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Selective capture of cesium and thallium from natural waters and simulated wastes with copper ferrocyanide functionalized mesoporous silica

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ABSTRACT

Copper(II) ferrocyanide on mesoporous silica (FC-Cu-EDA-SAMMS^{TM}) has been evaluated against iron(III) hexacyanoferrate(II) (insoluble Prussian Blue) for removing cesium (Cs^+) and thallium (Tl^+) from natural waters and simulated acidic and alkaline wastes. From pH 0.1–7.3, FC-Cu-EDA-SAMMS had greater affinities for Cs and Tl and was less affected by the solution pH, competing cations, and matrices. SAMMS also outperformed Prussian Blue in terms of adsorption capacities (e.g., 21.7 versus 2.6 mg Cs/g in acidic waste stimulant (pH 1.1), 28.3 versus 5.8 mg Tl/g in seawater), and rate (e.g., over 95 wt% of Cs was removed from seawater after 2 min with SAMMS, while only 75 wt% was removed with Prussian Blue). SAMMS also had higher stability (e.g., 2.5–13-fold less Fe dissolved from 2 to 24 h of contact time). In addition to environmental applications, SAMMS has great potential to be used as orally administered drug for limiting the absorption of radioactive Cs and toxic Tl in gastrointestinal tract.

1. Introduction

Removal of large monovalent cations, including radioactive cesium (Cs) and highly toxic thallium (Tl), from the environment and nuclear wastes is a subject of significant interest due to the hazards they pose. Radioactive Cs ion is a significant component of nuclear waste and nuclear fallout [1]. For example, in the Hanford site (located in Washington State and operated by the U.S. Department of Energy), 53 million gallons of high-level radioactive wastes are currently stored in 177 underground steel tanks [2]. Some of these tanks are known to have leaked [2], and the waste is still waiting for final disposition. A significant component of radioactivity in spent nuclear fuel arises from ^{137}Cs [3]. It is often a component of dirty bombs. Radiocesium presents serious threat, both to the environment and to humans, as a result of its relatively long half-life ($T_{1/2} = {\sim}30$ years), high solubility/mobility (up to 186, 209, 261, and 400 g/100 g of water at ~20 °C for CsCl, $CsHCO_3$, Cs_2CO_3, and CsOH, respectively), and strong γ-emitting radiation [4]. If exposed *via* ingestion route, Cs is 100% absorbed from the gut to the body and is distributed fairly uniformly throughout the body's soft tissues. ^{137}Cs is the major cause of Thyroid Cancer in Belarus, which took 70% of the fallout from the Chernobyl Nuclear Disaster. Because of its high mobility (it can travel in airborne dust particles, and can be present in food and water), the cleanup of ^{137}Cs is difficult. In this regard, selective removal of Cs from complex mixtures clearly has value in terms of environmental remediation, pollution prevention in the processing of nuclear waste, and biomedicines (e.g., decorporation and chelation therapies of radioactive Cs).

Thallium has been released to the ecosystem as a by-product from the extraction of iron, cadmium and zinc [5,6] as well as from reactions of alloys, dyes, pigments, optical lenses, semiconductors and low-temperature thermometers, where it is used as a catalyst [7,8]. Also, Tl compounds have been used as insecticides and rodenticides because of its highly toxic effects, which are more severe than mercury, lead, copper and cadmium. Thallium is a non-essential toxic element that is bioavailable and has been associated with a number of adverse health effects including: alopecia, psychic disturbances, acute ascending paralysis and cardiovascular effects [9]. Thallium (Tl^+) is also fairly soluble and mobile in environment; the solubility (in g/100 g water) at ~15–20 °C is 0.3, 4.0, 4.9, or 25.9 for TlCl, Tl_2CO_3, Tl_2SO_4, or TlOH, respectively. The United States Environmental Protection Agency has set the maximum Tl levels of 2 μg/L in drinking and 140 μg/L in wastewater [10]. Because of its toxicity, the removal of Tl from groundwater and surface water is very important.

Selective capture of Cs and Tl from aqueous systems is chemically challenging task. These monovalent ions lack chemically unique characteristics and can be competed for the reactive sites by monovalent Group I and divalent Group II cations, which typically are found in much higher concentration. Selective capture

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of monovalent Tl and Cs from contaminated liquid wastes has been performed using co-precipitation, solvent extraction, and solid phase extraction. However, the co-precipitation and solvent extraction have drawbacks such as low selectivity in the presence of competing ions and generation of large amounts of secondary wastes. Therefore, solid phase extraction method that employs inorganic compounds including insoluble molybdates [11], bentonite [12], and mostly metal ferrocyanides [13–16] has attracted a lot of attention due to high selectivity, rapid separation, high thermal and radiation stabilities, and high efficiency in reduction of the waste volumes. However, these sorbents are typically available as fine powders, which have issues with slow filtration rate, making them unsuitable for deployment.

Ordered mesoporous silica (MCM-41) has particle size of ~20 μm and exhibits open pore hexagonal structure, with parallel cylindrical pores, that lead to surface area of ~1000 m^2/g. MCM-41 has been modified with a wide variety of chemical functionalities using molecular self-assembly forming a new class of nanoengineered sorbents called self-assembled monolayers on mesoporous supports (SAMMS^{TM}). SAMMS containing ligands for the selective removal of heavy metals [17,18], lanthanides [19–21], actinides [22,23], radioiodine [24] were reported by our research group. Copper ferrocyanide self-assembled on MCM-41 (FC-Cu-EDA-SAMMS) has been reported previously [25], but the work was focused on design and synthesis of the materials and the sorption performance was focused only on Cs in simple laboratory buffers. Since matrix effects are known to have a significant impact on metal sorption properties of sorbent materials, the study herein is extended to real matrices in which the sorbent materials are intended to be used. Also in this work, Tl sorption is evaluated along with Cs. For the first time, the performance of SAMMS is evaluated against insoluble Prussian Blue, a commercial ferrocyanide resin sorbent counterpart. Prussian Blue is used for environmental cleanup of Cs and Tl and is approved by the FDA for chelation therapies of Cs and Tl. Therefore, this work lays a foundation for using FC-Cu-EDA-SAMMS in chelation therapies of Cs and Tl in order to search for the better materials than the FDA-approved one.

