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Removal of oils from water surface via useful recyclable $CoFe_2O_4$/sawdust composites under magnetic field

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ABSTRACT

In this study, the poplar sawdust was used as a recyclable, low cost, environmentally friend and highly selective oil absorbent material. The sawdust with high hydrophobicity, superoleophilicity and magnetic property was obtained by precipitating $CoFe_2O_4$ on sawdust surface and chemically modifying the low surface energy polysiloxane layers. These composites were able to absorb lubrication oil up to 11.5 times of the sawdust weight while completely repelling water. In addition, the oil-absorption composites were able to collect oils conveniently from water surface with the help of an external magnet due to its exceptional magnetic property. Furthermore, the sawdust could be cleared up and re-used for water–oil separation at least 10 times. This work provides a potential platform for developing a water-protection strategy using natural waste resources.

1. Introduction

Interest has recently arisen in the development of a facile method for fast removing oils from water surface, driven by the problem of oil contaminants causing severe environmental pollution and health problems [1–3]. Especially an increasing attention is being devoted to the utilizing of natural waste resources to replace chemicals in the sustainable society. Treatments for oil spillage included burning [4], using chemical dispersants [5] and absorbent materials [6], mechanically collecting [7], etc. Among these methods, the approach of using adsorbent material is attractive for some applications because of its easy collection and ready availability [8,9]. For examples, using superamphiphobic filter paper [10], carbon nanotubes [11], polymer films [12], metal nanoparticles [13], highly porous materials [14], etc., were reported to efficiently separate oils from water. However, the high costs and recycling operations limited the application.

Recently, high hydrophobicity, superoleophilicity and magnetism were introduced to synthetic absorbent in order to reduce the costs and improve the efficiency. It seems that the magnetic absorbent, possessing the capability to remove oil from water surface and being convenient for magnetic separation, are promising materials for oil–water separation [15]. Thanikaivelan et al. proposed a stable magnetic oil-absorbent of collagen and superparamagnetic iron oxide nanoparticles. These nanocomposites have selective oil absorption and magnetic property, allowing it to be used in oil removal applications [16]. Palchoudhury et al. prepared a kind of polyvinylpyrrolidone-coated iron oxide nanoparticles for fast and selective adsorption of oil from water surface [17]. As a solid waste product obtained from mechanical wood processing, wood sawdust has great quantities but largely underutilized presently and is available for conversion into value-added products. Furthermore, the porous appearances and abundant hydroxyl groups of the wood sawdust provide an essential capability for further modification [18,19].

In this study, using the poplar sawdust, a recyclable, low cost, environmentally friend and highly selective oil absorbent material was developed. These magnetic $CoFe_2O_4$/sawdust composites could selectively absorb lubricating oils and organic solvents while completely repelling water. Moreover, the oil-absorbed composites were able to be quickly cleared up by a magnet bar and the absorbed oils were easily desorbed in the ethanol solution, which provided a possibility to be re-used for the oil-removal from water.

2. Experimental section

2.1. Materials

Poplar sawdust used for this experiment was obtained from a local saw mill in Heilongjiang Province, China. The sawdust was first washed with distilled water, dried, cut, and sieved through100-mesh screen. The cobalt chloride hexahydrate ($CoCl_2 \cdot 6H_2O$), ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$), potassium nitrate (KNO_3), sodium hydroxide (NaOH) and vinyl triethoxysilane used in this study were

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supplied by the Shanghai Boyle Chemical Company Limited., and used without further purification.

2.2. Synthesis

Fig.1 shows the process for synthesizing highly hydrophobic $CoFe_2O_4$/sawdust composites. 5 g wood sawdust was added into a mixture of 80 mL freshly prepared aqueous solution of 0.2 mol/L $FeSO_4$ and $CoCl_2$ with a molar ration of $[Fe^{2+}] / [Co^{2+}] = 2$ before being transferred into a Teflon-lined stainless steel autoclave and the system was heated to 90 °C for 3 h. At the end of the reaction, the supernatant was poured out and 65 mL of 1.32 M NaOH solution with 0.25 M KNO_3 was added into the Teflon-lined stainless-steel autoclave. After the additional hydrothermal processing for 8 h at 90 °C, the precipitated precursors were converted into ferrite crystal nanoparticles, and the magnetic $CoFe_2O_4$/sawdust composites were collected by an external magnet, rinsed with deionized water for 3 times, and dried at 90 °C for over 24 h in vacuum. Finally, the obtained powder was treated with the 2 wt% vinyl triethoxysilane ethanol solution containing 95 mL anhydrous ethanol, 5 mL H_2O and 1 mL glacial acetic acid at room temperature for 3 h. After the filtration, these composites were dried at 110 °C for another 24 h.

2.3. Adsorption and recyclability study

The oil absorbent ability of the composites was determined by weight measurements. The weights of composites before and after the oil absorption were measured as m_1 and m_2 by an electronic balance with an accuracy of 0.1 mg, respectively. The oil absorbent capacity q of the composites was calculated using the formula $q = (m_2–m_1) / m_1$. Three replicates were utilized for each experiment and the mean values were used for the analyses.

