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Magnetic fluid modified peanut husks as an adsorbent for organic dyes removal

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Abstract

Magnetically responsive nanocomposite materials, prepared by modification of diamagnetic materials by magnetic fluids (ferrofluids), have already found many important applications in various areas of biosciences, medicine, biotechnology, environmental technology etc. Ferrofluid modified biological waste (peanut husks) has been successfully used for the separation and removal of water soluble organic dyes and thus this low cost adsorbent could be potentially used for waste water treatment.

Keywords: magnetic fluid; ferrofluid; peanut husks; dyes; adsorption

1. Introduction

Nanocomposites are materials that are usually created by introducing appropriate nanoparticles into a macroscopic sample material. The resulting nanocomposites may exhibit drastically changed properties, resulting e.g., in enhanced mechanical, optical or magnetic properties. Such materials are of great importance for new scientific and technological applications [1].

Materials whose physical properties can be varied by application of external magnetic fields belong to a specific class of smart materials. In many cases magnetically responsive composite materials can be formed by modification of originally diamagnetic materials by magnetic nanoparticles (most often formed by magnetite, maghemite or various ferrites), present in different types of magnetic fluids (ferrofluids). Such composite materials have already found many important applications in various areas of biosciences, biotechnology, medicine and environmental technology [2]. In addition to traditional inorganic or synthetic organic materials, recently also materials of biological origin, such as microbial and algae cells, or lignocellulose particles, have been transferred into magnetically responsive nanobiocomposite materials after magnetic fluid treatment. Such materials could be used

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for the separation and removal of both organic and inorganic xenobiotics or for the construction of magnetically responsive, whole cells biocatalysts [3,4].

Recently, the possible use of agricultural products and by-products has been widely investigated as a replacement for current costly methods of removing different types of xenobiotics (e.g., heavy metals ions, hydrocarbons and dyes) from water and wastewater. Some of the agricultural waste materials can be effectively used as low-cost adsorbents. Modification of agricultural by-product could enhance their natural adsorption capacity or add another additional value to the by-product.

In order to improve manipulation during the adsorption process, magnetic modification of the low-cost adsorbents by magnetic fluids can be used, leading to the formation of "magnetic adsorbents", which can be easily removed from the treated solutions using an appropriate magnetic separator.

Peanut husks are one of the biggest food industry waste products. It has been shown recently that peanut husks can efficiently remove copper ions from waste water [5]. In this paper magnetic fluid modification of peanut husks and subsequent application of this magnetic nanobiocomposite material for dyes removal is described.

2. Experimental

2.1. Materials

Peanut husk was colleted from locally available roasted peanuts; the husk was milled in a coffee mill and fraction smaller than ca 0.5 mm was collected and used for magnetic modification. Water-based ionic magnetic fluid stabilized with perchloric acid was prepared using a standard procedure [6]. The ferrofluid was composed of magnetic iron oxide nanoparticles with diameters ranging between 10 and 20 nm (electron microscopy measurements). The relative magnetic fluid concentration (25.2 mg ml^{-1}) is given as the iron(II,III) oxide content determined by a colorimetric method [7].

2.2. Preparation of magnetic adsorbent

Magnetically responsive peanut husk was prepared in a similar way as magnetic sawdust [8]. Three grams of powdered husk in a 50 ml polypropylene centrifuge tube were suspended in 40 ml of methanol and then 6 ml of ferrofluid was added. The suspension was mixed on a rotary mixer (Dynal, Norway) for 1 h. The magnetically modified peanut husk particles were then twice washed with methanol and air dried.

2.3. Adsorption of dyes on magnetically modified peanut husk

30 mg of the magnetically modified peanut husk particles were suspended in 8 mL of water in test tubes. Then 0.01–2.0 mL portions of stock water solutions (1–2 mg/mL) of tested dyes were added and the total volume of the suspension was made up to 10.0 mL with water. The suspension was mixed for 3 h at room temperature. Then the magnetic peanut husk particles were separated from the suspension using a magnetic separator (MPC-1 or MPC-6, Dynal, Norway) and the clear supernatant was used for the spectrophotometric measurement. The concentration of free (unbound) dye in the supernatant (C_{eq}) was determined from the calibration curve. The amount of dye bound to the unit amount of the adsorbent (q_{eq}) was calculated using the following formula:

$$q_{eq} = D_{tot} - 10C_{eq} / 30 \quad \text{(mg/g)} \qquad (1)$$

where D_{tot} is the total amount of dye used in the experiment.

