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Novel nano-Fe_3O_4-encapsulated-dioctylphthalate and linked-triethylenetetramine sorbents for magnetic solid phase removal of heavy metals

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ABSTRACT

A simple and solvent-free method is proposed for synthesis of novel magnetic nano-sorbents. Dioctyl phthalate (DOP) was used to encapsulate nano-Fe_3O_4 and produce a nano-Fe_3O_4-DOP sorbent. This was treated with triethylenetetramine (TETA) in another solvent-free procedure for the formation of a novel nano-Fe_3O_4-DOP-TETA. The synthesized nano-sorbents were characterized by FT-IR, TGA, SEM and HR-TEM (3.0–12.0 nm). The magnetic solid phase sorption characteristics were studied and optimized. The potential applications of these magnetic solid phase extractors for removal of Ni(II), Cd(II) and Pb(II) from drinking tap water, industrial wastewater and sea water samples were accomplished using a multi-stage micro-column technique.

Introduction

Engineered nano-materials in the form of nano-metal oxides have been designed for the purposes of heavy metals removal, extraction and remediation from aqueous solutions. Such recent interests are mainly related to their high surface area, efficient adsorption capacity, incorporated selectivity, fast equilibration time and excellent recovery values if compared to other bulk materials [1,2].

Nano-magnetic iron oxide, nano-Fe_3O_4, is an example of the widely used metal oxides. The implementation of magnetic nano-particles, as sorbents, for heavy metals has recently received high attentions in environmental and chemical engineering fields in order to solve the associated problems with the separation process from contact medium. The high interests in magnetic nano-materials are mainly due to their simple isolation from the medium by using an external magnetic field [3]. The free magnetic nano-Fe_3O_4 is characterized by the presence of surface hydroxyl groups which limit chemical and physical reactivities toward interaction with other contacted species [4]. In addition, magnetic nanoparticles are subjected to agglomeration due to several modes of interactions and therefore, the high capacity and selectivity of these nano-materials would be greatly decreased or lost [5]. In order to overcome such limitations along with the maintenance of the magnetic properties of nano-particles, various selected approaches are generally used to modify the surface via loading of other target chemical species or biological materials with potential applications in heavy metal removal from various matrices.

The following is a survey of some recently reported magnetic nano-sorbents with their applications for removal of heavy metals. A natural biodegradable and renewable resin with abundant hydroxyl and carboxylic groups was used as a coating layer on the surface of iron oxide magnetic nano-material and reported as a newly synthesized effective adsorbent for cadmium removal from aqueous solution [6]. Adsorption of arsenate on iron(III) oxide-coated-ethylenediamine and functionalized multi-wall carbon nano-tubes was recently reported [7]. The sorptive removal of arsenic from water by magnetic Fe-hydrotalcite (MFeHT) seeding by nano-magnetite was investigated [8]. Magnetic binary oxides (MBOP) were synthesized by using chitosan template and investigated for the uptake of arsenic(III) [9]. A magnetic composite nano-material was synthesized from pectin-iron oxide adsorbent and used for removal of copper(II) [10]. Magnetite nano-particles synthesized through the co-precipitation method with

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(NCM) or without (CM) nitrogen gas passing through them were used to remove Pb(II) and Cr(III) both individually and simultaneously [11]. Magnetic nano-iron oxide modified with 2-mercaptobenzothiazole was reported as an efficient adsorbent and used for the effective removal of mercury(II) ions from contaminated surface waters [12]. Nano synthesized $MnFe_2O_4$ was investigated as a potential adsorbent for removal of selenium oxo-anions, selenite and selenate, from aqueous solutions using batch techniques and DRC–ICP–MS spectroscopy [13]. Removal of cobalt from aqueous solution was studied and reported by magnetic multi-walled carbon nano-tube/iron oxide composites [14]. An efficient procedure for decontamination of U(VI) was proposed by using β-cyclodextrin conjugated magnetic iron oxide composite [15]. A novel magnetic adsorbent was synthesized from α-ketoglutaric acid-modified magnetic chitosan (α-KA-Fe_3O_4/CS) for highly efficient adsorption of Cd(II) from aqueous solution [16]. A magnetic ion-imprinted polymer (Fe_3O_4@SiO_2-IIP) functionalized with–SH group for the selective removal of Pb(II) ions from aqueous samples was synthesized by surface imprinting technique combined with a sol–gel process using 3-mercaptopropyl trimethoxysilane as a monomer, tetraethyl orthosilicate as a cross-linking agent, Pb(II) ion as a template [17]. Various modified iron oxide magnetic nano-sorbents were also reported for removal of some dyes [18,19] and other organic compounds [20–23].

Dioctyl phthalate (DOP) is characterized by a number of comprehensive properties, such as high plasticizing efficiency, low volatility and excellent UV-resisting [24]. Therefore, DOP was used in solvent-free procedure to design and synthesize two novel magnetic nano-sorbents. The first was based on surface encapsulation of nano-Fe_3O_4 by DOP for the formation of nano-Fe_3O_4-DOP sorbent. This magnetic nano-sorbent was further treated with triethylenetetramine (TETA) as an example of nitrogen donors containing sequestering reagent to produce nano-Fe_3O_4-DOP-TETA via also a solvent-free procedure. The produced magnetic nano-sorbents were characterized by scanning electron microscopy (SEM), high resolution transmission electron microscopy (HR-TEM), thermal gravimetric analysis (TGA), and Fourier transform-infrared spectroscopy (FT-IR). The metal sorption behaviors and characteristics of the newly designed magnetic nano-sorbents as magnetic solid phase extractors were investigated and explored by Ni(II), Cd(II) and Pb(II) under different experimental controlling factors and conditions.

