



# High performance nano-zirconium silicate adsorbent for efficient removal of copper (II), cadmium (II) and lead (II)



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## ABSTRACT

In this research paper, zirconium silicate material, in the form of nanoparticles (ZrSiO<sub>4</sub>-NPs), was explored as a high performance, novel and efficient adsorbent for extraction and removal of some divalent metal ions. The metal selectivity properties of ZrSiO<sub>4</sub>-NPs were studied and evaluated from the distribution coefficients of a series of divalent metal ions. The incorporated selectivity characters were found to follow the order: Cu(II) > Cd(II) > Pb(II) > Ni(II) > Co > Mg (II) > Ca(II). The metal binding and uptake capacity values of Cu(II), Cd(II) and Pb(II) as the highest extracted metal ions by ZrSiO<sub>4</sub>-NPs were investigated as a function of pH, contact time, adsorbent dosage and initial metal ion concentration using the batch equilibrium technique. The adsorption capacity values of Cu(II), Cd(II) and Pb(II) were characterized as 4.500, 2.100 and 1.400 mmol g<sup>-1</sup>, respectively using 5.0 mg of the adsorbent at pH 7.0. The adsorption processes were studied, evaluated and found to follow the postulates of Langmuir and BET isotherm models. The surface reaction between metal ions such as Cu(II) and ZrSiO<sub>4</sub>-NPs was confirmed using FT-IR, SEM and TGA.

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## Introduction

Rapid industrialization has created a major global concern about the environmental toxicity of heavy metals due to their direct release into the environments. Heavy metals such as arsenic, cadmium, lead, mercury, chromium, zinc, copper and nickel, etc. are often found in industrial wastewaters due to metal plating, smelting, battery manufacture, tanneries, petroleum refining, paints, pesticides and pigments manufactures, etc. [1,2]. Cadmium can cause renal dysfunction, liver damage, bone degeneration, lung insufficiency and hypertension in humans [3]. Lead is harmful to children and can cause mental retardation [4–6]. The excessive release of copper (II) in the environment can cause serious health problems such as liver and kidney failure, nausea, headache, respiratory difficulty, hemolytic anemia, massive gastrointestinal bleeding as well as death and the other toxic heavy metals are also well known for their serious impact on the human health [7–10].

Several treatment and separation techniques were used to minimize the concentration levels of heavy metal contents in wastewater effluents. These include ion-exchange, coagulation, lime precipitation, solvent extraction, electrolytic processes,

membrane separation and adsorption [11–13]. In recent years, adsorption technology has been known as one of the most popular methodology to control such pollutants in water due to its emergence as an alternative low cost and highly efficient approach for removal of trace metals from wastewater and water supplies [14,15]. The applications of activated carbon, zeolite, clays and other materials in wastewater treatment have been reported [16–18]. However, these types of traditional adsorbents have lost their effectiveness and recently replaced by other nano-organic, nano-inorganic and nano-composite materials due to their high surface area, adsorption capacity and magnetic properties [19]. In addition, recent advances as well as research interests are now focused on the growing designing fields of novel nano-metal oxides as efficient adsorbents for water treatment [20]. Nano-magnetite (γ-Fe<sub>2</sub>O<sub>3</sub>) has emerged as a highly selective adsorbent for removal of Cr(VI) from water [21]. Nano-sized manganese oxides (NMnOs) was found to exhibit high adsorptive performance compared to the bulk counterpart due its polymorphic structure and higher specific surface area and thus were used for removal of some heavy metal ions such as cadmium(II) and mercury(II) [22,23]. Nano-sized Al<sub>2</sub>O<sub>3</sub> with certain functional donor groups such as oxygen, nitrogen, sulfur and phosphorus were found to improve their sorption efficiency toward heavy metals as previously reported [24]. Nano-sized TiO<sub>2</sub> exhibited 15.3 and 7.9 mg g<sup>-1</sup> at pH 9.0 as the adsorptive capacity values of Zn(II) and