2.4. Equilibrium data processing

Equilibrium adsorption data were fit to Langmuir and Freundlich adsorption isotherms using SigmaPlot software.

3. Results

Peanut husk particles were magnetically modified by simple contact with a water-based magnetic fluid. The adsorption of iron oxide nanoparticles onto the particles surface proceeded within a few minutes. Magnetically modified peanut husk could be easily separated by rare earth permanent magnets or commercially available magnetic separators.

The presence of both individual magnetic nanoparticles and their aggregates on ferrofluid modified peanut husk particles was observed on SEM images (Fig. 1).

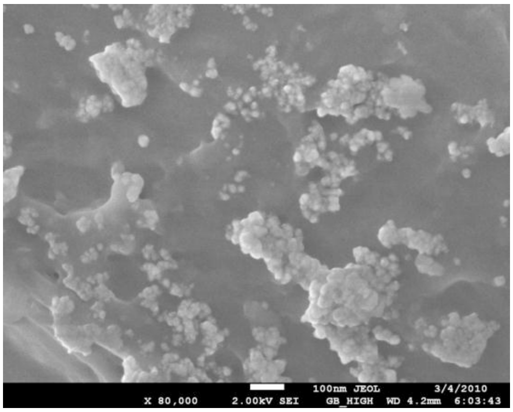

Fig. 1. SEM image of ferrofluid modified peanut husk particle (bar = 100 nm).

Magnetically modified peanut husk particles were used as an adsorbent to study the binding of several water-soluble dyes (acridine orange, Bismarck brown, crystal violet and safranin O). The adsorption of the tested dyes reached equilibrium in approximately 60–90 min. Incubation time of 3 h was used for adsorption experiments. The equilibrium adsorption isotherms for the tested dyes are shown in Fig. 2.

In order to study the adsorption process, Langmuir and Freundlich isotherm equations were used for experimental data analysis. The dyes adsorption could be successfully described by the Langmuir isotherm. Such a description allows a simple calculation of the maximum adsorption capacity Q_{max} (see Table 1), which is a very important parameter describing the adsorption process. In the case of tested dyes, the highest Q_{max} was found for Bismarck brown (95.3 mg/g), while the lowest Q_{max} value was obtained for acridine orange (71.4 mg/g).

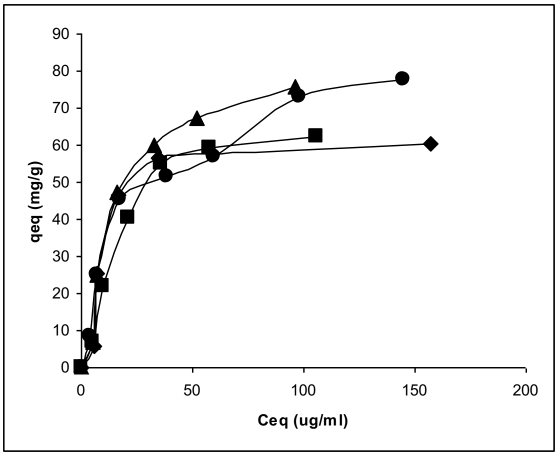

Fig. 2. Equilibrium adsorption isotherms of the tested dyes using magnetically modified peanut husk as adsorbent. C_{eq}: equilibrium liquid-phase concentration of the unadsorbed (free) dye (mg/L); q_{eq}: equilibrium solid-phase concentration of the adsorbed dye (mg/g). (♦) acridine orange; (▲) Bismarck brown; (■) crystal violet; (●) safranin O.

Table 1. Maximum adsorption capacities of the tested dyes.

Dye	Maximum adsorption capacity (mg/g)
Acridine orange	71,4
Bismarck brown	95,3
Crystal violet	80,9
Safranin O	86,1

4. Conclusions

As can be seen from the results, peanut husk is a promising adsorbent for the removal of different types of xenobiotics including dyes. Magnetic modification of this material enables to use magnetic separation techniques for its rapid separation from complex samples containing different impurities, including suspended solids. Simple magnetic modification was performed with the perchloric acid stabilized ferrofluid. Magnetic nanoparticles precipitated on the peanut husk surface both in the form of individual particles and agglomerates of particles. The maximum adsorption capacities of tested dyes on this magnetically labeled material are relatively high. Magnetically modified peanut husk particles can thus be a promising magnetic adsorbent which may be used to the removal of dyes and other xenobiotics.

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