Experimental

Materials

Iron(III) chloride hexahydrate, $FeCl_3\cdot 6H_2O$ (purity > 98%) and iron(II) sulfate heptahydrate, $FeSO_4\cdot 7H_2O$ (purity > 98%), sodium chloride, NaCl, potassium sulphate (K_2SO_4), magnesium sulphate ($MgSO_4$), copper acetate, $Cu(CH_3COO)_2$) and zinc acetate, $Zn(CH_3COO)_2$ were all of analytical grade and purchased from Sigma-Aldrich, USA and BDH Limited, Poole, England. Dioctyl phthalate, DOP, (purity > 99.55%), sodium hydroxide (NaOH) and triethylenetetramine (TETA) was purchased from BDH, UK. Lead nitrate, $Pb(NO_3)_2$, cadmium nitrate, $Cd(NO_3)_2$ and $NiCl_2\cdot 6H_2O$ was purchased from oxford, India.

Synthesis

Synthesis of magnetic nano-Fe_3O_4 sorbent

The magnetic nano-iron oxide was first synthesized according to a previously reported method [2]. A 6.1 g sample of $FeCl_3\cdot 6H_2O$ and 4.2 g $FeSO_4\cdot 7H_2O$ were dissolved in 100 mL of distilled water. A total of 25.0 mL of 6.5 M-NaOH was slowly added to the above solution. The reaction mixture was stirred for 4 h using a magnetic stirrer. After the complete addition of NaOH, the formed black precipitate, nano-Fe_3O_4, was then washed several times with distilled water, collected in a pure form by the assistance of an external magnetic field and dried in an oven at 70 °C.

Synthesis of nano-Fe_3O_4-DOP sorbent

The Fe_3O_4-encapsulated-DOP nano-sorbent was prepared by the addition of 20.0 mL of DOP to 10.0 g of nano-Fe_3O_4 sorbent. This mixture was heated under stirring at 80–90 °C for 3 h and the product nano-Fe_3O_4-DOP sorbent was filtered, washed with methanol, collected in a pure form by a magnetic field and dried in an oven at 70 °C until complete dryness.

Synthesis of magnetic nano-Fe_3O_4-DOP-TETA sorbent

A 10.0 g sample of nano-Fe_3O_4-DOP was added to 7.5 mL of TETA and these two reactants were combined together by heavy grinding and mixing in a mortar for 3 h. The produced nano-Fe_3O_4-DOP-TETA sorbent was heated to dryness in an oven at 70 °C.

Sorption characteristics of metal ions using magnetic nano-sorbents by the batch equilibrium technique

The applicability of newly synthesized and functionalized magnetic nano-sorbents for extraction of heavy metal ions, viz. Ni(II), Cd(II) and Pb(II) was studied by the batch equilibrium technique under several experimental controlling factors. These include the effect of pH, contact time, sorbent dosage, initial metal ion concentration and interfering ions. The sorption procedure was repeated three times and the average metal sorption capacity values of the examined metal ions were determined according to the following procedures.

Effect of pH

A 30.0 ± 1.0 mg sample of nano-magnetic sorbent was placed in a 50.0 mL measuring flask and 1.0 mL of 0.1 mol L^{-1} metal ion was then added and followed by 9.0 mL of the selected acidic or buffer solutions (pH 1.0, 2.0, 3.0, 4.0, 5.0, 6.0 and 7.0). The reaction mixture was shaken by an automatic shaker for 30 min at room temperature. The adsorbed metal ion on the surface of nano magnetic sorbent was separated from solution by the action and attraction of an external magnet. The free metal ion in solution was transferred to a conical flask and titrated against 0.01 mol L^{-1} of EDTA by using the appropriate buffer solution and indicator for each metal ion.

Effect of contact time

The effect of shaking time on the sorption characteristics of magnetic nano-sorbent was studied using the batch equilibrium technique. A 1.0 mL solution of 0.1 mol L^{-1} of the examined metal ions, Ni(II), Cd(II) and Pb(II), was mixed with 30.0 ± 1.0 mg of the selected nano-sorbent in a 50.0 mL measuring flask and 9.0 mL of the optimum buffer solution was then added. The reaction mixture was shaken by an automatic shaker for the time intervals of 1.0, 5.0, 10.0, 15.0, 20.0, 25.0, 30.0, 40.0, 50.0 and 60.0 min at room temperature. The adsorbed metal ion on the surface of magnetic nano-sorbent was separated from solution by the action of an external magnet. The free metal ion in solution was titrated against 0.01 mol L^{-1} of EDTA using the appropriate buffer solution and indicator for each metal ion.

Effect of sorbent dosage

The effect of sorbent dosage was also studied by using 5.0, 10.0, 15.0, 20.0, 25.0, 30.0, 40.0, 50.0, 60.0, 70.0, 80.0, 90.0, 100.0 ± 1.0 mg of the selected magnetic nano-sorbent. The optimum conditions were applied by using pH 7.0 and contact time 30 min. A 1.0 mL solution of 0.1 mol L^{-1} of the metal ion was added to the selected sorbent mass. 9.0 mL of the optimum buffer solution was then added and this reaction mixture was automatically shaken for