Facile microwave-assisted fabrication of nano-zirconium silicate-functionalized-3-aminopropyltrimethoxysilane as a novel adsorbent for superior removal of divalent ions

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ABSTRACT

A method is described for functionalization of nano-zirconium silicate with 3-aminopropyltrimethoxysilane by a fast solvent-free reaction using microwave-assisted fabrication approach to produce a novel Nano-ZrSiO$_4$–NH$_2$ adsorbent. The structure was confirmed from the FT-IR, SEM, TGA and surface area analysis. The metal adsorption and selectivity properties were examined and evaluated from the distribution coefficients (K_d) of a series of metal ions. Nano-ZrSiO$_4$–NH$_2$ was identified to exhibit 6.300, 4.000 and 2.100 mmol g^{-1} as the highest capacity values for Cu(II), Cd(II) and Pb(II), respectively using 0.005 g of the adsorbent per 10.0 mL solution. Other important controlling factors were also explored.

Introduction

Water pollution represents a problem of global concern. Heavy metals, even at relatively low concentration levels can cause serious hazardous effects to humans owing to their non-biodegradability properties, high toxicity and carcinogenic effects. The divalent ions of copper, cadmium and lead are examples of heavy metals which are well known for their high toxicity when released to the aquatic systems from some industrial activities. Copper has been listed as one of the most widespread heavy metal contaminants [1]. Copper pollution results from electroplating industries, mining and smelting, brass manufacture, and excessive use of Cu based-chemicals. Exposure to high levels of copper in water and diet can lead to liver and kidney diseases [2]. The health effects of cadmium may include vomiting, nausea, diarrhea, salivation, muscle cramp, loss of calcium from bones, reduction of red blood cells, damage of bones, yellow coloration of teeth, hypertension, kidney failure following oral ingestion, lung irritation, chest pain, and loss of smell sense after inhalation [3]. Lead is among the highly toxic heavy metals and it transfers to the environment from the effluent of many industrial activities such as storage batteries, pigments, mining, painting, coating, electroplating, insecticides, petrochemicals and photographic materials [4]. The permissible level of lead in drinking water is 0.05 mg L^{-1} according to the Environmental Protection Agency (EPA) [5]. Lead exhibits harmful effect to the developing brains of children and may affect children's mental and physical health. Moreover, it affects children's learning abilities and causes behavioral problems and mental retardation. Lead can also cause severe dysfunction of kidneys, liver, nervous system, reproductive system as well as anemia, headache, chills, diarrhea, reduction in hemoglobin formation and high blood pressure [6]. Therefore, a strong need is emphasized to develop economic and eco-friendly methods in order to minimize and remove such toxic pollutants from water.

There is a worldwide concern nowadays about the development of new water and wastewater treatment technologies. The utilization and applications of nano-materials and nano-adsorbents in treatment processes have received much attention as promising targets from the scientists and engineers due to their unique properties. The advantages of these materials are mainly based on their extremely small particle size, ability to chemically or physically modify, high surface area to volume ratio and excellent biocompatibility [7–10]. Nano-materials are mainly divided into several main categories based on their surface properties, surface functionalization and adsorption applications. Water treatment by adsorption techniques using various nano-adsorbents may include modified or unmodified metallic nano-particles such as silver and gold [11,12], metal oxide nano-particles

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such as silicon oxide [13], aluminum oxide [14], magnetic iron oxide [15] and titanium oxide [16]. In addition, different structures of carbonaceous nano-materials such as carbon nano-tubes, carbon nano-sheets and carbon nano-particles are representing an important class of nano-adsorbents [17].

Zirconium silicate or zircon ($ZrSiO_4$) is generally manufactured by electric/thermal fusion of zirconium oxide (ZrO_2) and silicon oxide (SiO_2). The major applications field of zirconium silicate is mainly focused on surface cleaning, nuclear reactor components, surface preparation of stainless steel parts, food industries and other medical applications. Zirconium silicate was also reported as an efficient fire retarding and heat shielding material [18]. Zirconium silicate is highly insoluble in aqueous, acidic and alkaline solutions and this property can help in application of this material as a promising adsorbent for removal of various pollutants from aqueous solutions. However, the use of zirconium silicate for removal and solid phase extraction of organic and inorganic species is limited to a number of published papers [19–21]. A method was reported for using pure zirconium silicate and bismuth citrate powders as packing materials inside micro spin columns to establish a solid-phase extraction procedure for galloyl- and caffeoylquinic acids from natural sources (Galphimia glauca and Arnicae flos) [19]. Chromatographic separation of sodium, cobalt and europium on the particles of zirconium molybdate and zirconium silicate ion exchangers was also reported [20]. The sorption mechanisms of Cs(I), Co(II) and Eu(III) on the surface of amorphous zirconium silicate as a cation exchanger was investigated and evaluated [21]. Surface modification of zirconium silicate via physical or chemical impregnation of certain functional groups is limited [22]. Therefore, the objective of this research study is devoted to explore and investigate the potential functionalization of nano-zirconium silicate (Nano-$ZrSiO_4$) with 3-aminopropyltrimethoxysilane for the formation of a novel Nano-$ZrSiO_4$–NH_2 adsorbent using microwave assisted approach. The feasibility of Nano-$ZrSiO_4$–NH_2 as an efficient adsorbent for removal of some selected divalent metal ions, viz. copper (II), cadmium (II) and lead (II) was also explored in this work. The contributions of experimental controlling parameters such as pH, contact time, adsorbent dosage and initial metal ion concentration were also studied and optimized using the batch adsorption technique.

