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Magnetic fibrous sorbent for remote and efficient oil adsorption

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ABSTRACT

Oil spill accident and oily water have potential risks to environment and human health, thus need to be imperatively treated. Herein, a magnetic fibrous sorbent was designed *via* electrospinning of suspension containing polymer and magnetic nanoparticles in one step for remote and efficient oil adsorption. The morphology of the magnetic fibrous sorbent was characterized by scanning electron microscopy. The magnetic property and the wetting behavior were measured by vibrating sample magnetometer and contact angle system, respectively. The results showed that the morphology of the fibers was homogeneous and the magnetic nanoparticles were well dispersed within the fibers. It was also found that this composite sorbent had good magnetic response, special wettability, and remote oil adsorption capacity. We believed this novel polymer/Fe_3O_4 fibrous sorbent could be used as a promising material for the remote oil/water separation.

1. Introduction

Exploration, transportation, storage and usage of oil are desperately needed as the consequence of the rapid development of industrialization, which also aggravate the oil spill pollution simultaneously, such as the oil spill in the Gulf of Mexico (Lin and Mendelssohn, 2012; Liu et al., 2016). Ocean oil pollution not only leads to enormous loss in economy and environment, but also threatens human health as the poisonous chemicals produced from the deterioration of oil may get into our body through food chains (Solomon and Janssen, 2010). Nowadays, three strategies have been commonly used for the oil spill cleanup, including physical methods (sorbents, booms, and skimmers, et al. (Broje and Keller, 2006; Crick et al., 2014)), chemical methods (*in situ* burning and solidifiers, et al. (Mullin and Champ, 2003; Rosales et al., 2010)), and bioremediation (Crisafi et al., 2016). However, secondary pollution induced by chemical methods and low efficiency of bioremediation hinder their further application in oil spill cleanup. In contrast, the physical recovery of oil by sorbents is an ideal method because of its convenience and high efficiency. Oil sorbents, which can concentrate and transform liquid oil to a semi-solid or solid form, followed by being removed from the polluted areas, are able to avoid adverse effects to the environment and make the separated oil recyclable (Wu et al., 2014).

As it is known that, severe ocean weather such as wind and storm is frequently occurred, which has the adverse influence on the oil adsorption. Since the oil adsorption process by the conventional sorbents is easily disturbed due to the severe weather conditions. In addition, these sorbents may be blown away by the ocean wind, and the sorbents will not be withdrawn, which will cause the secondary ocean pollution (Montewka et al., 2013). In order to solve these problems, researchers have endowed the sorbent with magnetic property, such as construction of hydrophobic magnetic nanoparticles and magnetic sponges (Banerjee et al., 2012; Calcagnile et al., 2012; Peng et al., 2016; Wang et al., 2010; Zhang et al., 2012; Zhu et al., 2010). However, the potential secondary pollution caused by the inevitable nanoparticles residual and the relatively poor mechanical property of the sponges have seriously limited their further applications. Fabrication of magnetic fibrous sorbents by the electrospinning technique can effectively solve the problems mentioned above, as the fibrous sorbents are mechanical robust and the fibers within the sorbents are interconnected with no residual after oil adsorption. It is worth noting that the electrospinning approach is relatively simple and versatile as compared with other fibrous sorbents fabrication process. Moreover, the fibrous sorbents fabricated by this method can show large surface areas and high porosity due to the very small fiber diameters ranging from several nanometers to several micrometers, which is of great importance for the oil adsorption process (Yan and Gevelber, 2010; Zhao et al., 2016). However, few works have been devoted to construct magnetic fibrous sorbents for oil spill treatment so far. Wu and coworkers have fabricated electrospun poly (vinylidene fluoride) fibers, followed by anchoring Fe_3O_4 nanoparticles onto the fiber surface for oil adsorption (Wu et al., 2015). Unfortunately, the complicated procedures and the unpolished pore structures might limit the further application of this material. Since both the micropores created by the interlaced fibers and the nanopores within the single fiber have greatly influence the oil

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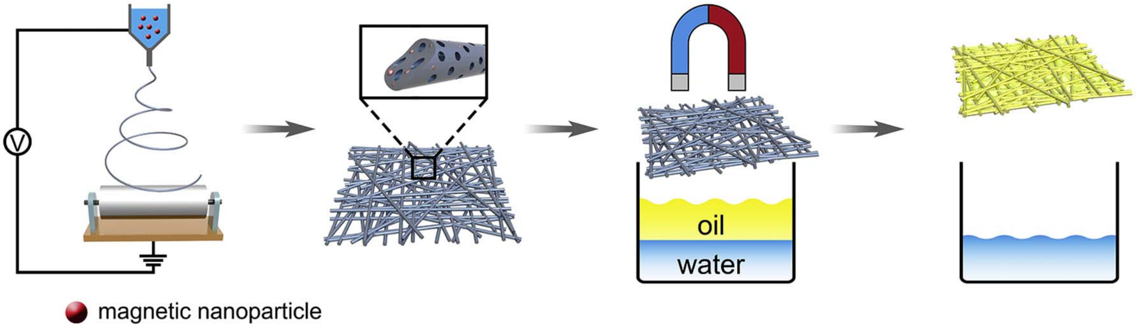

Fig. 1. Illustration of the electrospinning process for the fabrication of magnetic fibrous sorbent and the remote oil adsorption process.

adsorption property (Zhang and Hsieh, 2006; Zhang et al., 2016), it is of great importance to develop a simple yet powerful method to fabricate magnetic fibrous sorbent with hierarchical pore structure for efficient separation of oil from the oil/water mixtures.