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Cd(II), respectively and the presence of common cations and anions showed no significant influence on the adsorption process of targeted metal ions [25]. Magnesium oxide and zinc oxide nanoparticles were recently employed as excellent adsorbents for removal of copper from wastewater [26]. Cerium oxide (CeO<sub>2</sub>) was also synthesized as nano-crystals and shown an apparent adsorption for heavy metal ions as 15.4 mg g<sup>-1</sup> for Cr(VI) and 9.2 mg g<sup>-1</sup> for Pb(II) which are nearly 70 times higher than that of the commercial bulk ceria material [27]. On the other hand, ZrO<sub>2</sub> as an adsorbent has been demonstrated and reported by its strong affinity to negatively charged moieties such as arsenic [28,29], antimony (V) [30] and phosphate ion [31].

Zirconium silicate or zircon (ZrSiO<sub>4</sub>) is generally manufactured by electric/thermal fusion of silicon oxide (SiO<sub>2</sub>) and zirconium oxide (ZrO<sub>2</sub>). Zirconium silicate is widely used in surface cleaning, nuclear reactor components, surface preparation of stainless steel parts, food industries and other medical applications. Zirconium silicate was also reported as efficient fire retarding and heat shielding material [32]. Zirconium silicate is highly insoluble in aqueous, acidic and alkaline solutions. The use of zirconium silicate as an adsorbent for removal and solid phase extraction of organic and inorganic species is limited to a number of published papers [33–35]. Therefore, the objective of this research work is devoted to explore and investigate the potential application of zirconium silicate in the form of nano-particles (ZrSiO<sub>4</sub>-NPs) as an efficient adsorbent for removal of some selected divalent metal ions, viz. copper (II), cadmium (II) and lead (II). The contributions of experimental controlling parameters such as pH, contact time, adsorbent dosage and initial metal ion concentration were also studied and optimized.

## Experimental

### Instrumentations

The pH-measurements of all metal ions and buffer solutions were carried out by an Orion 420 pH-meter which is calibrated against standard buffer solutions of pH 4.00, 7.00 and 9.21. Atomic absorption analysis for determination of the concentration of Cu (II), Cd(II) and Pb(II) was performed using Shimadzu model AA-6650. Fourier transform-infrared (FT-IR) spectra were recorded from KBr pellets using Bruker Tensor 37 Fourier transform infrared spectrophotometer in the range of 400–4500 cm<sup>-1</sup>. Thermal gravimetric analysis (TGA) and thermoanalytical curves of ZrSiO<sub>4</sub>-NPs and ZrSiO<sub>4</sub>-NPs-Cu(II) were measured by PerkinElmer TGA7 Thermobalance using the temperature heating range = 20–600 °C, heating rate = 10 °C min<sup>-1</sup>, flow rate = 20 mL min<sup>-1</sup> pure nitrogen atmosphere and sample mass was taken in the range of 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 to examine the morphology of ZrSiO<sub>4</sub>-NPs and N-ZrSiO<sub>4</sub>-NPs-Cu(II).

### Chemical and solutions

The metal salts are all of analytical grade and used as received. Zirconium silicate nano-powder (ZrSiO<sub>4</sub> < 100 nm, FW = 183.31, 98.5% purity) was purchased from Sigma-Aldrich chemical company, St Louis, MO. Copper acetate ((CH<sub>3</sub>COO)<sub>2</sub>Cu·H<sub>2</sub>O, FW = 199.65 and 98.0% purity), cadmium nitrate (Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, FW = 308.47 and 99.1% purity) and lead nitrate (Pb(NO<sub>3</sub>)<sub>2</sub>, FW = 331.21 and 99% purity) were purchased from BDH Chemicals Ltd, Poole, England. Hydrochloric acid (HCl, FW = 36.46 and 37% purity), sodium acetate trihydrate (CH<sub>3</sub>COONa·3H<sub>2</sub>O, FW = 136.10 and ≥99.0% purity) were purchased from Riedel-de Haën, AG, Seelze, Hannover, Germany. The metal ion solutions were

prepared from distilled water (DW). Acidic and buffer solutions (pH 1.0–7.0) 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 pH-value of the resulting solution was adjusted by a pH meter.