The removal of the lubrication oil from water surface was carried out according to the procedure illustrated in Fig. 2. Firstly, the 0.1 g treated wood sawdust were scattered on the surface of the mixture (6 mL oil on the surface of 20 mL water). The oil was absorbed by the composites quickly. After 1 min, the oil-absorbed composites were collected from the water surface by a magnet bar. The adsorbed oil was removed from the wood sawdust by vigorously stirring in ethanol solution for 5 min. After being dried at 110 °C for 12 h, the sawdust was re-used for the removal of oil from water surface. The recyclability was investigated by the measurements of the water contact angles, magnetic property and oil absorbent ability.

2.4. Characterization

The morphology of the specimen was examined by the scanning electron microscopy (SEM, FEI, and Quanta 200) and transmission electron microscopy (TEM, FEI, and Tecnai G20). The crystalline structure of these composites were identified using the X-ray diffraction (XRD, Rigaku, and D/MAX 2200) operating with Cu Kα radiation (λ = 1.5418 A) at a scan rate (2θ) of 4°/min, an accelerating voltage of 40 kV, and an applied current of 30 mA ranging from 5° to 80°. The X-ray photoelectron spectroscope (XPS) was recorded on Thermo ESCALAB 250XI. The deconvolution of the overlapping peaks was performed using a mixed Gaussian–Lorentzian fit program. The surface chemical compositions of the samples were determined via the Fourier transformation infrared spectroscopy (FTIR, Nicolet, Magna-IR 560). The magnetization measurements were carried out at room temperature using a superconducting quantum interference device (MPMS XL-7, Quantum Design Corp.). The water contact angles were measured by the commercial instrument (Analyzer JC2000C, Beijing code tong technology co., LTD) at ambient temperatures. Before the measurements, the sawdust was placed on a slide and pressed into a flat film. A distilled water droplet and an oil droplet of 5 μL were employed as the indicators. The average of the five measurements taken at different locations on each sample was used to calculate the final WCA angle.

3. Results and discussion

3.1. Preparation of highly hydrophobic $CoFe_2O_4$/sawdust composites

Fig.1 shows the reactive scheme of the highly hydrophobic $CoFe_2O_4$/sawdust composites. The hydrophilic sawdust was immersed in an aqueous $FeSO_4/CoCl_2$ solution at room temperature before the system was heated to 90 °C to thermally precipitate the insoluble Co/Fe oxyhydroxide complexes on sawdust surface [20]. Then the precipitated precursors were converted into ferrite crystal nanoparticles upon the

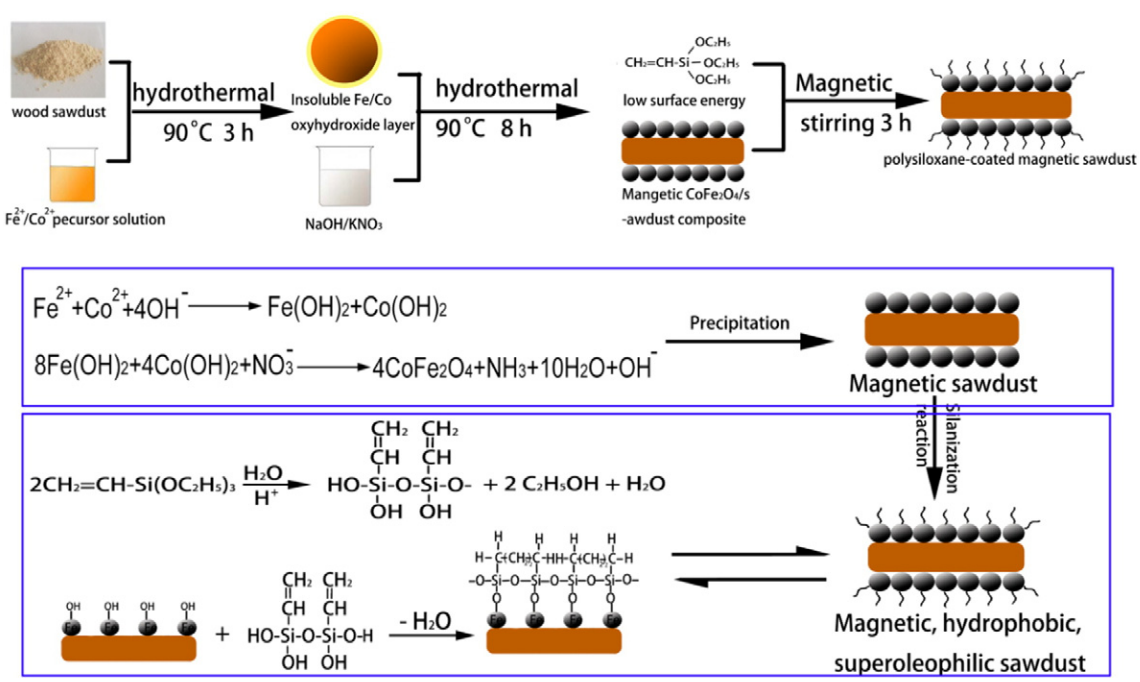

Fig. 1. Experimental strategy for the fabrication of highly hydrophobic $CoFe_2O_4$/sawdust composites.