In this study, we fabricated a magnetic fibrous sorbent with hierarchical pore structure based on polystyrene (PS) and Fe_3O_4 nanoparticles through one-step electrospinning (Fig. 1). The PS was chosen as the fiber matrix because of its featured superiorities such as low density, hydrophobicity, and oleophilicity, and all of them were required for the oil pollution cleanup (Lee et al., 2013; Lin et al., 2012; Zhu et al., 2011). Besides, the Fe_3O_4 nanoparticles were incorporated into the fibers due to the environmental friendly property and excellent magnetic response (Peng et al., 2016; Wang et al., 2015; Wang et al., 2016; Wu et al., 2015; Yang et al., 2014). The physicochemical properties of the obtained magnetic fibrous sorbent were systematically investigated. The oil adsorption capacity of this kind of magnetic fibrous sorbent was further evaluated using edible oil, saxoline, and dimethicone.

2. Materials and methods

2.1. Materials

Both PS and Fe_3O_4 nanoparticles were purchased from Aladdin Chemical Reagent Company. *N*, *N*-dimethylformamide (DMF) and tetrahydrofuran (THF) were supplied by Tianjin Tianli Chemical Reagent Company. The edible oil, saxoline, and dimethicone were obtained from Arowana Company, Tianjin Tianli Chemical Reagent Company, and Hangzhou Yongsheng Organosilicon Chemical Co. Ltd., respectively. All the reagents were used as received without further treatments.

2.2. Fabrication of magnetic fibrous sorbent by electrospinning

1 g PS was dissolved in a mixed solvent containing 3 mL of DMF and 1 mL of THF to form a transparent solution, followed by ultrasonically dispersing 0.5 g Fe_3O_4 nanoparticles into the solution for 20 min. Then, the suspension was transferred into a syringe for further electrospinning. A drum about 9 cm in diameter covered with aluminium foil was used as a collector with the rotation speed of 450 rpm.

The electrospinning parameters were shown as follows. The feeding rate of the suspension in the syringe was controlled at 1.8 mL/h and the supplied voltage was ranged from 9 to 12 kV. Distance between the needle and the collector was 15–20 cm. The electrospinning process was carried out at room temperature and the relative humidity was about 60%.

The pristine PS fibrous sorbent was also fabricated with the similar procedures.

2.3. Characterization

The morphology of the magnetic fibrous sorbent was observed by scanning electron microscopy (SEM, S-4800, HITACHI Ltd., Japan). The wettability of the fibrous sorbent was measured on a Dataphysics OCA 20 contact angle system. During each contact angle test, the distilled water and edible oil droplet (5 μL) were respectively dripped onto the surface of the fibrous sorbent. Each sample was tested for three times and the average contact angle was calculated. The composition of the fibrous sorbent was examined by Fourier Transform Infrared Spectrometer (FTIR, TENSOR 27, BRUKER Ltd., Germany). The average pore size of the fibrous sorbent was measured by using a microscope (Nikon Eclipse Ti−U). The fibers in the same focal plane were firstly focused with the microscope and the software of the microscope was used to measure the diameter of a virtual inscribed circle among the fibers. Finally, the diameter of the virtual inscribed circle was recorded as the pore size of the fibrous sorbent. 50 virtual inscribed circles were selected to determine the average pore size of the fibrous sorbent. In order to quantify the magnetic property, the vibrating sample magnetometer (VSM, MPMS-XL-7, Quantum Design Ltd., USA) was applied. Oil viscosities were measured by a viscometer (NDJ-55, Shanghai Fangrui Company).

2.4. Oil absorption test

Firstly, we put a piece of fibrous sorbent on a metal wire mesh and transferred them to the top of a beaker which was used to collect the effusive oil. Then, the oil was dripped onto the sorbent by a dropper. When the sorbent was fully saturated, it was drained for 2 min and then weighed. The oil adsorption capacity of the sorbent was determined by the following equation:

$$q = (m_{ws} - m_s)/ms$$

where q is the adsorption capacity of the fibrous sorbent (g/g), m_{ws} is the weight of the sorbent and the adsorbed oil (g), m_s is the initial weight of the sorbent (g). The results were expressed as mean ± standard deviation ($n = 3$).

To determine whether the fibrous sorbent can be applied to adsorb various oils, three kinds of oil including edible oil, saxoline, and dimethicone were utilized and the corresponding oil adsorption capacities were systematically studied.

3. Results and discussion

3.1. Morphology of the magnetic fibrous sorbent

As depicted in Fig. 2A, the pristine PS sorbent exhibited white color and was prepared in a large area. Moreover, from the SEM images it could be observed that the sorbent was composed of lots of bead-free continuous ultrathin fibers, which had a rough surface with numerous protruding ‘nanopillars’. By further surveying the cross section morphology of the fibers, a highly porous interior that was consisted of a