorbent were studied. The results showed that the prepared sorbent exhibited high sorption capacity and excellent oil/water selectivity. 1 g of the prepared sorbent could adsorb more than 100 g of motor oil, while it only picks up less than 0.1 g of water from an oil–water interface under both static and dynamic conditions. More than 70% of the sorption capacity remained after 15 successive sorption–squeezing cycles, which suggests an extraordinary high reusability. The prepared sorbent is a better alternative of the commercial polypropylene sorbent which are being used nowadays.

1. Introduction

Oil-sorbent plays an important role in many fields such as oil spill cleanup, oil/water separation and environmental remediation (Gui et al., 2010; Yuan et al., 2008; Su et al., 2005; Whitfield, 2003; Moura and Lago, 2009; Fingas, 2000; Adebajo et al., 2003). Disasters such as the oil spill in Mexico Gulf in 2010 remind us again the importance of oil-sorbents in spilled oil cleanup and environmental remediation (Kerr et al., 2010; Aguilera et al., 2010). High oil sorption capacity, low water pickup, and excellent reusability are the most important criteria for selecting oil sorbent (Adebajo et al., 2003). To date, several types of materials, such as inorganic sorbents, natural organic sorbents, and synthetic organic sorbents, have been extensively studied (Adebajo et al., 2003; Gurav et al., 2010; Carmody et al., 2007; Abdullah et al., 2010; Srinivasan and Viraraghavan, 2008; Annunciado et al., 2005; Ceylan et al., 2009; Duong and Burford, 2009; Lin et al., 2010; Wei et al., 2003; Zhang et al., 2009). However, it is still a challenge to get ideal oil sorbents that could meet all the three criteria. Generally, the oil sorption capacities of inorganic sorbents and natural organic sorbents are only tens of grams per gram of sorbent and the oil/water selectivity is basically not very high. Commercial polypropylene (PP) oil sorbents have good oil/water selectivity because of their oleophilic–hydrophobic properties, but their oil sorption capacities are only 15–25 g g^{-1}. Recently, oil sorbents made of polymer fibers prepared via a one-step electrospinning process, such as polyvinyl chloride/polystyrene fibers (Zhu et al., 2011), were reported to have very high oil sorption capacity up to 146 g g^{-1}. However, these electrospun oil sorbents have poor reusability. Once they are compressed to remove oil, they will lose most of their sorption capacities and it is difficult to recover. Another kind of newly developed oil sorbents is carbon base sponges and aerogels. For example, Gui et al. reported a type of carbon nanotube sponges with sorption capacities of about 125 and 143 g g^{-1} for pump oil and diesel oil, respectively (Gui et al., 2010). Sun et al. (2013) and Hu et al. (2013) reported that graphene aerogels not only had extremely high sorption capacities but also were reusable. The reported aerogels kept their initial shape and absorption capability after more than 10 cycles of compression. However, the oil/water selectivity of these graphene aerogels has not yet been reported. Furthermore, these materials are still synthesized in a lab scale. The research for high performance oil sorbents at low cost and scalable production remains a challenging issue and needs urgent attention.

In the current paper, we report the preparation of ideal oil sorbents that can meet the three mentioned criteria. Polyurethane (PU) sponges are chosen as raw materials because they are durable, cheap, available in large scale, and above all, they have huge sum of connected holes that can provide very high oil sorption capacity. Furthermore, polyurethane sponges have excellent elastic property and can recover to the initial state after many times of compression. The only obstacle is that polyurethane sponges are hydrophilic, thus surface modifications are required to improve the

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oil/water selectivity. In this work, polyurethane sponges are treated with SiO_2 sol and subsequently gasoline to develop hydrophobic surface. Then their performances as oil sorbents are characterized in terms of oil sorption capacity, oil/water selectivity, reusability and oil retaining ability. Particularly, the oil sorption mechanism is studied by way of investigating the microstructures, the fiber surface property and the contact angles of the prepared sorbent.

2. Materials and methods

2.1. Preparation of sorbents

Polyurethane sponges were obtained from Jinhua Duxiu Technology Co. Ltd. In a typical preparation process, the sponges were cut into blocks of $45 \times 20 \times 15$ mm, and then immersed completely into an aqueous SiO_2 sol containing 0.5 wt.% of SiO_2 nanoparticles. After being soaked in the SiO_2 sol for 30 min, the sponges were centrifuged to remove liquid, dried naturally, and then immersed completely into gasoline for another 15 min. The sponges were then centrifuged and dried at room temperature to get the final oil sorbents.

Scanning electron microscopy (SEM) images were taken on a FESEM-6700 field-emission microscope. An OCA20 contact angle system was applied to measure the contact angle of the obtained sorbent with water or motor oil.

