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Heavy metal ions extraction from aqueous media using nanoporous silica

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ABSTRACT

Nanoporous silica (NP) was synthesized and modified with thiol moiety [NPSi-SH]. Thermal gravimetric analysis (TGA) of [NPSi-SH] proved its high thermal stability in the temperature range of 25–600 °C. Structural identification of surface modification of [NPSi-SH] was also confirmed on the basis of surface coverage value from the study of thermal desorption method and FT-IR as well as electron impact-mass spectrometry (EI-MS) by the direct insertion probe. A study was performed to explore the metal adsorption, chelating and selectivity properties of [NPSi-SH] toward a series of di- and tri-valent toxic and nontoxic metal ions via determination of the metal capacity and distribution coefficient values. The incorporated selectivity characters of [NPSi-SH] were studied based on determination of the distribution coefficient and separation factor and the results have strongly referred to high affinity toward binding and up-take of anionic and cationic Hg(II) species in all the studied pH range (1.0–7.0). Also, The proposed mechanisms of adsorption of Hg(II) were suggested at different pH. The selective removal and extraction of Hg(II), via micro-column packed with [NPSi-SH], versus other toxic and nontoxic metal ions from drinking tap water samples were also explored. Excellent percentage extraction values of Hg(II) were characterized as 98.1 ± 4.0%, 98.0 ± 4.0% and 97.7 ± 3.0% from water samples buffered to pH 1.0, 2.0 and 7.0 respectively. The other tested metal ions were found to exhibit percentage extraction values of 94.0 ± 5.0% for Cd(II), 93.6 ± 4.0% for Cu(II) and 90.5 ± 5.0% for Zn(II) from pH 7.0 water samples. Different important analytical factors were applied to compare and show superiority of synthesized [NPSi-SH] phase with other previously reported silica gel phases-loaded-thiol [Si-SH].

1. Introduction

A fundamental requirement for safe human life and protected green environments is mainly based on the abundance of clean, uncontaminated water. However, in the past century, a huge number of contaminants have found their ways by direct release into water resources via the massive industrial activities and technological applications including burning of fossil fuels, mining, nuclear energy, electroplating, steel production and many others. Heavy metal species derived from mercury, lead, arsenic, cadmium, chromium and copper are of major concern as contaminants [1,2].

Considerable research efforts have been made in the previous few decades to search for the best ways to overcome the environmental pollution problems caused by improper disposal and spillage of these toxic heavy metals [3–5]. In addition, a strong emphasis on finding and developing new and greener analytical methods is aimed and led to a continuous growth in the analytical methods for various metals determination [6]. A wide variety of analytical techniques have been developed to determine trace metal concentrations in natural waters. The most important step in heavy metal determinations is mainly based on the initial extraction and preconcentration procedures [7,8]. The traditional metal extraction techniques are dependent on applications of liquid–liquid extraction, co-precipitation and ion exchange. However, these methods require large amounts of high-purity solvents and some of these are causing severe health and/or environmental problems [9–12]. On the other hand, solid phase extraction approach (SPE) has emerged as the most effective multi-elemental extraction and preconcentration technique due to its well documented advantages. Selective SPE of metal ions are mainly focused on the utilization of chelating and ion exchange organic or inorganic sorbents [13–15]. The advantages of high surface areas and increased stability as well as reactivity of chelating silica gel as an example of inorganic sorbents versus others are also well reported [16–18].

Chemisorption of chelating functional groups or donor atoms containing compounds on the surface of silica gel offers a unique advantage due to the strong covalent bonding of the molecule as well as increasing efficiency, sensitivity and selectivity characteristics [19,20]. The first step in chemisorption technique is to modify

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the surface with salinization reagents that end up with a terminal amino-, chloro-, hydroxyl- or mercapto- group for providing silica-NH_2, silica-Cl, silica-OH and silica-SH, respectively [21,22]. Silica-SH is characterized by its simultaneous capability of both ion exchanger and metal chelation properties that were used in a number of publications. Silica-SH phase was previously reported for extraction of Cd(II) and Cu(II) [23], Co(II) and Ni(II) [24] and Cu(II), Zn(II), Cd(II) and Pb(II) [25]. A series of seven thiol-functionalized adsorbents were prepared and characterized as completely disordered amorphous solids to highly ordered mesostructures and variable density of organic ligands for the examination of Hg(II) [26]. Therefore, silica-SH as a sulfur containing solid phase extractor may be expected to show high affinity and selectivity for successful binding with mercury ion or species based on the hard-soft acid-base phenomenon [27]. Heavy metal ion adsorbents such as MCM-41 with an initially anionic silicate framework [28–34] and HMS [32–34] with an electrically neutral framework, was functionalized by 3 mercaptopropylsilyl groups to the framework pore walls of nanoporous silica for Hg(II) removal [28–34]. More detailed studies are available in literatures that were focused on MCM-41 rather than HMS. However, the grafting process was much more effective for HMS than for MCM-41 owing to a higher surface concentration of surface hydroxyl groups [33]. Consequently, the functionalized HMS derivative was able to bind quantitatively more Hg(II) ions from aqueous solution compared to MCM-41 [33]. The Hg(II) adsorption capacities for HMS were interpreted in terms of the size and accessibility of the framework pore structure [33].

