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Use of macadamia nut shell residues as magnetic nanosorbents

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ABSTRACT

Nanosorbents have been increasingly used for targeted contaminant removal; however, handling and separation of spent sorbents from treated water remains a challenge. To address these drawbacks, a hybrid magnetic nanosorbent was prepared from waste macadamia nut shell and magnetite nanoparticles. The novel nanosorbent had primarily meso- and macroporous structure with 70 $m^2\ g^{-1}$ specific surface area. Batch sorption tests using methylene blue model pollutant found sorption capacities increasing from 33 to 42 mg g^{-1} with temperature in the 25–45 °C range. Nonlinear regression analyses found that process kinetics was accurately described by a fractal-like pseudo first order model. The isotherms showed excellent fits to the Langmuir model and implied monolayer adsorption mechanism. The thermodynamic parameters confirmed that the process was spontaneous, endothermic, and involved physisorption. The point of zero charge was 7.4, which is advantageous in the removal of anionic aquatic pollutants. The ferrimagnetic sorbent had 48 emu g^{-1} saturation and 0.65 emu g^{-1} remanence that allowed easy handling and rapid separation by magnetic field. Spent sorbents were effectively regenerated by acidic wash for subsequent reuse over four cycles. The intrinsic characteristics of the magnetite/carbon nanosorbent befit tailored water and wastewater treatment applications.

1. Introduction

Textile industries undergo increasing growth worldwide to meet increasing demand for their products. The production of dyes amounts to more than 7×10^5 metric ton per year to supply over 100,000 commercially available products (Robinson et al., 2001). Unfortunately, the expansion of the textile sector invariably has brought about environmental degradation due to the discharge of diverse chemicals used in manufacturing processes. Discharge of highly coloured wastewater into surface waters causes harmful effects downstream, mainly through increased chemical oxygen demand and impeded light penetration (Mcmullan et al., 2001). Many dyes, especially the azo types, are toxic to humans and cause nausea, vomiting, eye and skin irritation, chest pain, high fever, headache, increased sweating, and mild bladder irritation (Hildenbrand et al., 1999). In recognition of the harmful effects caused by the discharge of highly–coloured, organic-rich and toxic dye wastes on the environment, regulations have been imposed globally to compel some degree of waste treatment before discharging into natural water resources (O'Neill et al., 1999).

Adsorption onto the sorbents is one of the most reliable and versatile conventional process for removing dyes and other pollutants from aqueous solutions (Mezohegyi et al., 2012). Activated carbon is the most common material used in adsorption processes, but its price is of concern in applications providing low-value or undervalued end-products, like water and wastewater treatment. Its viability and cost-effectiveness can be helped by the local availability of low-cost adsorbents produced from various waste products (Pollard et al., 1992). Low-cost and other non-conventional adsorbents that have been successfully explored for the treatment of dye wastewaters include zeolite, fly ash, sawdust, rice husk, coffee waste and coconut shell, and many others (McKay et al., 1999; Yagub et al., 2014). While many agricultural wastes have been recommended and thoroughly investigated to produce activated carbons, macadamia nut shells have so far received limited attention (Martins et al., 2015; Poinern et al., 2011).

Australia produces around 47,000 ton of macadamia nuts annually, representing about 10,800 ton of nutshell waste (Su et al., 2013). Part of the residual nutshell is utilised as solid fuel in nut processing, and the rest is disposed on land and in landfills creating environmental concern. Clearly, there is a potential to use

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Nomenclature

α	Fractal constant of FL-PFO and FL-PSO models
b_t	Temkin isotherm constant related to the heat of adsorption (J mol^{-1})
C_0	Initial concentration of MB (mg L^{-1})
C_e	Concentration of MB at equilibrium (mg L^{-1})
k_1	PFO and FL-PFO rate constant (min^{-1})
k_2	PSO and FL-PSO rate constant (g mg^{-1} min^{-1})
k_b	Bangham rate constant (g mg^{-1} $min^{-\vartheta}$)
k_{DC}	Diffusion-chemisorption constant (mg g^{-1} min^{-n})
K_e	The distribution coefficient adsorption affinity
k_f	Freundlich isotherm constant (mg g^{-1})(L g^{-1})^n
k_l	Langmuir isotherm constant (L^{-1} mg^{-1})
k_s	Pseudo-second-order rate constant (g mg^{-1} min^{-1})
k_t	Temkin equilibrium binding constant (L mol^{-1})
m	Mass of MCM adsorbent (g)
n_f	Heterogeneity factor
q_e	Predicted mass of adsorbed MB at equilibrium (mg g^{-1})
q_{ex}	Mass of adsorbed MB at equilibrium (experimental) (mg g^{-1})
q_m	The maximum adsorption capacity (mg g^{-1})
q_t	Mass of MB adsorbed at t time (mg g^{-1})
R^2	Nonlinear coefficient of determination
T	The absolute temperature (K)
t	Adsorption contact time (min)
V	Volume of solution (mL)
α_e	Initial adsorption rate of Elovich model (mg g^{-1} min^{-1})
β_e	Elovich desorption constant (g mg^{-1})
ΔG°	Gibbs free energy change
ΔH°	Enthalpy change
ΔS°	Entropy change
ϑ	Bangham constant (<1)
χ^2	Chi-square test

