



Metal ion adsorption using polyamine-functionalized mesoporous materials prepared from bromopropyl-functionalized mesoporous silica

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ABSTRACT

Mesoporous silicas carrying di-, tri-, or penta-amine functional groups were prepared by prior functionalization of a mesoporous silica with bromopropyl-functional groups followed by nucleophilic displacement of the bromine atoms by ethylenediamine, diethylenetriamine, or tetraethylenepentamine, respectively. A synthetic method was developed that gave a starting material with very high surface coverage by the 3-bromopropyl groups. Batch tests were conducted to investigate the capabilities of the prepared adsorbents for the removal of copper, zinc, and cadmium from aqueous solutions. The metal adsorption capacities for these metals were determined as a function of the polyamine group used and the total nitrogen content. The tendency to chemisorb divalent metal ions was found to follow the order: $\text{Cu}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+}$. It was found that the ethylenediamine derivative unexpectedly exhibited the highest capacities. The metal sorption by the ethylenediamine functionalized silica was found to follow first order kinetics with rate constants for Cu^{2+} , Zn^{2+} and Cd^{2+} uptake of 0.028, 0.019, and 0.014 min^{-1} , respectively. The substituted mesoporous silicas showed high resistance to leaching of the grafted polyamine groups. Copper ions that were adsorbed at the surface of the mesoporous silicas can be recovered by washing with an aqueous solution of 1.0 M HNO_3 . The activities of the recovered mesoporous silicas were between 80 and 90% of the original materials.

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1. Introduction

Mineral processing and metal finishing industries produce large amounts of waste effluents containing copper, nickel, cobalt, zinc, cadmium, and other harmful elements [1]. The removal of heavy metal ions from wastewater has been the subject of extensive industrial research since the toxic nature of the heavy metal ions, even low at trace levels, has been a public health problem for many years [2]. Therefore, increasing pressure from environmental authorities forces the establishment of discharge limits, which in turn, requires more effective decontamination and purification methods such as the use of porous materials to remove metal ions from aqueous solution [3]. Notably, the recovery of heavy or valuable metals from process water or wastewater can often result in considerable cost savings [4,5] due to recycling of the materials. High concentrations of heavy metal ions can be precipitated as hydroxides and removed by filtration, while low concentrations of metal ions can be removed from aqueous solutions using ion exchange resins, membranes, or adsorbents [6]. A number of adsorptive compounds are capable of capturing metal ions from

aqueous solution, among which are activated charcoal and clays [7]. The inherent disadvantages of these materials are their wide distribution of pore size, heterogeneous pore structure, low selectivity for heavy metal ions, and relatively low loading capacities. In order to circumvent these limitations, some promising heavy metal adsorbents have been prepared via the immobilization of ion-chelating agents on inorganic supports [5], or via the coupling of chelating ligands to a solid support, such as inorganic oxides and organic polymers [8–10]. These adsorbents have relatively high loading capacities and the selectivity for a targeted metal ion can be increased by the proper selection of chelating ligands. The discovery of mesoporous molecular sieves has stimulated a renewed interest in adsorbent and catalyst design, and a number of papers have been published in this area [11]. Applications of mesoporous silicas as heavy metal ion adsorbents have also been reported in the literature [8–10]. Functionalized mesoporous silica with a high density of diamino groups and well-defined mesochannels that can enhance the accessibilities of molecules is required to achieve high production when applied as a catalyst [12] and to reach high capacity and selectivity when applied as an adsorbent for harmful heavy metal cations [9,13].

This investigation has focused on the application of the functionalized silica as adsorbents for the separation and removal of pollutant metal ions. Amino-functionalized mesoporous silicas

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show notable adsorption capacities for heavy and transition metal ions from solution [12,14].

Promising sorbents can be prepared by anchoring chelating agents on mesoporous silica. In this work, immobilization of the bromopropyl-functional groups and their amine derivatives is explored. The importance of the bromopropyl-functionalized mesoporous silica results from the facile addition of nucleophiles by displacement of the terminal bromide group [15]. The aim of the present investigation was the incorporation of di-, tri-, or pentamine groups onto a modified silica gel surface and testing of the ability of this new adsorbant for removal of divalent metal ions from water.

2. Experimental

2.1. Reagents and materials

The chemicals used in this work are as follows: 3-bromopropyltrichlorosilane [(Cl₃Si(CH₂)₃Br) (96.0%), ethylenediamine, diethylenetriamine and tetraethylenepentamine were purchased from Aldrich and used as received. Toluene, 99.8% HPLC grade, acetone and diethyl ether were dried using anhydrous sodium sulfate for three days. Solutions of divalent metals of the appropriate concentration were prepared by dissolving the metal(II) nitrates in deionized water. Different pH ranges were prepared. Acetate solutions were prepared using hydrochloric acid/sodium acetate for pH 2–4, acetic acid/sodium acetate (buffer for pH 4–6), and acetic acid/NaOH for pH 6.5–8.0. The mesoporous silica used as the starting material (OSU-6-W) was synthesized using the procedure reported in our previously published paper [13].

2.2. Characterization of mesoporous materials

X-ray powder diffraction (XRD) patterns were obtained on a Bruker AXS D-8 Advance diffractometer using Cu K_α radiation ($\lambda = 0.154056$ nm) at 40 kV and 30 mA within the 2θ range of 1.2–10°. The samples were prepared as a thin, flat layer in a plastic holder. Data were collected with the resolution of 0.02° with step time of 8.2 s at 25 °C. The interplanar spacing (d , nm) was calculated using Bragg's equation of the formula: $d_{100} = \lambda/2 \sin \theta$, where d_{100} is the interplanar distance (nm), λ is a wavelength of Cu K_α radiation and θ is the position of the first low-angle peak (°).