The focus of this study is detailed investigation of the removal of Hg(II) as well as other metals ions such as Mg(II), Ca(II), Mn(II), Cr(III), Fe(III),Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Pb(II) from micro-column and natural water samples via a single step modification route of a nanopouros silica (NP) or HMS modified with SH phase.

2. Experimental

2.1. Reagents and solutions

All chemicals used in this work, were of analytical reagent grade and were used without further purification. Reagents used for the synthesis are NaOH, tetraethyl-orthosilicate (TEOS) $Si(OC_2H_5)_4$, n-dodecylamine and (3-mercaptopropyl)trimethoxysilane. These were supplied by Aldrich Chemical Company Milwaukee, WI, USA. The metal salts are in chloride, acetate or nitrate form and all of analytical grade and purchased from Aldrich Chemical Company, and BDH limited, Poole, England. The metal ion solutions were prepared from doubly distilled water (DDW). 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-values of resulting solutions were adjusted by a pH meter.

2.2. Synthesis of [NPSi-SH]

Nanoporous silica was synthesized according to the following method [35]. Briefly, nanoporous silica (NP) was prepared by mixing 99% EtOH, deionized H_2O and n-dodecylamine ($C_{12}H_{27}N$, MW 185.36) and a silicate source, tetraethyl orthosilicate (TEOS, $Si(OC_2H_5)_4$, MW 208.33). Both solutions were separately stirred to homogeneity and TEOS was then added to the surfactant template solution. The mixture was stirred overnight at 23 °C and the product was dried for 4 h and rinsed several times with deionized H_2O and EtOH through Fisher Scientific qualitative P2, 5.5 cm filter paper. Nanoporous silica was air-dried and finally calcinated at 650 °C for 6 h [35].

The synthesized [NPSi-SH] phase was prepared according to the following procedure. Nanoporous silica (5.0 g) was suspended in 100 ml toluene and 12.0 g of (3-mercaptopropyl)trimethoxysilane. This reaction mixture was refluxed with stirring for 6 h. [NPSi-SH] phase was filtered, washed with toluene, ethyl alcohol and finally with diethyl ether and allowed to dry in an oven adjusted to 60 °C for 8 h (see details in Supplementary materials).

2.3. Determination of surface coverage

The determination of surface coverage values of [NPSi-SH] phase was performed by thermal desorption method. In this method, 100 ± 1 mg of dry silica was ignited in a furnace at 550 °C for 1 h and left to cool down at 70 °C. The sample was transferred to a desiccators and left to reach the room temperature. The weight loss was determined by the difference in the sample masses before and after thermal desorption process. Blank samples of silica phase were also subjected to the same procedure.

2.4. Determination of the metal adsorption capacity

The metal adsorption capacity values (mmol g^{-1}) of [NPSi-SH] for the extraction of different metals including this series of ions Mg(II), Ca(II), Mn(II), Cr(III), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II) and Pb(II) in various buffer solutions were determined in triplicate by the static equilibrium technique. In this method, 20.0 mg of dry phase was added to a mixture containing 1.0 ml of 0.1 M metal ion solution and 9.0 ml of the selected buffer solution. This mixture was shaken at room temperature for 30 min by an automatic shaker. The mixture was filtered and washed with 100 ml of DDW. The free metal ion was determined by complexometric titration and/or atomic absorption spectrophotometric analysis.

2.5. The effect of shaking time on metal adsorption capacity

The following time intervals (1, 5, 10, 15, 20, 25 and 30 min) were applied. Hg(II) was tested under these time intervals in presence of buffer solutions with pH values 1, 2, 4, 6 and 0.1 M-NaOAc while Cu(II), Cd(II) and Pb(II) were only tested in 0.1 M-NaOAc by the static technique according to the following procedure. A sample of dry silica phase (20.0 mg) was added to a mixture containing 1.0 ml of 0.1 M-metal ion and 9.0 ml of the selected buffer solution. The reaction mixture was then shaken by an automatic shaker for the selected time, filtered, washed with 100 ml-DDW and the unextracted metal ion was determined by flame atomic adsorption analysis.

2.6. Determination of the percentage extraction of metal ions by [NPSi-SH] from drinking water samples

A concentration of selected metal ions (~1.0 μg ml^{-1}) were spiked into drinking tap water samples and determined by atomic absorption spectrophotometry. A sample of 25.0 mg of [NPSi-SH] was added to 250 ml of water.

2.7. Instrumentation

FT-IR spectrum of [NPSi-SH] was recorded by FT-IR 8400-S Shimadzu Spectrophotometer, Moubarak. Thermolyne 47900 furnace was used to determine the mmol g^{-1} surface coverage values. The thermogravimetric analysis (TGA) and thermoanalytical curves were obtained using a Thermo Gravimetric Analyzer TGA-50 Shimadzu. pH-measurement of metal ions and buffer solutions were carried out by an Orion 420A pH-meter. Determination of the metal concentration was performed using A Perkin-Elmer Optima