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Synthesis and characterization of thiol-functionalized silica nano hollow sphere as a novel adsorbent for removal of poisonous heavy metal ions from water: Kinetics, isotherms and error analysis

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ABSTRACT

In this study, a strategy has been provided for the preparation of silica nano hollow spheres and its functionalization with the thiol group. Scanning electron microscopy, energy dispersive spectroscopy, X-ray diffraction, N_2 adsorption and Fourier transform infrared spectroscopy have been used to characterize the structure of nanoparticles before and after functionalization. This new synthesized nano hollow sphere was applied to remove heavy toxic metals such as Hg^{2+}, Pb^{2+} and Cd^{2+} from water samples. The effect of initial concentration of heavy metals and interaction time were investigated in batch mode. In order to determine the best fit model for each system, non-linear regressions was carried out. For this, three error functions were applied to predict the optimum model. The goodness of fit of experimental data was observed with Sips and Redlich–Peterson isotherms. The pseudo-second order kinetic model represented our experimental data very well. Adsorption data showed that the adsorption capacity of thiol functionalized silica nano hollow sphere (thiol-SNHS) for Hg^{2+} is higher than Pb^{2+} and Cd^{2+}.

1. Introduction

Metals with specific gravity of about 5 g cm^{-3} or greater are generally defined as heavy. Heavy metals such as lead, mercury and cadmium, often are found in industrial wastewater. The stricter environment regulation on the discharge of heavy metals makes it necessary to develop various technologies for their removal. Waste streams containing low to moderate levels of heavy metals are often encountered in metal plating industries and mining, chemical pharmaceutical, electroplating corrosion of galvanized piping, pigments and alloys, battery manufacture, fertilizer, electronic device manufactures and many others.

Most of heavy metals are dangerous to health or to the environment and are not biodegradable and tend to accumulate in living organisms, thus causing different disorders; therefore it is necessary to remove them from the polluted streams in order to meet increasingly stringent environmental quality standards. A wide range of methods including chemical precipitation, solvent extraction, vacuum evaporation, membrane technologies, adsorption, ion exchange and membrane separation have been used to treat such streams [1–3]. Traditional chemical precipitation is the most economic but is inefficient for dilute solution. Adsorption is one of the best available environmental control technologies for the heavy metal removal from water resources [2], especially using low-cost natural adsorbents such as agricultural wastes, clay materials, zeolite, biomass, and seafood processing wastes [4,5]. Improvement of adsorbent materials into nanoporous structures has shown to significantly enhance their performance in metal removal when compared to conventional adsorbents [6].

For analytical purposes, functionalized silica particles with organic functional groups are commonly used since the material silica provides many advantages such as inert, good adsorption and cation exchange capacity, easy to prepare with chemical compound and particular impregnate medium to create several modified silica surfaces, high mechanic and thermal stability [2,7,8]. For environmental applications, the development and introducing of new functionalized nanoporous materials is necessary, especially for the preparation of heavy metal adsorbents. Synthesis and characterization of nano hollow structures have been extensively done in recent years. The nano hollow particles often exhibit substantially different properties such as low density, large specific surface area, stability, and surface permeability, from those of common particles [9]. This is making them attractive from both scientific and technological viewpoints.

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In this article, we report an easy and versatile method for fabrication of well-defined silica nano hollow sphere in nanometer range via surfactant template assisted and then functionalized with 3-mercaptopropyltrimethoxysilane (MPTMS). Functionalized silica nano hollow spheres (SNHS) were prepared as heavy metal ion adsorbents. These materials were characterized using energy dispersive spectrometer (EDS), X-ray diffraction (XRD), scanning electron microscopy (SEM), BET specific surface area and Fourier transform infrared spectroscopy (FT-IR) analysis.

The other aim of this work is to investigate the usefulness of the fabricated thiol-SNHS as a new nanostructure adsorbent for removal of chosen heavy metal ions (Hg^{2+}, Pb^{2+} and Cd^{2+}) from water solutions. Also the kinetics, isotherm and error analysis for the adsorption of Hg^{2+}, Pb^{2+} and Cd^{2+} onto thiol-SNHS were evaluated. On the other hand, a comparison of three different error functions in minimizing the error distribution between the experimental and predicted isotherms was discussed using the experimental data of adsorption.

2. Materials and methods

2.1. Materials

The chemicals are pro analysis grade consist of ethanol (≥99.9%, Merck), tetraethyl orthosilicate (TEOS, ≥98%, Merck) as a silica source, ammonia solution (25%, Scharlau), 3-mercaptopropyltrimethoxysilane (MPTMS, ≥95%, Merck), *n*-butyl amine (≥99%, Merck), toluene (≥99%, Merck), lead nitrate ($Pb(NO_3)_2$, ≥99.5%, Merck) as a lead source, mercury nitrate ($Hg(NO_3)_2 \cdot H_2O$, 99%, Merck) as a mercury source, cadmium nitrate ($Cd(NO_3)_2 \cdot 4H_2O$, 99%, Merck) as a cadmium source. All aqueous solutions were made with double distilled water $\leq 1.49\ \mu S\ cm^{-1}$.

