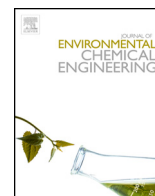




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Coconut shell based activated carbon–iron oxide magnetic nanocomposite for fast and efficient removal of oil spills

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ABSTRACT

An efficient magnetic adsorbent nanocomposite material is prepared by simple chemical methods using coconut shell based activated carbon and iron oxide nanoparticles. The composite material shows good oil retention capacity with fast kinetics and can be recovered along with the adsorbed oil by using an external magnet. The adsorbent material can be reused after recovering either by heat treatment or by solvent extraction. Hence, the magnetic nanocomposite is shown to be an efficient and recyclable potential candidate for removal of oil spills by magnetic separation.

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Introduction

Our aquatic ecosystem is under constant threat due to the possibility of oil spillage from different sources. Massive and momentary oil spillages come from the wreckage of ships and oil tankers, whereas a slow and steady contribution comes from the industrial effluents or by the oil leakage from machineries and pipe lines which eventually reaches the rivers and other subterranean water systems [1]. Different techniques like skimmers, floating barriers, synthetic organophilic sorbent materials like polypropylene, polyethylene terephthalate, silica aerogels, zeolites, organophilic clays, exfoliated graphite, graphene frameworks, cellulose fiber, collagen fibers etc. have been employed in cleaning up the oil spills [1–5]. The most important criteria that should be met by any material to be used on large scale for such an environmental application are the efficiency, recyclability and biocompatibility. Even though many of the currently available sorbent materials satisfy these criteria, they suffer a major disadvantage that the removal of sorbent materials along with the adsorbed oil from the aquatic system after the oil adsorption is tedious and time consuming task considering that large quantity of oil has to be removed quite quickly and efficiently to prevent further spreading. This disadvantage can be surpassed by adding a magnetic functionality to the sorbent material which facilitates the fast recovery in the presence of a magnet and

thereby increasing the total efficiency of the process [5,6]. Therefore, a composite made from a magnetic material and a suitable adsorbent serves as a potential candidate for a fast oil clean up. However, the composite as a whole and especially the magnetic material should be biocompatible to avoid any secondary pollution in aquatic systems by the adsorbent/composite material, along with the cost effectiveness of the whole process and the ease of production of the composite material in required bulk quantities.

Superparamagnetic iron oxide nanoparticles, SPIONs (Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$), due their good magnetic properties, biocompatibility and low cytotoxicity, find applications in targeted drug delivery, magnetic hyperthermia, as MRI contrast enhancement agent, etc. [7], and they have been studied as the magnetic part of the sorbent material [5,6]. Different types of magnetic sorbents such as collagen fiber-SPION composites [5], Fe_2O_3 @C core-shell nanoparticles [6], Fe–Carbon nanocomposites [8], magnetic floating foams [9], iron incorporated carbon nanotube sponges [10], metal-organic framework (MOF) derived porous carbon–iron oxide nanocomposite [11], magnetic exfoliated graphite [12], epoxidized natural rubber–magnetite nanocomposites [13], polystyrene–iron oxide nanocomposites [14], palm shell based activated carbon–iron oxide composite [15] etc., have been studied for the removal of oil by magnetic separation. Many of these materials like the macroporous carbon nanotubes, magnetic floating foams, magnetic exfoliated graphite, MOF derived porous carbon–iron oxide composite and polystyrene–iron oxide composite are good in terms of their oil retention capacity. However, the synthesis of these materials includes relatively complex procedures and costly chemicals, with low yield, so that a cost effective bulk production for real time application is impossible [9–12,14]. Comparatively

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cheaper natural sorbent materials like collagen fibers, epoxidized natural rubber and palm shell based chemically activated carbon have been proposed to overcome the major issues, after incorporating with different magnetic nanoparticles. However, they also suffer with either a low oil retention capacity or a very slow response time which reduces the efficiency of the process [5,13,15]. Therefore, search for a cheap and efficient material which can actually be used for immediate containment and/or sudden removal of large oil spills is still an open area of research.

Coconut shell based carbon has been extensively used as an adsorbent for various applications because of its high surface area and porosity. The microstructure of pyrolyzed carbon is known to depend critically on the carbon source and hence a porous carbon source like coconut shell can produce highly porous carbon with high surface area and good sorption properties, on pyrolysis [16,17]. In this manuscript, we report the use of a composite made from coconut shell derived activated carbon and SPIONs for containment and removal of oil spills. The main reason for the selection of coconut shell as the carbon source in the present work is its easy availability and cost effectiveness which makes the material an ideal source for large scale production of activated carbon. In order to prepare stable composites with iron oxide and to enhance the oil retention capacity by increasing the porosity and surface area, the carbon material was activated by two different activation techniques before incorporating iron oxide nanoparticles, a liquid phase acid activation and a solid phase KOH activation at high temperatures.

