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Magnetic accumulation and extraction of Cd(II), Hg(II) and Pb(II) by a novel nano-Fe_3O_4-coated-dioctylphthalate-immobilized-hydroxylamine

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ABSTRACT

A magnetic nano-sorbent was synthesized via direct surface impregnation of dioctyl phthalate (Dop) on magnetic nano-iron oxide (nano-Fe_3O_4) for the formation of (nano-Fe_3O_4-Dop). The produced material was further functionalized with nitrogen and oxygen donor atoms by surface immobilization of hydroxylamine for the formation of a novel magnetic nano-sorbent (nano-Fe_3O_4-Dop-HA). This was identified using SEM, HR-TEM, TGA, FT-IR and surface area determination. The average particle size was found in the range of 5–16 nm based on the HR-TEM analysis. The incorporated selectivity was examined for removal of Cd(II), Hg(II) and Pb(II) from aqueous solutions by the static and dynamic techniques. Nano-Fe_3O_4-Dop-HA was identified by high Hg(II) uptake capacity values (1433.3–1633.3 $\mu mol\ g^{-1}$ in pH 1.0–7.0) compared to Cd(II) and Pb(II). The contributions of pH, contact time and nano-sorbent dosage, initial metal ion concentration and interfering ions on the magnetic solid phase extraction by nano-Fe_3O_4-Dop-HA were also studied and optimized. The potential applications of nano-Fe_3O_4-Dop-HA for removal of Cd(II), Hg(II) and Pb(II) from industrial wastewater, sea water and drinking tap water samples were successfully accomplished using a multistage micro-column technique.

Introduction

Pollution of surface water and ground water is now known as a worldwide critical issue. This problem has resulted due to high population growth and rapid developments in industrialization [1]. Persisting contaminants and pollutants in water and wastewater may include various components such as heavy metals, organic and inorganic derivatives as well as other complex compounds [2]. Consequently, it is necessary to prevent or control the harmful effects of these pollutants in order to improve the human living environments [3,4]. Direct applications of treatment processes are generally controlled by several factors including processing efficiency, operational method, economical benefits and energy requirements. Recently, nano-materials have been proposed in various disciplines as efficient, cost effective, environmental friendly alternative to existing treatment materials from the standpoints of both resource conservation and environmental remediation [5]. Applications of nano-materials for wastewater treatment have been focused on magnetic nano-materials [6], carbon nano-tubes [7], activated carbon [8] and nano zero-valent iron [9] as well as other metal oxides [10–14]. Among these materials, magnetic iron oxide (NMs) exhibited good capacity for treatment of large volumes of wastewater as well as ability to use in magnetic removal of heavy metal from different matrices [15].

Iron oxides are existing in nature in several forms including magnetite (Fe_3O_4), maghemite (γ-Fe_2O_3) and hematite (α-Fe_2O_3) as the most common forms [16]. Iron oxide nano-particles have been widely used in water treatments due to their important properties such as nano-size range, high surface area to volume ratios and super-magnetism [17] as well their easy synthesis, possible surface modification and ability to control [18]. In addition, iron oxides are characterized by low toxicity, chemically inertness and biocompatibility [19]. It has been reported that the preparation method and surface coating medium can play a major role in determining the size distribution and morphology, magnetic properties and surface chemistry of these nano-

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materials [20]. However, the stability of nanoparticles is generally affected by the electrostatic and van der Waals interactions. Therefore, more work is needed to enhance and improve the stability of magnetic nano-materials by deceasing surface energy which limits their large scale applications [21]. One attractive potential approach is the modification of nano-materials by the direct reaction with different functional groups and coating materials. Some aimed stabilizers, electrostatic surfactants and polymers have been widely proposed to coat nano-materials with some specific moieties such as ligands [22]. In addition, the stability of nano-iron oxide colloid suspensions could be enhanced by surface modifications with functional groups such as carboxylic acid and amines [23].

The practical applications of nano-iron oxides in water treatments are generally dependent on the modified form [24]. Moreover, to find out the best method and material for treatment of water and wastewater, it is important to identify and evaluate the efficiency, quality standards, security and friendship to the environment as well as cost [25,26]. Dioctylphthalate (DOP) which is known as one of the most extensively used plasticizers in plastics processing. It is also characterized by several comprehensive properties [27]. Therefore, Dop was recently used to coat and protect the surface of Fe_3O_4 nano-particles to provide some functional groups on the surface of this nano-material [28].

The aim of this work is devoted to apply Dop as a potential good coating and protection material for nano-Fe_3O_4 in order to design a newly functionalized magnetic nano-sorbent with hydroxylamine as the simplest sequestering agent. The produced adsorbent (nano-Fe_3O_4-Dop-HA) is aimed to characterize by high-resolution transmission electron microscopy (HR-TEM), surface area analysis (BET), scanning electron microscopy (SEM), thermal gravimetric analysis (TGA) and FT-IR spectroscopy. The objective of this study is also directed to explore the potential applications of this novel magnetic nano-sorbent in water treatment of heavy metal ions such as Cd(II), Hg(II) and Pb(II) and study the contribution of important experimental controlling parameters on the uptake processes.