Experimental

Instrumentations

The FT-IR spectra were acquired from KBr pellets using a Bruker Tensor 37 Fourier transform infrared spectrophotometer in the range of 400–4500 cm^{-1}. Thermal gravimetric analyses were recorded by a Perkin-Elmer TGA7 Thermobalance using the following operating conditions. Heating range = 20–600 °C, heating rate = 10 °C min^{-1}, flow rate = 20 mL min^{-1} of pure nitrogen atmosphere and the sample mass was 5.0–6.0 mg. Scanning electron microscope (SEM) (JSM-6360LA, JEOL Ltd.), (JSM-5300, JEOL Ltd.) and an ion sputtering coating device (JEOL-JFC-1100E) were used. The atomic absorption analysis was performed using a Shimadzu model AA-6650. The pH-measurements were carried out by an Orion 420 pH-meter and this was calibrated against standard buffer solutions of pH 4.0, 7.00 and 9.21. Nokia Egypt microwave instrument, NG23LS-BS with output 900 W and 2450 MHz was used. The surface area analysis was accomplished using the BET method by a Nova 3200 Nitrogen physisorbtion Apparatus, USA.

Chemicals and solutions

3-Aminopropyltrimethoxysilane (FW = 179.29 and 97%) and zirconium silicate nano-powder (Nano-$ZrSiO_4$, <100 nm, FW = 183.31, 98.5%) were purchased from Sigma–Aldrich chemical company, St Louis, MO. The selected metal salts were all of analytical grade and used as received. Copper acetate (($CH_3COO)_2$-Cu·H_2O, FW = 199.65 and 98.0%), cadmium nitrate ($Cd(NO_3)_2$·$4H_2O$, FW = 308.47 and 99.1%) and lead nitrate ($Pb(NO_3)_2$, FW = 331.21 and 99%) were purchased from BDH Chemicals Ltd, Poole, England. Hydrochloric acid (HCl, FW = 36.46 and 37%), sodium acetate trihydrate (CH_3COONa·$3H_2O$, $3H_2O$, FW = 136.10 and ≥99.0%) were purchased from Riedel-de Haën, AG, Seelz-Hannover, Germany. Acidic and buffer solutions were prepared from 1.0 M hydrochloric acid solution and 1.0 M sodium acetate trihydrate solution by mixing the appropriate volumes of the two solutions and diluting to 1.0 L. The metal ion solutions were prepared from distilled water (DDW).

Synthesis of Nano-$ZrSiO_4$–NH_2 and $ZrSiO_4$–NH_2–Cu(II) materials

A 10.0 g sample of Nano-$ZrSiO_4$ was added to 30 mL of 3-aminopropyltrimethoxysilane and the reaction mixture was heated into the microwave system for 3 min. The produced Nano-$ZrSiO_4$–NH_2 adsorbent was filtered, washed with 50 mL of ethanol and dried in an oven for 6 h at 70 °C. Nano-$ZrSiO_4$–NH_2–Cu(II) material was prepared by mixing 0.250 g of Nano-$ZrSiO_4$–NH_2 adsorbent with 50.0 mL of 0.1 mol L^{-1} Cu(II) and this mixture was shaken for 30.0 min by an automatic shaker. The product Nano-$ZrSiO_4$–NH_2-Cu(II) material was filtered, washed with distilled water and dried in an oven at 70 °C for 4 h.

Determination of the distribution coefficient

The distribution coefficient values of a series of metal ions were determined using 2.0 μg mL^{-1} metal ion solutions as the studied concentration. 0.010 ± 0.001 g of the dry Nano-$ZrSiO_4$–NH_2 adsorbent was added to 10 mL solution of 2.0 μg mL^{-1} metal ion in a 25 mL measuring flask. This mixture was shaken for 30.0 min and filtered. The concentration of metal ion in the sample, standard and blank solutions were determined by atomic absorption analysis.

Determination of metal adsorption capacity by Nano-$ZrSiO_4$–NH_2

Three selected metal ions, viz. Cu(II), Cd(II) and Pb(II) were used to determine the metal adsorption capacity values (mmol g^{-1}) by Nano-$ZrSiO_4$–NH_2 adsorbent in different experimental controlling factors as a function of pH, contact time, adsorbent dosage and initial metal ion concentration using the batch equilibrium technique.

Effect of pH on the metal adsorption capacity

Various acidic and buffer solutions (pH 1.0, 2.0, 3.0, 4.0, 5.0, 6.0 and 7.0) were used to conduct this study. In this method, 0.010 ± 0.001 g of Nano-$ZrSiO_4$–NH_2 adsorbent was added to a mixture of 1.0 mL of 0.1 mol L^{-1} of metal ion and 9.0 mL of the selected acidic or buffer solutions into a 50 mL measuring flask. This mixture was then automatically shaken for 30.0 min. After equilibration, the mixture was filtered and washed three times with 100 mL-DW and the free metal ion in solution was subjected to complexometric titration against 0.01 mol L^{-1} of EDTA solution using the appropriate buffer and indicator. The metal adsorption capacity value of each metal ion was determined in triplicate.

Effect of contact time on the metal adsorption capacity

The effect of shaking time intervals (1, 5, 10, 15, 20, 25 and 30 min) on the metal adsorption capacity was also studied for the same three metal ions by the batch equilibrium technique. A sample of 0.010 ± 0.001 g of dry Nano-$ZrSiO_4$–NH_2 was weighed and added to a mixture of 1.0 mL of 0.1 mol L^{-1} of each metal ion and 9.0 mL of the optimum buffer solution (pH 7.0). This mixture was