Abbreviations

BET	Brunauer-Emmet-Teller
DFT	Density Functional Theory
FL-PFO	Fractal-like pseudo first order
FL-PSO	Fractal-like pseudo second order
ICDD	International Centre for Diffraction Data
MB	Methylene blue
MCM	Magnetite/carbon materials
MNS	Macadamia nut shell
PFO	Pseudo first order
PSO	Pseudo second order
SSE	The sum of squared error (residuals)

macadamia nut shells already discarded in large masses as a promising precursor for the production of granular and powdered activated carbons. Although powdered activated carbon is commonly used in wastewater treatment, it is difficult to handle and to eventually separate the spent adsorbent from the treated water. Magnetite (Fe_3O_4) products long have been used to adsorb pollutants from water (Anderson et al., 1982; Bolto, 1996; Liu et al., 2015) due to their affordability, good performance and magnetic property. The use of magnetic fields allows the rapid and efficient separation of the exhausted particles from aqueous solutions (Ambashta and Sillanpää, 2010). Hybrid activated carbon with iron oxide adsorbents showed good performance in removing various contaminants, including dyes (Yang et al., 2008), arsenate (Zhang and Kong, 2011), p-nitrophenol (Bastami and Entezari, 2012), and selenium (Kwon et al., 2015) from aqueous solutions.

The overall aim of our investigation is to explore improved nanosorbents comprised mainly of synthetic magnetite deposited activated carbon to serve both as a carrier and complementary adsorbent. This approach is promising to address the main shortcoming of natural magnetite, namely (low surface area (Schwertmann and Cornell, 2000)), while retaining its favourable characteristics such as desirable surface charge characteristics, high volumetric density, and minimal risk to the environment. In this research, the specific objective is to investigate hybrid magnetite/carbon materials (MCM) using waste macadamia nut shell as a carbon precursor. The magnetic compound is characterised via physical and chemical surface properties and evaluated for the removal of a methylene blue (MB) model dye from water. Treatment performance and the involved mechanisms are examined through adsorption kinetic and isotherm models, and thermodynamic study.

2. Materials and methods

2.1. MCM composite preparation

There are several methods of synthesis described in the literature for the preparation of activated carbon/magnetite hybrid compounds (Gu et al., 2007; Kwon et al., 2015; Yang et al., 2008). The present method was aimed at achieving high magnetite content in the product. It involved impregnation and coating of hydrophilic bio-char using separately prepared magnetite nanoparticles and consequent carbon activation during pyrolysis in the presence of carbon dioxide gas.

Waste macadamia nut shell (MNS) of the Integrifolia species was provided by a factory in Southeast Queensland, Australia. The shells were washed with distilled water and dried at 105 °C for 24 h. About 100 g of dry MNS was loaded in an iron reactor for carbonisation in a furnace (F62730, Thermolyne), the temperature was raised to 400 °C at 5 °C min^{-1} heating rate, and maintained for 2 h. After cooling, the carbonized shells (char) were impregnated with 98% sulphuric acid at 80 °C for 3 h in water bath to render them hydrophilic for strong bonding. The solids were filtered under vacuum and dried at room temperature. Dried hydrophilic char (10 g) was added to 400 mL water containing 80 g Fe_3O_4 nanoparticles, which were prepared by the acidic peptization method of Massart (1981), and the mixture was shaken in a water bath at 80 °C for 3 h. After particle deposition, the sample was filtered under vacuum and dehydrated in an oven at 100 °C for 1 h. Next, the processed sample was loaded in a quartz tube reactor (OD 60 mm × 10 mm wall thickness × L 100 mm). The tube reactor was placed inside a vertical tube furnace (STF55433C-1 model, Lindberg/Blue M), which was connected to nitrogen and carbon dioxide gas lines. The temperature of the furnace was increased from 30 °C to 900 °C at 30 °C min^{-1} heating rate under N_2 flow rate of 0.30 L min^{-1}, followed by activation using 0.3 L min^{-1} CO_2 gas flow rate over 1 h. After cooling down to room temperature, the solids were powdered in a ball mill (Pulverisette 5, Fritsch) to obtain the MCM for characterization and adsorption studies.

2.2. MCM composite characterization

Specific surface area, pore volume, and pore size distribution were determined by physical adsorption of nitrogen at 77 K using