### Determination of the distribution coefficient [36]

A series of metal ions, viz. Mg(II), Ca(II), Co(II), Ni(II), Cu(II), Cd (II) and Pb(II) was used to determine the distribution coefficient values by ZrSiO<sub>4</sub>-NPs adsorbent via a single component system by the batch adsorption technique. The concentration of each metal ion solution was prepared as 2.0 µg mL<sup>-1</sup>. A 10 ± 1 mg sample of the dry adsorbent was weighed and added to 10.0 mL solution of the selected metal ion in a 25.0 mL measuring flask. This mixture was shaken by an automatic shaker for 30 min and filtered using cellulose nitrate filter with pore size 0.2 micron. The concentrations of each metal ion in the filtrate, standard and blank solutions were determined by atomic absorption analysis. This procedure was repeated three times and the average values were considered.

### Determination of metal adsorption capacity [16,36–38]

The metal adsorption capacity values (mmol g<sup>-1</sup>) of Cu(II), Cd (II) and Pb(II) by ZrSiO<sub>4</sub>-NPs adsorbent in various acidic and buffer solutions (pH 1.0–7.0) were determined in triplicate by the batch equilibrium technique. In this method, 10 ± 1 mg sample of the dry adsorbent was weighed and added to a mixture of 1.0 mL of 0.1 M-metal ion and 9.0 mL of the selected acidic or buffer solution into a 50 mL measuring flask. This mixture was then automatically shaken at room temperature for 30 min. After equilibration, the mixture was filtered using cellulose nitrate filter with pore size 0.2 micron and washed three times with 100 mL of DW. The unbounded metal ion in the filtrate was subjected to complexometric titration by a 0.01 M EDTA solution using the appropriate buffer and indicator for each metal ion. This experiment was repeated three times and the average value was calculated.

The effect of shaking time intervals (1, 5, 10, 15, 20, 25, 30, 40, 50 and 60 min) on the metal adsorption capacity was also studied for the same metal ions, viz. Cu(II), Cd(II) and Pb(II) by the batch equilibrium technique according to the following procedure. A sample of dry ZrSiO<sub>4</sub>-NPs adsorbent (10 ± 1 mg) was added to a mixture of 1.0 mL of 0.1 M each metal ion and 9.0 mL of the optimum buffer solution (pH 7.0). This mixture was shaken for the selected period of time, filtered using cellulose nitrate filter with pore size 0.2 micron, washed with 100 mL of DW and the unextracted metal ion in the filtrate was determined by complexometric EDTA titration. This experiment was repeated three times and the average values were calculated.

The effect of adsorbent dose (5, 10, 25, 50 and 100 ± 1 mg) was also studied by the batch equilibrium technique. A mixture of 1.0 mL of 0.1 M of each metal ion and 9.0 mL of the optimum buffer solution was added to the selected ZrSiO<sub>4</sub>-NPs adsorbent dose into a 50 mL measuring flask. These were then shaken at room temperature for 30 min by an automatic shaker. After equilibration, the mixture was filtered using cellulose nitrate filter with pore size 0.2 micron and washed three times with 100 mL of DW. The unbounded metal ion in the filtrate was subjected to complexometric titration using 0.01 M EDTA solution. This experiment was repeated three times and the average values were calculated.

A batch equilibrium technique was also used to investigate the effect of different metal ion concentrations on the adsorption capacity values of ZrSiO<sub>4</sub>-NPs. In this method, a 10 ± 1 mg sample of the dry adsorbent was weighed and added to a mixture of 1.0 mL of the selected metal ion concentrations (0.010, 0.025, 0.050, 0.100,

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