Experimental

Materials

Iron (III) chloride hexahydrate ($FeCl_3{\cdot}6H_2O$, FW = 270.29 and assay = 98%) and iron (II) sulfate heptahydrate ($FeSO_4{\cdot}7H_2O$ FW = 278.01 and assay = 98%), sodium hydroxide (NaOH, FW = 40 and assay > 99%), disodium ethylene diamine tetraacetate dihydrate (EDTA) ($C_{10}H_{14}N_2Na_2O_8{\cdot}2H_2O$, FW = 372.24 and assay > 99.0%), hydrochloric acid (HCl, FW = 36.46 and assay = 37%), sodium dodecyl sulfate (SDS) ($C_{12}H_{25}NaO_4S$, FW = 288.38 and assay > 90%), sodium chloride (NaCl, FW = 58.44 and assay > 99%), dioctyl phthalate (Dop and assay = 99.55%) and magnesium sulfate heptahydrate ($MgSO_4{\cdot}7H_2O$, FW = 246.47 and assay = 99.0%) were purchased from Riedel-de Haën AG, Seelze, Hannover, Germany. Cadmium nitrate ($(Cd(NO_3)_2{\cdot}4H_2O$, FW = 308.47 and assay = 99.1%) was purchased from RECTAPUR, CE-EMB. Lead nitrate ($Pb(NO_3)_2$, FW = 331.21 and assay = 99%) was purchased from Oxford, India. Mercuric chloride ($HgCl_2$, FW = 271.52 and assay = 98%) was purchased from Ubichem Limited, Egypt. Zinc powder (Zn, AW = 65.39 and assay = 99%) was purchased from Arabic Laboratory Equipment Company, Egypt. Potassium chloride (KCl, FW = 74.55 and assay = 99.5%) was purchased from VWR International Ltd., England. Copper acetate monohydrate ($(CH_3COO)_2Cu{\cdot}H_2O$, FW = 199.65 and assay = 98%) was purchased from United Company, Egypt. Zinc acetate dihydrate ($(CH_3COO)_2Zn{\cdot}2H_2O$, FW = 219.50 and assay = 98.5%) was purchased from BDH Chemicals Ltd., Poole, England. Hydroxylamine hydrochloric acid ($NH_2OH{\cdot}HCl$, FW = 69.49 and assay > 99%) was purchased from Sigma–Aldrich, USA.

Synthesis of nano-Fe_3O_4-Dop-HA

The magnetic iron oxide nano-material (nano-Fe_3O_4) was initially synthesized by the co-precipitation method [29]. 6.1 g of $FeCl_3{\cdot}6H_2O$ and 4.2 g of $FeSO_4{\cdot}7H_20$ were dissolved in 100 mL distilled water and 25 mL of 6.5 mol L^{-1} of NaOH was then slowly added drop wise. This system was mixed by a magnetic stirrer after the complete addition for 4 h. The produced black precipitate (nano-Fe_3O_4) was collected by a magnet, washed several times with distilled water and dried in an oven at 70 °C.

Nano-Fe_3O_4-coated-dioctyl phthalate (nano-Fe_3O_4-Dop) was prepared by the addition of 20.0 mL of Dop to 10.0 g of nano-Fe_3O_4. This mixture was heated under stirring for 3 h at 80–90 °C and the product nano-Fe_3O_4-Dop was filtered, washed with methanol and dried in an oven at 70 °C until complete dryness. A 10.0 g sample of nano-Fe_3O_4-Dop was mixed with 3.0 g of hydroxyl amine hydrochloride (HA) in presence of 10 mL ethanol. The two reactants were combined together by heavy mixing and grinding in a mortar for 3 h. The produced (nano-Fe_3O_4-Dop-HA) sorbent was heated to dryness in an oven at 70 °C.

Instrumentations

Scanning electron microscope (JSM-636LA, JEOL Ltd.), (JSM-5300, JEOL Ltd.) and the ion sputtering coating device (JEOL-JFC-1100E) were used to image the studied magnetic nano-sorbent. A high resolution transmission electron microscopy (HRTEM) model JEM-2100 was used to image and determine the particle size of the magnetic nano-sorbent. The HR-TEM technique includes scanning image observation device to give bright and dark-field STEM images at 200 kV. Also, the unit comprises energy dispersive X-ray analyzer model JED-2300T to examine the images and particle size of nano-Fe_3O_4-DOP-HA. Thermal gravimetric analysis (TGA) and thermoanalytical curve of nano-Fe_3O_4-DOP-HA was acquired by using a PerkinElmer TGA7 thermobalance. The selected operating conditions were 20–600 °C as the heating temperature range, 10 °C min^{-1} as the heating rate, 20 mL min^{-1} as the flow rate of nitrogen atmosphere and 5–7 mg as the range of sample mass.

The FT-IR spectrum of nano-Fe_3O_4-DOP-HA sorbent was measured using a BRUKER Tensor 37 Fourier transform infrared spectrophotometer (400–4000 cm^{-1}). The surface area of nano-Fe_3O_4-DOP-HA sorbents was measured using NOVA 3200 N_2 physisorption, USA. A calibrated CRISON pH-meter using three different standard buffer solutions, viz. 4.01, 7.00 and 9.21 was used to measure the pH of various aqueous solutions. The concentrations of Cd(II) and Pb(II) in water samples were detected by a Perkin Elmer flame atomic absorption spectrophotometer, model 2380. A single beam spectrophotometer was used to determine the concentration of Hg(II) using Unico 7200 spectrophotometer. In this method, 1.0 mL of mercury(II) solution was placed in a 10.0 mL measuring flask and 5.0 mL of sodium dodecylsulfate (0.6 mol L^{-1}) was then added. A 1.0 mL of H_2SO_4 (1.0 mol L^{-1}) and 1.0 mL of dithizone (1.95×10^{-4} mol L^{-1}) solution were then added and mixed with the above mixture. The absorbance value of mercury(II) in this solution was measured using a single beam spectrophotometer at 490 nm from which the concentration value was determined.

Sorption of metal ions by nano-Fe_3O_4-Dop-HA using the static technique

The sorption properties of functionalized nano-Fe_3O_4-Dop-HA toward some heavy metal ions, viz. Cd(II), Hg(II) and Pb(II) by using the static or batch equilibrium technique were studied in presence of various experimental controlling factors such as the effect of pH,