2.2. Sorption experiments

Three types of oils including motor oil, peanut oil and diesel were employed to study the sorption capacity of the sorbents. The sorption experiments were conducted in dynamic simulated system and static system at 20 ± 4 °C. In dynamic simulated system, different amount of oil was poured into four 5 L glass beakers, containing 800 mL tap water each, to obtain oil films of 1–4 mm in thickness on water surface, respectively. The mixture of oil and water were constantly agitated (~500 rpm) by magnetic stirrer. Then blocks of sorbent were weighed and placed in each of the glass beakers, respectively. After 30 min of sorption, the sorbents were taken out and allowed to drain for 2 min. The saturated sorbents were squeezed and the recovered liquids were centrifuged to separate water from oil according to the standard method D4007-81 (ASTM-1998a). Thus the amounts of sorbed water and sorbed oil were determined. The sorption capacity of oil and water can be calculated using Eq. (1),

$$C_{s,o} = m_o/m_i, \text{ or } C_{s,w} = m_w/m_i \quad (1)$$

where $C_{s,o}$ and $C_{s,w}$ represent oil and water sorption capacity (g g^{-1}) of the sorbent, m_i is the initial weight (g) of the sorbent, m_o is the weight (g) of the sorbed oil, and m_w is the weight (g) of the sorbed water. Four independent experiments were conducted to get average value for each test. In static system, the magnetic stirrer was turned off while keeping all other experimental parameters unchanged as in the dynamic system.

The saturated sorbents were squeezed and then reused as sorbent. The sorption–squeezing procedure was repeated many times under identical conditions to evaluate the reusability of the sorbent.

3. Results and discussions

3.1. Sorption capacity and oil/water selectivity of the sorbents

Fig. 1 shows the sorption capacity of motor oil and water measured when sorbents were placed in beakers containing motor oil films of different thickness on the top of tap water, under both static and dynamic conditions. Taken the reasonable experimental fluctuation into account, the sorption capacity of motor oil was determined to be around 103 ± 3 g g^{-1} under static condition and 106 ± 3 g g^{-1} under dynamic condition, which showed less relevant to the thickness of oil films. In comparison, water pick up under both static and dynamic conditions was measured to be less than 0.1 g per gram sorbents, not affected by the thickness of oil films. The results suggest high oil sorption capacity for both thick oil films and thin oil films. As the thickness of oil films is not relevant to the oil sorption capacity, it should be emphasized that the sorbents are especially applicable at the final stage of oil spill cleanup when there is very thin oil film remained and it is difficult to handle with traditional methods. The results also indicate that the sorbents have not only high sorption capacity, but also have very good oil/water selectivity, which means the water pickup is negligible in comparison to the oil sorption. This is of great significance because it suggests a very high efficiency of a single sorption cycle when the sorbents pick up large amount of oil without further efforts required for oil–water separations.

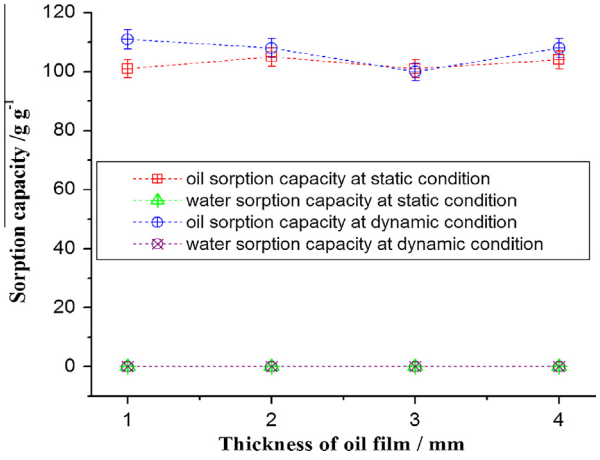

Fig. 1. Sorption capacities of the prepared sorbents at static and dynamic conditions (motor oil at oil–water interface).

The sorption capacities of the prepared sorbents for different kinds of oils determined by putting the sorbents on 3 mm oil film at oil–water interface under static condition are presented as Fig. 2, together with the data of commercial PP sorbents measured under identical conditions. The sorption capacities of the prepared

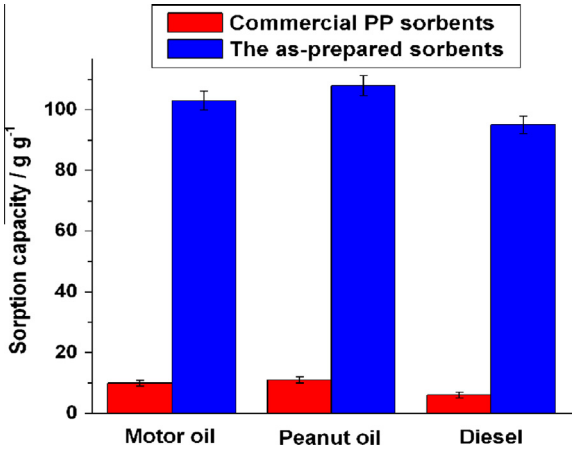

Fig. 2. Sorption capacities of the prepared sorbents and commercial PP sorbents for various oils (3 mm oil film at oil–water interface, static condition).

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