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Magnetically modified peanut husks as an effective sorbent of heavy metals

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ABSTRACT

Magnetically modified peanut husks were used as an adsorbent of cadmium and lead ions from aqueous solutions. Sorption and desorption experiments were carried out and adsorption isotherm models were calculated to assess the sorption capacity of the material. Langmuir adsorption isotherm was the best fitting model both in one-metal ion and two-metal ions solutions suggesting monolayer adsorption taking place. The observed desorption rate was very low, metals are therefore strongly bound on the surface of the adsorbent. Magnetically modified peanut husks were found to be suitable adsorbent for removal of heavy metal ions from water.

1. Introduction

Despite the recent reduction of industry-related pollution in many countries, the use of metals and chemicals in various industries still results in production of large quantities of wastes (i.e. fly ash, liquid effluents or sludge) with high heavy metal content. Since the elements in wastes are often bio-available, mobile and thus toxic ionic species, heavy metal pollution is still one of the most important environmental problems [8].

A number of new technologies for removal of heavy metals from waste water have been developed. The predominant applied methods are coagulation [39], flocculation, precipitation [9,10,15,39], electrochemical processes, ion exchange, extraction etc. [12,15]; using a suitable sorbent is another favourable way of removing pollutants from waste water. Price, availability, adsorption capacity and strong affinity to pollutants are limiting factors for sorbent application in waste water treatment [1,23,37] hence new materials to be used as sorbents are evaluated constantly.

Apart from inorganic or organic sorbents, it is also viable to use certain biological materials (bio-sorbents). Various bio-sorbents were tested for the ability to remove heavy metal ions from water solution. Most of the studies focused on the bio-sorbents based on unprocessed plant waste such as waste tea, already-used ground coffee, nut and walnut shells [31], papaya wood [34], peanut hull pellets [20], teak leaf powder [22], lalang (*Imperata cylindrica*) leaf powder [17],*Coriandrum sativum* [21], grape stalks wastes generated in the wine production process [44], hazelnut shells [7] etc.

Some processed biological materials – for example rice husk ash (which is a solid obtained by burning rice husks) [3], peanut husk carbon [33], leaf powder [16], saltbush (*Atriplex canescens*) leaves [38], rubber maize (*Hevea brasiliensis*) leaves [2], etc. were also used as sorbents of various pollutants.

Since production of peanuts leads to vast amount of organic waste, the peanut husks were subject of various studies regarding their possible utilization in metal sorption from aqueous solutions. Peanut husks, either ground [45] or in the form of pellets were used and it was found out that, although their capacity is lower than that of commercial grade ion-exchange resins, their low cost makes them an attractive adsorbent for metal ions removal [5]. Carbon prepared from peanut husks (PHC) was also assessed in the adsorption of Pb^{2+}, Zn^{2+}, Ni^{2+}, and Cd^{2+}. The results show that Pb^{2+} has better affinity to prepared carbon than other investigated ions [33].

Modified peanut husks were used as well – Charmathy et al. used citric and phosphoric acid modified husks [6] and found

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preference (among other metal ions) for Cu^{2+} and Pb^{2+}. Peanut husks modified by formalin (about 40 vol.% water solution of formaldehyde) – in order to reduce organic pigment – were found to be favourable sorbent of Pb^{2+}, Cr^{3+} and Cu^{2+} with both Langmuir and Freundlich equations describing the process [26].

Magnetic derivatization of adsorbents is a very important modification which was proven to improve the manipulation and increase their adsorption capacity – magnetically modified montmorillonite [29], zeolite [4]; [28], or bentonite [30,43] have been already used for adsorption of heavy metal ions. Biological materials are mainly diamagnetic, which means they do not interact significantly with an external magnetic field; however, their magnetic modification significantly improves the whole adsorption and separation process. Uzun et al. [42] described the adsorption of Cu^{2+} on magnetized *Saccharomyces cerevisiae* subsp. *uvarum* (bottom-brewer's yeast). Magnetically modified yeast cells were also used for bio-sorption of mercury [47] and removal of water-soluble dyes [36]. Magnetic modification has been applied on peanut husks already [35], nevertheless, only adsorption of organic dyes was considered, adsorption of heavy metals has never been assessed before.

The present study focuses on description of the sorption properties of both unmodified and magnetically modified peanut husks and their comparison with other sorbents. The experiments were focused on the removal of Cd, Pb and Zn ions from aqueous solutions as well as on their desorption from the sorbent.

