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Coco peat powder as a source of magnetic sorbent for selective oil–water separation

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ABSTRACT

Coco peat powder (CPD), the main by-product of the coconut palm, is an excellent source of environmentally friendly magnetic sorbent with potential application in oil-spill cleanup. In order to develop the best resource for the agricultural crop and alleviate environmental stress caused by disposal of natural CPD, Fe_3O_4 nanoparticles were immobilized on coco peat powder (CPD) with the aid of mussel-inspired polydopamine (PDA) and then chemically modified by low-surface-energy octadecylamine (ODA) to fabricate a novel magnetic coco peat powder (MCPD) for selective oil–water separation. The obtained MCPD, which had high hydrophobicity (water contact angle: $135 \pm 3^{\circ}$) and saturation magnetization of 27.6 emu/g, exhibited remarkable sorption efficiency for convenient removal of oils from water and displayed excellent separating performance under an auxiliary magnetic field. The results indicated that the highest amount of oil sorption on MCPD reached 8.57 times of its own weight, and the oil could be desorbed from the oil-loaded MCPD and easily recycled for at least 11 cycles. The oil-loaded MCPD also exhibited high recyclability, with a loss of less than 15.32% in oil-sorption capacity after 11 cycles, which suggests that the MCPD prepared through the proposed synthesis process has high potential for application in large-scale removal of spilled oils from water. This work also provides a universal strategy for developing an oil-pollution treatment using natural resources from the waste stream.

1. Introduction

With the rapid development of a wide range of industries and transportation elements, increasing oil spills have become the most widespread contaminant in marine and aquatic environments as a result of natural seepage and anthropogenic activities on ships and in harbors and oil terminals. Continued pollution caused by crude oil leakage has jeopardized human health and the marine ecosystem (Ivshina et al., 2015). To address this problem, considerable efforts have been made to remove spilled oils from water, including burning (Aurell and Gullett, 2010), biodegradation (Boopathy et al., 2012), sorption (Yang et al., 2016a), and the use of oil skimmers (Broje and Keller, 2007). Compared with other degreasing methods, sorption is getting more attention because of its low cost, simple operation, and high efficiency. Various sorbents such as polypropylene fibers (Zhao et al., 2013), polyurethane foams (Shi et al., 2014), vermiculite (da Silva et al., 2003), and kapok fibers (Wang et al., 2013b) have been studied and tested extensively in the removal of spilled oil. However, obvious drawbacks such as non-biodegradation, poor buoyancy, and recyclability limit their practical application. Therefore, it is necessary to launch further research on simple and convenient fabrication of novel oil-sorbent materials with superior properties. Currently, more focus has been directed on magnetic oil sorbents owing to the convenient magnetic separation process, high oil-sorption capacity, and good reusability in practice (Pan et al., 2011; Zhai et al., 2016). However, most of the current methods designed to prepare magnetic oil-sorbent materials are complicated and costly because of the tedious synthesis processes such as pre-emulsification and hydrothermal treatment (Konwar et al., 2015; Song et al., 2015).

For decades, humans have been designing and fabricating efficient and low-cost materials by employing natural chemical ideologies and mimicking structures originating from nature. For example, mussels strongly adhere to many types of surface by depositing *Mytilus edulis* foot proteins. A study proved that dopamine from the protein can undergo self-polymerization when

Abbreviations: CPD, coco peat powder; MCPD, magnetic coco peat powder; ODA, octadecylamine; PDA, polydopamine; Tris, tris(hydroxymethyl)aminomethane; Tris-HCl, Tris(hydroxymethyl)aminomethane hydrochloride.

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immersed in alkaline- or oxidant-containing aqueous solutions, and the resultant polydopamine (PDA) layer has strong covalent and noncovalent interfacial interactions with substances in the solutions (Lee et al., 2007). Mussel-inspired PDA has been reported as an extremely versatile platform for secondary reactions or the immobilization of functional materials. For example, Wang et al. (2015b) prepared superhydrophobic cotton fibers by depositing PDA films on cotton fibers and then modifying them with dodecyltrimethoxysilane. Wang et al. (2015a) combined mussel-inspired chemistry with the Michael addition reaction to synthesize CNT-reinforced polyurethane sponges, which demonstrated high hydrophobicity and oil-sorption capacity. Nevertheless, there have been very few reports on the utilization of PDA in the fabrication of magnetic oil-sorbent materials with stable nanostructured layers for selective oil–water separation.

As the byproduct of coconut palm, coco peat powder (CPD) is naturally abundant in many Asian countries, including China, Malaysia, Philippines, and Thailand (Keerthika et al., 2016; Owolabi et al., 1985). For years, large amounts of CPD have been discarded as agricultural waste or, at best, used as cheap fertilizer. Since waste CPD has considerable untapped advantages that include low cost, high availability, biodegradability, and renewability, exploring effective use of waste CPD is of particular importance for sustainable development. Particularly worth mentioning is its high potential for application as an oil-sorbent material. The main constituent of CPD is lignocellulose, which is composed of cellulose (~43%), hemicellulose (~8%), and lignin (~49%) (Marcos and Francisco, 2012; Thakur et al., 2015). Many studies attributed the remarkable performance of lignocellulose-based materials in fast oil trapping to the strong capillary force between oil and lignocellulose (Galblauba et al., 2016; Likon et al., 2013; Yang et al., 2016b). The abundant reactive functional groups in lignocellulose, such as hydroxyl, carboxyl, ether, phosphate, and amino groups allow further modification of CPD (Wang et al., 2015c; Xu et al., 2015).

