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Magnetically superhydrophobic kapok fiber for selective sorption and continuous separation of oil from water

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ABSTRACT

Magnetically superhydrophobic oil sorbent was prepared by directly immobilization of Fe_3O_4 nanoparticles on the surface of kapok fiber and subsequent hydrophobic modification. The results show that the as-prepared fibers demonstrated excellent superhydrophobicity and magnetic responsivity. They also exhibited high separation efficiency for oil/water mixtures and can quickly absorb floating oils on water surface via magnetic driving. Compared with raw fiber, the oil sorption capacity of as-prepared fiber for *n*-hexane, toluene, chloroform, paraffin oil, gasoline, and diesel can increase by 70.8%, 58.5%, 96.1%, 23%, 37.3%, and 30.5%, respectively. Furthermore, the fibers can be used to continuously separate a large quantity of oil contaminants from water surface by means of a vacuum pump. Importantly, the water contact angel still can reach above 143° after being repeatedly used several times and immersed in various oils and harsh water environments for long time period, implying excellent recyclability and chemical durability in the oil sorption. The findings suggest that the magnetically superhydrophobic kapok fiber has the prospect of potential applications in the removal and recovery of spilled oil contaminants.

1. Introduction

In recent years, the frequent occurrence of oil spill accidents during the oil exploitation and utilization process has resulted in harmful consequences to water environment (Barbier et al., 2014; Nihous, 2011). Various methods (dispersants, burning in situ, and sorbents) have been currently employed for oil spill prevention and cleanup. Among these approaches, the cleanup of oil by sorbent is considered as one of the most economical, rapid, and effective technique. Sorbents used to the cleanup of oil should have characteristics of low cost, high sorption capacity, good oil/water selectivity, quick oil sorption rate, and environmentally friendliness (Liu et al., 2014; Chen and Pan, 2013; Jiang et al., 2013; Zhu et al., 2013; Nguyen et al., 2013; Wahi et al., 2013).

So far, three kinds of common sorbents, namely synthetic materials (polystyrene fiber and oil-absorbing resin) (Avila et al., 2014; Wang et al., 2013a), inorganic materials (exfoliated graphite, silica aerogel, and clay nanocrystals-based absorbent) (Wang et al., 2010; Hayase et al., 2013; Liang et al., 2014), and natural materials (cotton fiber, kapok fiber, sawdust, and wheat straw) (Singh et al., 2013; Wang et al., 2012; Choi and Cloud, 1992; Zang et al., 2015) have been employed for oil removal. For synthetic materials, the high cost and the poor biodegradability restrict their wide application. Most of inorganic materials have low oil sorption capacity, while the production cost of inorganic aerogels with superior oil sorption capacity is so high that it is difficult to be applied on a large scale. In this sense, the inexpensive, renewable, and sustainable sorbents based on natural materials show attractive application prospects in the cleanup of spilled oil. Natural fibers such as cotton fiber (Singh et al., 2013), milkweed (Choi and Cloud, 1992), kapok fiber (Wang et al., 2012; Abdullah et al., 2010), bagasse (Said et al., 2009), cotton grass fibre (Suni et al., 2004), and wheat straw (Sidiras et al., 2013) have been used as oil sorbents, but most of natural materials are poor in oil sorption capacity and oil/water selectivity. To solve these shortcomings, hydrophobic natural materials for absorbing oil in water have been fabricated by the modification for hydroxyl groups of the cellulose

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(Sun et al., 2003). However, the hydrophobicity and oil sorption capacity of the resulting materials is still unsatisfactory. Hence, it is necessary to develop renewable and sustainable sorbents with excellent hydrophobicity and high oil sorption capacity.

Superhydrophobic surfaces (water contact angles of >150°) with special wettability have attracted much attention in the field of oil/water separation. A series of superhydrophobic sorbents, such as superhydrophobic calcium carbonate powder (Arbatan et al., 2011), graphene-based sponges (Nguyen et al., 2012), metallic foam (Jin et al., 2014), carbon nanotube sponges (Gui et al., 2010), and candle soot coated nickel foam (Zhao et al., 2014) have been developed for absorbing oil from water. However, the high cost and complicated fabrication processes limit their practical applications. Moreover, most of micro/nanoscale coatings fabricated on the surface of substrates are mechanically instable. In our previous study, superhydrophobic kapok fiber was also fabricated by sol–gel method (Wang et al., 2012), and the resulting fiber exhibit excellent oil affinity and water repellency in oil/water surroundings. Nevertheless, owning to weak interaction between silica coating and kapok fiber surface, superhydrophobic fiber exhibited unsatisfactory recyclability. In addition, the movement of the sorbents toward the oil-polluted area and their removal from water surface after absorbing the oils are also another challenge.