Experimental

Materials used

Analytical grade iron(II) chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), iron(III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), 25% ammonia solution, Conc. H_2SO_4 , Conc. HNO_3 and KOH were purchased from Merck Chemicals and used as-received. Locally available coconut shell was used as the carbon source. For oil removal studies, two kinds of oils were used, red colored new premium oil and black colored used oil.

Preparation of activated carbon

Dried coconut shell was pyrolyzed at 1000°C in a horizontal tubular furnace under flowing nitrogen atmosphere. The pyrolyzed carbon obtained was crushed and ground to fine powder using an agate mortar and pestle. For liquid phase acid activation, 10 g of the pyrolyzed carbon powder was refluxed with 125 ml of 20% (v/v) HNO_3 and 125 ml of 20% (v/v) H_2SO_4 at 110°C for 90 min [18]. The activated sample was washed several times with double distilled water till neutral pH and then dried in an oven (sample code AC). The base activation was carried out by a liquid state KOH impregnation of the pyrolyzed carbon (5 g) at 1:3 carbon to KOH (15 g) weight ratio for 24 h, followed by drying and heating at 1000°C under argon atmosphere in a tubular furnace [17]. The activated sample was washed till neutral pH with double distilled water and dried in an oven (sample code KC).

Preparation of activated carbon–iron oxide composite

Activated carbon/iron oxide composites were prepared by in situ co-precipitation technique using both AC and KC [19]. The activated carbon to iron oxide weight ratio in the final composite material was fixed as 1:1. 0.5 g of AC was first dispersed in water to which a 2:1 molar mixture of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (11.6770 g) and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (4.2943 g) was added and stirred for 2 h, after de-aerating with argon gas. The argon flow was maintained and the pH was

then adjusted to 12 using 25% ammonia solution to precipitate the iron oxide nanoparticles. The precipitate was then heated in the mother liquor at 80°C for 1 h to facilitate the binding of the nanoparticles to the surface functionalities of activated carbon [19]. The final magnetic composite was magnetically separated from a small fraction of light weight non-magnetic part present in the supernatant solution and then washed several times till neutral pH. The weight of this discarded portion was less than 0.5% of the weight of KC or AC used during the synthesis. Hence, the quantity of this small portion lost during the preparation of the composite was neglected during the calculation of the oil retention capacity of ACf and KCf with respect to the amount of activated carbon present in the material. The product was then dried in an oven to obtain AC–iron oxide composite material (sample code: ACf). KC–iron oxide composite material was prepared by a similar procedure using the same amount of KC and iron oxide precursors (sample code: KCf).

Determination of oil adsorption capacity

The oil adsorption capacities of AC, KC, ACf and KCf were determined by using weight measurements. For oil removal studies, 2 g oil was poured on top of 10 ml water taken in a petri dish to create an artificial oil spill. A weighed amount of the material was smeared over the oil and then waited for a specific time before the oil adsorbed material was separated from the artificial spill. On performing the experiment with magnetic composite ACf and KCf, the oil adsorbed composite was recovered by magnetic separation using a permanent magnet and then dried overnight at 100°C to remove water. However, when AC and KC were used to remove the oil from the artificial spillage, the oil adsorbed material was separated by filtration, and the filtered material was then dried under similar conditions as in the case of using ACf and KCf. The oil retention capacity (k) of ACf, KCf, AC and KC, per gram of carbon, was determined by using the relation $k = (b - a)/a$, where 'a' is the weight (in gram) of the adsorbent material smeared on top of the oil layer and 'b' is the weight (in gram) of the oil adsorbed material recovered from the artificial oil spill after drying. The retention capacity (k) of ACf and KCf was calculated with respect to the weight of carbon present in the composites in order to compare the results with that of AC and KC.

Characterization techniques

All materials were characterized using powder X-ray diffraction (XRD) on a Phillips X'pert Pro diffractometer using $\text{Cu K}\alpha$ radiation. Infrared (IR) spectra were recorded on a Bruker Tensor-27 FT-IR spectrometer and the magnetic measurement was performed using a Quantum Design MPMS 7T SQUID VSM. TEM images were obtained using a FEI, TECNAI G2 TF 30 transmission electron microscope. The surface area and porosity measurements were performed using a Quantachrome Quadrasorb automatic volumetric instrument. Temperature dependent oil adsorption studies were performed after maintaining the temperature using a refrigerated circulating EQUIBATH.

Results and discussion

Characterization of the materials

Both acid and base activations are known to introduce different types of oxygen functionalities on the carbon surface by partial oxidation of carbon [20,21]. However, during KOH activation, apart from the surface modification, large numbers of pores are also formed by gasification of carbon through a series of chemical reactions [22,23]. Below 700°C , the main products are potassium oxide, carbon monoxide, carbon dioxide, hydrogen and potassium

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