The diffuse reflectance infrared Fourier transform (DRIFT) spectra were recorded on a Nicolet Magna 750 FTIR. The spectra were collected for all samples in the range from 400 to 4000 cm⁻¹. The samples were ground powders diluted with potassium bromide in an approximate ratio of 1:4.

Textural properties (surface areas, pore sizes, pore volumes, and pore size distribution) were determined at -196 °C using Brunauer–Emmett–Teller (BET) multilayer nitrogen adsorption method in a conventional volumetric technique by a Quantachrome Nova 1200 instrument and Quantachrome Autosorb-3B automated gas adsorption system. All samples were degassed for 16 h at 100–150 °C prior to adsorption. This temperature range was chosen from the TGA data in order to avoid the degradation of the immobilized surface groups or templating organic molecules while at the same time removing adsorbed gases and water. The surface area was calculated using the BET six-point surface area measurement method based on adsorption data in the partial pressure (P/P_0) range from 0.05 to 0.3 and the pore volume was determined from the amount of N₂ adsorbed at $P/P_0 = \text{ca. } 0.99$. The calculation of pore size was performed using the Barrett–Joyner–Halenda (BJH) method applied to the adsorption data of the N₂ sorption isotherms. Elemental analysis for C and N was used to measure the

amount of functional groups in the samples and was carried out on a LECO TruSpec Carbon and Nitrogen Analyzer. Solid-state ¹³C and ²⁹Si NMR spectra were obtained with a Chemagnetics CMX-II 300 MHz solid-state NMR spectrometer. The experimental details for these measurements were published previously [13]. Metal concentrations were measured using either by UV–Visible spectrophotometer or by inductively-coupled plasma atomic emission spectroscopy. UV–Visible spectra were recorded on a Perkin Elmer (Lambda EZ 201) spectrometer in the range from 200 to 800 nm, while the ICP analysis was performed on a Spectro CIROS ICP Spectrometer. A JEOL JXM 6400 Scanning Electron Microscope (SEM) equipped with an Evex Analytical Imaging System was used to study the morphology, shape, and size of the particles of the synthesized mesoporous materials. A JEOL JEM 100 CX II Transmission Electron Microscope (TEM) was used to study the shape, and size of the pores of the mesoporous materials. Samples for analysis were prepared by placing a small amount of the mesoporous material samples into a beam capsule. Each capsule was then filled top with Polybed 812 resin and polymerized at 60 °C for 48 h in a polymerization oven. The blocks were sectioned in thin sections of about 70 nm thickness using a Sorvall MT 5000 Ultramicrotome with a Diatome diamond knife. The sections were taken and placed on 150 mesh Formvar-coated nickel grids.

2.3. Surface derivitization of the surface of the mesoporous silica with bromopropyl groups

A solution of 50 mmol (~13.0 ml) of 3-bromopropyltrichlorosilane was prepared in 10 ml of dry toluene under a dry atmosphere within a 50 ml round-bottom flask that was sealed with a rubber septa, under a dry atmosphere. Next, the resulting solution was added drop-wise over 30 min via a syringe to a stirred suspension of 3.0 g (~50.0 mmol) of the activated OSU-6-W mesoporous silica in 50 ml of dry toluene in a 125 ml round-bottom flask which was also closed with rubber septa. The mixture was then stirred gently for 48 h at room temperature to ensure complete reaction. The resulting solid was recovered by filtration in a sintered funnel and washed with dry toluene (3 × 50 ml) to rinse away any surplus 3-bromopropyltrichlorosilane. The resulting white solid was dried at 80 °C under vacuum for 24 h to give a yield of 4.97 g. IR (cm⁻¹) (KBr): 3734 (m, sh), 3597 (m, br), 2923 (m, sh), 2852 (m, sh), 1436 (m, sh), 1346 (w), 1311 (w), 1234 (s), 1089 (s, br), 978 (m, br), 798 (m, sh), 683 (w), 574 (w), and 450 (m). Elemental analysis yielded C (11.32 wt%) and N (0.09 wt%).

In order to increase the surface coverage with bromopropyl groups, a second treatment with 3-bromopropyltrichlorosilane was used after an intermediate step in which the initial bromopropyl-derivitized silica was stirred with 50 ml of distilled water for 5 h. After filtration, washing with dry toluene and drying at 80 °C under vacuum for 24 h, the resulting hydrolyzed solid was treated with 3-bromopropyltrichlorosilane as described above. This 3-step derivitization process gave a final yield of 5.69 g of white solid. IR (cm⁻¹) (KBr): 3562 (w, br), 3241 (s, br), 2966 (w), 2933 (s, sh), 2892 (w), 2856 (s, sh), 1455 (w), 1436 (s, sh), 1350 (w), 1303 (m), 1245 (s), 1097 (s), 1045 (m), 976 (m), 804 (m, sh), 692 (m, sh), 614 (w), 559 (w), and 468 (m). Solid-state ²⁹Si CP/MAS NMR δ (ppm) are -57.3 (T²), -65.3 (T³), -101.5 (Q³), and -110.6 (Q⁴). Solid-state ¹³C CP/MAS NMR δ (ppm) are 12.0 ($\equiv\text{Si}-\text{CH}_2-$)[1], 27.2 ($\equiv\text{Si}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{Br}$)[3], and 35.3 ($\equiv\text{Si}-\text{CH}_2-\text{CH}_2-$)[2]. Elemental analysis yielded C (14.72 wt%) and N (0.16 wt%) Scheme 1.

2.4. Preparation of mesoporous silicas with immobilized polyamine ligands

The preparation of mesoporous silica with polyamine functional groups was performed by utilizing nucleophilic displacements of

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