2. Materials and methods

2.1. Reagents and test matrices

Manganese (Mn^{2+}), iron (Fe^{3+}), copper (Cu^{2+}), selenium (Se^{4+}), molybdenum (Mo^{6+}), Zinc (Zn^{2+}), sodium (Na^+), magnesium (Mg^{2+}), calcium (Ca^{2+}), potassium (K^+), cesium (Cs^+) and thallium (Tl^+) were purchased as standard solutions containing 1000 mg/L of appropriate element in ~2% HNO_3 or HCl (Aldrich). Batch metal sorption experiments were performed in natural sea water obtained from the Sequim Bay (WA), which was filtered with 0.45 μm cellulose acetate membranes prior to use. Other test matrices included river water (Columbia River, Richland, WA), groundwater (Hanford, WA), 0.085 M HCl with 0.32% (w/v) pepsin (pH 1.1), and 0.2 M $NaHCO_3$ (pH 8.6); the last two served as waste simulants. Commercially available reagents of highest purity grade (Aldrich Co) were used throughout this study.

2.2. Sorbents

Synthesis of FC-Cu-EDA-SAMMS sorbent was described previously [25]. The substrate was MCM-41 silica with surface properties shown in Table 1. Ethylenediamine (EDA) terminated silane was deposited in refluxing toluene to produce EDA-SAMMS. Next, the EDA-SAMMS were treated with an excess of $CuCl_2$ solution in water, filtered and dried. The Cu-EDA-SAMMS were thermally cured in refluxing toluene (Dean-Stark trap) for 2 h. The Carolina blue powder was collected by filtration and air-dried. Next, a solution of excess sodium ferrocyanide was prepared and the Cu-EDA-SAMMS was added with vigorous stirring. The suspension turned a deep violet color as the ferrocyanide anion reacted with the Cu complex. The FC-Cu-EDA-SAMMS was collected by filtration, washed with water and alcohol and air-dried. The ligand loading capacity (shown in Table 1) of FC-Cu-EDA-SAMMS measured gravimetrically was 3.71 silanes/nm^2. Based on elemental analysis of Cu (e.g., after conc. HNO_3 digestion followed by ICP-MS analysis of Cu of the digestant, and by assuming that one mole of FC-Cu-EDA contains one mole of Cu, one mole of Fe, and three moles of EDA), the ligand loading capacity was 0.81 mmol FC-Cu-EDA/g sorbent or 3.6 silanes/nm^2, which is in good agreement with the number from gravimetric method. Insoluble Prussian Blue, $Fe_4[Fe(CN)_6]_3$, was purchased from Aldrich Co.

Table 1
Surface properties of FC-Cu-EDA-SAMMS.

Properties	Values
Surface area	900 m^2/g (of MCM-41)
Pore size	3.5 nm (of MCM-41)
Ligand loading capacity	3.7 silanes/nm^2 (gravimetric) 3.6 silanes/nm^2 (elemental)

2.3. K_d measurements

The metal sorption performance of FC-Cu-EDA-SAMMS and Prussian Blue was evaluated in term of the distribution coefficient (K_d, mL/g), which is a mass-weighted partition coefficient between solid phase and liquid supernatant phase. The distribution coefficients of Cs and Tl in filtered seawater that contained challenging metals, including 4500 ppm Na, 1000 ppm Mg, 200 ppm Ca, 100 ppm K, 1 ppm Se, and 0.5 ppm (each) of Mn, Fe, Co, Cu, Zn, and Mo, were measured in batch experiments with 0.5 ppm of starting concentrations of Cs and Tl. A 0.01 g weight of sorbent and 10 mL volume (sorbent per liquid, S/L, of 1.0 g/L) of the test solution was shaken in a polypropylene bottle at a speed of 200 rpm for 2 h at room temperature. The pH of multicomponent metal ion solution was adjusted to a desired pH values with HNO_3 and/or NaOH solutions. After the batch contacts, the suspension was filtered through 0.2 μm Nylon filter in a polypropylene housing in order to remove the metal-laden sorbent materials from the solution and left the unbound metal ions in the solution. Both initial and final solutions (before and after the batch experiments) were analyzed by an inductively coupled plasma-mass spectrometer (ICP-MS, Agilent 7500ce, Agilent Technologies, CA). The measurements were carried out in duplicates and triplicates and the average values were reported. The K_d values of Cs and Tl were also measured in river water, ground water, acidic and alkaline waste simulants. Along with the batch contact, the test solution without sorbent materials was shaken also for 2 h. After the shaking period, testing for precipitation or insolubility of the metal ions in the test solution was performed using 0.2 μm filters; reduced metal contents in the filtrate from those in the starting solution would indicate precipitation or insolubility of the metals in that solution. No precipitation/insolubility of Cs or Tl was detected.

2.4. Sorption isotherms

The sorption capacity of FC-Cu-EDA-SAMMS and Prussian Blue for metal ions was measured in the same fashion as with the K_d, but only a single element (e.g., Cs and Tl) was used and its concentration was varied in the solution until maximum sorption capacity was obtained. This was accomplished by using a large excess of metal ions to the number of binding sites on the sorbent materials (e.g.,