2. Experimental

2.1. Adsorbent preparation

Peanut husks (sample A) were collected from locally available roasted peanuts and were ground in a coffee mill. The particles with diameter less than 0.5 mm were prepared. Water-based ionic magnetic fluid stabilized with perchloric acid (analytical grade) was prepared using a standard procedure [27]. The ferrofluid was composed of magnetic iron oxide nanoparticles with diameters ranging between 10 and 20 nm (measured by electron microscopy). The relative magnetic fluid concentration (25.2 mg/ml) is given as the iron (II, III) oxide content determined by a colorimetric method [11]. Three grams of powdered peanut 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 in a rotary mixer (Dynal, Norway) for one hour. Then the sample was rinsed by methanol and dried at laboratory temperature [35].

2.2. Chemical analyses and material characterization

Chemical compositions of samples were determined using X-ray fluorescence spectrometry (SPECTRO XEPOS, Germany). Iron oxides in samples were detected by power X-ray difractometry (BRUCKER D8 ADVANCE, USA). The surfaces of the samples were characterized by scanning electron microscopy (SEM) combined with energy dispersive X-ray (QUANTA 450 FEG, FEI, Netherlands). Specific surface area was measured using nitrogen (Sorptomatic 1990, Thermo Fisher Scientific Inc., USA) and calculated by the Advance Data Processing software according to the BET isotherm. Particle size was measured by Laser Scattering Particle Size Distribution Analyzer (Horiba LA-950, France). Vibrating sample magnetometer (VSM) EV 9 (MICROSENSE Company, USA) was used to measure magnetic properties of the magnetically modified peanut husks.

The Cd, Pb, Zn and Fe concentration in aquatic solution was determined by atomic absorption spectroscopy with flame atomization F-AAS (UNICAM 969, United Kingdom).

2.3. Reagents

The preparation of adsorbate was carried out by preparing stock solutions containing 1 g/l of Cd, Pb, or Zn. The stock solutions were prepared from $Cd(NO_3)_2{\cdot}4H_2O$, $Pb(NO_3)_2$, and $Zn(NO_3)_2{\cdot}6H_2O$, respectively. Concentrations in the range of 1–700 mg/l were prepared by serial dilution in deionized water and then conserved with concentrated nitric acid, analytical grade (5 ml of 65 wt% acid added per one liter of solution).

Adsorption studies were carried out using the batch technique to obtain the equilibrium data. 0.2 g of magnetically modified peanut husks was suspended in 50 ml of metal solution with defined initial ion concentration. The adsorption isotherms were obtained with Pb^{2+} and Cd^{2+} ions separately as well as with the mixture of the two ions. Samples were stirred for 60 min at laboratory temperature using overturn shaker (Heidolph Reax 20 Heidolph, Germany); according to the preliminary study, the ions adsorption has reached equilibrium at that time. The adsorbent was then separated using 0.40 μm pore size membrane filter or using a magnetic separator and, after conservation, ion concentrations were determined. Adsorbent material was dried at laboratory temperature and studied by electron scanning microscopy; desorption experiment was carried out using the same apparatus as in adsorption study.

3. Results and discussion

3.1. Material characterization

Chemical compositions of peanut husks and their magnetic form (expressed as oxides) are shown in Table 1. As is apparent, process of magnetic modification lead to distinctively enhanced Fe content. Ignition loss of the magnetic peanut husks was 92.3%. From the results of X-ray diffraction analysis (Fig. 1), it can be concluded that iron in the magnetically modified peanut husks took forms of magnetite ($FeO{\cdot}Fe_2O_3$) or maghemite (which are difficult to distinguish), wüstite (FeO) and non-stoichiometric iron oxide γ-$Fe_{21.34}O_{32}$.

Fig. 2 shows the surface structures of magnetically modified peanut husks. The images were taken using electron scanning microscope. By mapping, magnetically modified material was proven to have adsorbed particles of iron oxides on the surface of peanut husks. The results of surface chemical analyses are in very good agreement with the results of phase analyses. Specific surface area was 7.99 m^2/g and the median particle size was 136 μm.

The SEM images of magnetically modified peanut husks after sorption of metal ions are shown in Fig 3. It is apparent that there were no significant visual changes in the surface structure.

Table 1
Chemical composition of original peanut husks (OPH) and magnetically modified peanut husks (MMPH). Content of elements expressed as oxides (wt.%).

Sample	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	TiO_2	MnO	Fe_2O_3
OPH	0.73	0.19	0.09	0.08	0.11	0.25	0.48	0.31	0.01	0.01	<0.01
MMPH	0.67	0.17	0.08	0.07	0.10	0.23	0.44	0.28	0.01	0.01	6.22