2.2. Methods

2.2.1. Apparatus

The XRD patterns of the prepared samples were recorded on an Ital structures XRD diffractometer model APD2000 using Cu Kα radiation wavelength 0.15405 nm. A step size of 0.01 and a time per step of 0.2 s were used. Diffraction patterns were taken over the 2θ range 0–60°. Average crystallite size of prepared particles was calculated by the Scherer's equation.

FT-IR spectroscopy was performed on a Perkin-Elmer Spectrum GX FT-IR spectrometer and spectra were recorded between 550 and 4000 cm^{-1} using KBr pellets.

SEM was carried out on a Philips SEM XL30 microscope operating at 30 kV.

BET surface area measurements were conducted using surface area analyzer (Nova 2000, Quantachrome Instruments, FL, USA) using nitrogen (99.99% purity) as the adsorption gas. The sample was slowly heated to 300 °C for 3 h under a nitrogen atmosphere. To obtain the BET specific surface area measurements, the different precursors were evacuated at −196 °C for 66 min.

The metal ion concentrations were determined by using an atomic absorption spectrometer (SpectrAA-220 Varian).

2.2.2. Preparation of SNHS

The SNHS particles were synthesized by ultrasound mediated process. The sonication was performed under ambient air conditions during the whole process. Initially 75 mL of CTAB solution (0.1000 g) was prepared and irradiated in an ultrasound water bath sonicator for 2 min. Then 1 mL of NH_3 solution was dropped into the solutions. Next 1 mL TEOS was added to the solution. After reaction was completed, the collected product was centrifuged repeatedly washed with distilled water and ethanol to remove surfactants and other impurities. The final sample was dried at 60 °C overnight in oven for further characterization. The obtained sediment was placed in furnace for 3 h and 400 °C.

2.2.3. Characterization techniques

The morphologies of particles and the shape and structure of SNHS were investigated through SEM, before and after functionalization. FT-IR was used to identify the functional group in the samples before and after functionalization. An X-ray diffractometer was used to measure the crystallinity of the prepared samples, before and after functionalization.

2.2.4. Surface modification of SNHS

1.0000 g of SNHS and 5 mmol of MPTMS and 25 μL of *n*-butyl amine as a catalyst and 50 mL of toluene as a solvent were refluxed for 150 min. The obtained liquid mixture was filtered and washed with toluene. Then it was dried at 150 °C in oven for 150 min. The thiol-modified SNHS was resuspended in water for 40 min, and then once again dried in oven at 100 °C [10].

2.2.5. Adsorption studies: kinetics and isotherms

Batch experiments were done to measure metal ion adsorption capacities. For the preparation of aqueous metal solutions, metal nitrate salts ($Hg(NO_3)_2$, $Pb(NO_3)_2$ and $Cd(NO_3)_2$) were used. A stock solution of 1000 $mg\ L^{-1}$ of Hg(II), Pb(II) and Cd(II) was prepared by dissolving the required amounts of Hg^{2+}, Pb^{2+} and Cd^{2+} in 1000 mL of double distilled water. Solutions of desired concentration were prepared by diluting the stock solution using double distilled water.

All sorption experiments were carried out in batch conditions using 10 mL of metal solution and 0.0100 g of thiol-SNHS as a nano adsorbent. Shaker was used to mix the suspensions (metal solution–adsorbent) at 150 rpm and 25.0 °C for all tested conditions.

2.2.5.1. Kinetic study (effect of contact time). In the first part, kinetic experiments were performed. For this purpose, initial identical concentrations of Hg^{2+} (350 $mg\ L^{-1}$), Pb^{2+} (40 $mg\ L^{-1}$) and Cd^{2+} (40 $mg\ L^{-1}$) were used. Adsorbent and each solution of Hg^{2+}, Pb^{2+} and Cd^{2+} were mixed and allowed to contact at different contact times. Then the samples were centrifuged at 11,000 rpm for 2 min and filtrated. The residual metal concentrations in the solutions were measured using an atomic adsorption spectrometer. The sorption capacity q_t ($mg\ g^{-1}$) of thiol-SNHS was calculated using [2]:

$$q_t = \frac{C_0 - C_t}{W} \times V \tag{1}$$

where C_0 is the initial ion concentration ($mg\ L^{-1}$) and C_t is the remaining metal concentration ($mg\ L^{-1}$) at time t, V is the volume of ion solutions (L), and W is the adsorbent amount (g).

2.2.5.2. Kinetic models. The sorption dynamics presented by thiol-SNHS were tested with the Lagergren pseudo-first order, the chemisorptions pseudo-second order and Elovich kinetic model.

The non-linearized form of the pseudo-first order equation (Lagergren) is generally expressed as follows [11]:

$$q_t = q_e(1 - e^{-k_1 t}) \tag{2}$$

where q_e and q_t are the adsorption capacity at equilibrium and at time t, respectively ($mg\ g^{-1}$) and k_1 (min^{-1}) is the rate constant of pseudo-first order adsorption.

The pseudo-second order kinetic model is represented by the following equation [12]:

$$q_t = \frac{k_2 {q_e}^2 t}{1 + k_2 q_e t} \tag{3}$$