Herein, inspired by the lotus leaf with self-cleaning and the bioadhesion of marine mussels (Josep et al., 2013), a kind of magnetically superhydrophobic oil sorbent based on kapok fiber was fabricated via in-situ immobilization of magnetic nanoparticles on fiber surface. The as-prepared fiber exhibited high oil sorption capacity and good selective sorption property for oils from water surface. More importantly, the floating oil from the polluted regions can be collected by simply moving the as-prepared fiber around oil-polluted water using a magnet. After finishing the oil sorption, superhydrophobic fiber can be recovered from water easily through using an external magnetic field. Although some investigations about magnetic materials for oil sorption have been carried out (Chen and Pan, 2013; Chin et al., 2014), there is little information known about the use of magnetically superhydrophobic kapok fiber for oil sorption. Therefore, the results from this study will provide a simple and inexpensive method for fabricating magnetically driven natural fiber that might be used for the remediation of oil spill accidents.

2. Experimental

2.1. Materials

Kapok fiber was purchased from market, Guangzhou, China. Dopamine hydrochloride (chemically pure) and Tris(hydroxymethyl)aminomethane (Tris–HCl, chemically pure) were supplied by Nanjin Aoduo Biotechnology Co., Ltd., China. Iron(III) chloride hexahydrate ($FeCl_3{\cdot}6H_2O$, chemically pure) and Iron(II) chloride tetrahydrate ($FeCl_2{\cdot}4H_2O$, chemically pure) were received from Tianjin Chemical Reagent Factory, China. *n*-Hexane, toluene, chloroform, and paraffin oil (analytical grade) were supplied by Ningxia Yaoyi Chemical Reagent Co., Ltd., China. Dodecyltrimethoxysilane (DTMS, chemically pure) was provided by Nanjin Chengong Organosilicon Co., Ltd., China. Diesel and gasoline was purchased from local gasoline station, Yinchuan, China.

2.2. Preparation process

Synthesis of Fe_3O_4 nanoparticles. Fe_3O_4 nanoparticles were prepared by a chemical co-precipitation method described previously (Liu et al., 2012). 150 mL of 1.5 M $FeCl_3{\cdot}6H_2O$ and 1 M $FeCl_2{\cdot}4H_2O$ were added into a three-necked flask under nitrogen gas with vigorous stirring at 60 °C. $NH_3{\cdot}H_2O$ (25 wt%) was added to the solution until pH 10–11. Then the solution was heated at 8 °C for 1 h, the resulting Fe_3O_4 magnetic fluid were isolated from the solvent by a magnet and repeatedly washed with deionized water until neutral. After the drying at room temperature under vacuum, Fe_3O_4 nanoparticles with average diameter of 10 nm will be obtained.

Preparation of magnetically superhydrophobic kapok fiber. Raw kapok fiber was treated with $NaClO_2$ according to the reported process (Wang et al., 2012). Briefly, raw fiber was placed into $NaClO_2$ solution (1.5 wt.%) to treat at 80 °C for 1 h, and then the treated fiber was used in the later modification. In a typical experiment, 1.76 g of Fe_3O_4 nanoparticles and 0.32 g of dopamine hydrochloride were ultrasonically dispersed into 160 mL of Tris–HCl solution for 10 min. Then, treated fiber was added into the dispersions to stir for 10 h at room temperature and then dried in an oven at 60 °C to constant weight. Finally, the obtained fiber was placed in a big glass bottle with a small open glass vial containing DTMS (1 mL) and water (1 mL), the glass bottle was capped and heated in an oven at 120 °C for 4 h for the silanation reaction, and then modified fiber will be obtained.

2.3. Measurements of oil sorption capacity

The dried sample (0.1 g) was put into a stainless-steel mesh weighed beforehand and immersed in the oils at room temperature. The sample and the mesh were taken out from the oil together after 1 min, drained several seconds, and wiped with filter paper to remove excess oil from the bottom of the mesh. The oil sorption capacity of the sample was determined by weighing the samples before and after the sorption, and calculated by the following formula:

$$Q = (M_t - M_i)/M_i$$

where Q is the oil sorption capacity of the sorbents calculated as grams of oil per gram of sample, M_t is the weight of the wet sorbents after draining (g), M_i is the initial weight of sorbents (g). All oil sorption capacity was measured three times, and an average value was used.

2.4. Duability

The as-prepared sample was immersed in various oils or acidic, alkaline, and salty solutions for different times. After that, the sample was washed with ethanol and dried in an oven at 60 °C. Finally, the water contact angle of resulting sample was measured. All water contact angle was measured three times, and an average value was used.

2.5. Recyclability

For the recyclability tests, the sample was immersed into the oils to reach sorption equilibrium and then placed on a sand core funnel and drained under vacuum for 3 min to remove the residual oils and dried in an oven at 60 °C. The sorption/desorption cycle was repeated for 16 cycles and then the water contact angle was evaluated.

2.6. Characterizations

Fourier transform infrared (FTIR) spectra were recorded on a Nicolet NEXUS FTIR spectrometer using KBr pellets. The micrographs of samples were examined using SEM (JSM-5600LV, JEOL). Before SEM observation, all samples were fixed on aluminum studs and coated with gold. Water 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.