Inspired by the afore-mentioned works, a simple strategy for the preparation of magnetic coco peat powder (MCPD) as an oil sorbent was devised in the study. The novel oil sorbent was fabricated by immobilizing individual Fe_3O_4 nanoparticles onto the surface of CPD through strong adhesion of the PDA layer and subsequent hydrophobic modification by octadecylamine (ODA). The as-prepared MCPD exhibited remarkable sorption performance for convenient removal of oils from water and excellent separation performance under an auxiliary magnetic field. The desorption capability and reusability of MCPD were also investigated.

2. Experiment

2.1. Materials and chemicals

The CPD used in this study was picked from the hard shell of coconut fruit purchased from local market in Hainan, China, and processed in a blender. Dopamine hydrochloride and tris(hydroxymethyl)aminomethane (Tris-HCl) were supplied by Tianjin Chemical Reagent Factory, Tianjin, China. ODA, ethanol, paraffin oil, silicone oil, toluene, chloroform, cyclohexane, ferric chloride hexahydrate ($FeCl_3{\cdot}6H_2O$), absolute ethanol, formaldehyde (HCHO), and hydrazine hydrate ($N_2H_4{\cdot}H_2O$) were provided by Xi'an Chemical Agent Corp., Xi'an, China. Cottonseed oil and machine oil were purchased from the local market in Xi'an, China.

2.2. Sample preparation

Fe_3O_4 nanoparticles were synthesized according to a method reported in the literature (Song et al., 2015). In brief, 1.20 g of $FeCl_3{\cdot}6H_2O$, 2 mL of HCHO, and 5 mL of $N_2H_4{\cdot}H_2O$ were dissolved in 40 mL of deionized water in a 100-mL beaker, and the solution was mechanically stirred at 700 rpm for 15 min at 25 °C. The mixture was then transferred to a Teflon-lined stainless steel autoclave and heated at 120 °C for 5 h. After the autoclave was cooled to 25 °C, the black Fe_3O_4 nanoparticles were collected magnetically and rinsed with ethanol and deionized water three times. The obtained samples were then dried at 80 °C for 1 h in a vacuum drying oven.

In a typical procedure for the synthesis of MCPD, a predetermined amount (0, 0.25, 0.5, 0.75, or 1 g) of Fe_3O_4 nanoparticles and 0.6 g of dopamine hydrochloride were added to 300 mL of the Tris-HCl buffer solution (pH = 8.5) in a 500-mL round-bottomed flask. After the solution was stirred at 700 rpm for 30 min, 1 g of CPD was placed into the above solution, which was then stirred at 700 rpm while kept at 25 °C for 24 h. After that, the sample was fetched and washed thoroughly with deionized water and ethanol to remove possible residues. The resulting sample was further modified with ODA in a 10 mM ethanol solution for 24 h at 25 °C under mechanical stirring. Finally, the as-prepared highly hydrophobic MCPD was washed with ethanol and dried in an oven at 50 °C.

2.3. Characterization

The morphology of the samples was analyzed with a scanning electron microscope (S4800, Hitachi, Japan) operating at 5.0 kV. Infrared spectra from 4000 to 400 cm^{-1} were obtained using an attenuated-total-reflectance Fourier-transform infrared spectrometer (ATR-FTIR; Nicolet NEXUS 670, Thermo-Nicolet, Waltham, MA) with a detector at 4 cm^{-1} resolution and a KBr pellet at 25 °C; 128 scans were performed on each sample. X-ray diffraction (XRD) analysis of the samples was performed using a powder diffractometer (D8, Bruker AXS GmbH, Karlsruhe, Germany) (Cu K_α radiation, $\lambda = 1.5406$ Å) operating at 40 kV in the 2θ range of 5–80° and at a scanning rate of 5°/min. The water contact angle was measured using an optical contact-angle measuring device (OCA-20, DataPhysics Instruments GmbH, Filderstadt, Germany) at 25 °C. Before the measurements, the MCPD was placed on a slide and pressed into a flat film. A 5 μL droplet of deionized water was released onto the surface of sample film; photographs were then taken and the water contact angle was measured. The magnetic properties were tested in fields between +20 and −20 kOe at 25 °C with a vibrating-sample magnetometer (VSM; Model 735, Lake Shore Cryotronics, Inc., Westerville, Ohio, USA).

2.4. Evaluation of oil-sorption capacity

The capacity of the MCPD samples for sorption of cottonseed oil, paraffin oil, machine oil, and silicone oil was measured in pure oil or oil–water mixtures. In the pure-oil uptake experiments, 0.1 g of MCPD was submerged in oil for a certain length of time, and then a magnet bar wrapped in PVC film was used to retrieve the sample from the oil. The sample on the PVC film was then easily transferred from the magnetic bar and weighed. In the oil–water test, the effect of NaCl concentration and pH on the oil-sorption capacity of MCPD was investigated in oil–water mixtures with an oil-to-water weight ratio of 1:30. To investigate the effect of NaCl concentration, oil was added to solutions with different NaCl concentrations (in the range of 0.0–0.5 M), while the amount of MCPD was kept constant at 0.1 g. The effect of pH value (in the range of 3–11) was studied in the oil–water mixtures and 0.1 g of MCPD. After oil sorption, the floating oil-loaded MCPD was separated by a magnetic bar wrapped in PVC film and then transferred by the PVC film for weight measurement.