

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-SAMMSTM) 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.

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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 ¹³⁷Cs [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 $\sim 20^\circ\text{C}$ for CsCl, CsHCO₃, Cs₂CO₃, 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. ¹³⁷Cs 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 ¹³⁷Cs 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 $\sim 15\text{--}20^\circ\text{C}$ is 0.3, 4.0, 4.9, or 25.9 for TlCl, Tl₂CO₃, Tl₂SO₄, or TlOH, respectively. The United States Environmental Protection Agency has set the maximum Tl levels of 2 $\mu\text{g/L}$ in drinking and 140 $\mu\text{g/L}$ 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 $\sim 20 \mu\text{m}$ and exhibits open pore hexagonal structure, with parallel cylindrical pores, that lead to surface area of $\sim 1000 \text{m}^2/\text{g}$. 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 (SAMMSTM). 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 $\sim 2\%$ 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 $0.45 \mu\text{m}$ 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 pow-

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	3.7 silanes/ nm^2 (gravimetric)
capacity	3.6 silanes/ nm^2 (elemental)

der 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, $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$, was purchased from Aldrich Co.

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 $0.2 \mu\text{m}$ 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 also 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 $0.2 \mu\text{m}$ 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.,

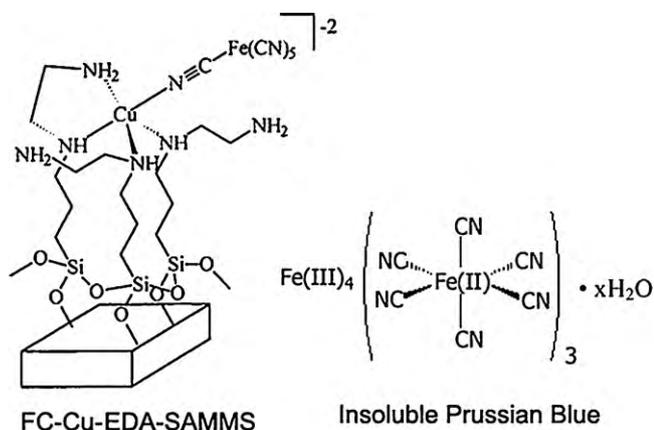


Fig. 1. Chemical structures of FC-Cu-EDA-SAMMS and Prussian Blue.

0.25–50 mg/L initial concentration of Cs⁺ or Tl⁺ at 0.1 g sorbent/L of solution).

2.5. Sorption kinetics

Kinetics experiments were carried out similarly to batch experiments except that a 0.1 g quantity of sorbent was dispersed in a 100 mL volume of filtered seawater containing 0.5 ppm (each) of Cs⁺ and Tl⁺. The aliquots were removed at 1, 2, 5, 10, 30, 60 min, 2, 8, and 24 h, filtered through a 0.2 μm Nylon filters and subjected to ICP-MS analysis along with the initial solution (zero min point).

2.6. Material stability

Along with the K_d measurements, Si, Fe and Cu were measured in the solutions before and after batch contacting with FC-Cu-EDA-SAMMS and Prussian Blue. The mg Si, Fe and Cu dissolved per gram of material was reported for each solution matrix as the average value of three replicates.

3. Results and discussion

In this study, the sorption performance of copper(II) ferrocyanide immobilized on mesoporous silica (FC-Cu-EDA-SAMMS) for Cs and Tl from aqueous media was evaluated in terms of adsorption affinity, rate, capacity, and materials stability. The performance was also evaluated against insoluble Prussian Blue, which is considered the best commercially available sorbent for Cs and Tl, and also FDA-approved in 2003 for radioactive Cs and Tl chelation therapies [26]. Fig. 1 illustrates the chemical structures of the FC-Cu-EDA-SAMMS and insoluble Prussian Blue.

3.1. Adsorption affinity for Cs and Tl

The adsorption affinity of the large monovalent Cs and Tl on FC-Cu-EDA-SAMMS and Prussian Blue have been investigated using seawater, the most challenging matrix among natural waters (sea, river, ground water) due to its highest ionic strength. The sorption affinity is often represented in term of the distribution coefficient, K_d (in the unit of mL/g), which is calculated as:

$$K_d = \frac{(C_o - C_f)}{C_f} \times \frac{V}{M} \quad (1)$$

where C_o and C_f are the initial and final concentrations in the solution of the target species determined by ICP-MS, V is the volume of solution in milliliters, and M is the mass of material in grams. The distribution coefficient expresses the chemical binding affinity of target metal ion to a sorbent and is most meaningful at dilute metal

concentrations. The higher the K_d values the stronger binding affinity. Generally speaking, a K_d value of 5000 and above is considered good, and a K_d value greater than 50,000 is considered excellent. The K_d values of Cs and Tl were evaluated as a function of solution pH and in the presence of competing cations.

3.1.1. The effect of pH

Metal sorption from aqueous solutions can be greatly affected by the solution pH, which impacts not only the binding sites (e.g., degree of protonation) but also the metal chemistry (e.g., speciation and precipitation). In order to determine optimal pH for the capture of Cs and Tl, their K_d values on FC-Cu-EDA-SAMMS and Prussian Blue were measured in pH-adjusted seawater containing various challenging metals. The results are presented in Table 2. Note that zero value of K_d in Table 2 is by approximation; it indicates no detectable change in solution metal concentrations before and after applying sorbent materials (e.g., no adsorption). In the pH 0.1–7.3 range (measured and reported as equilibrium solution pH since K_d are equilibrium values), Cs and Tl are present completely as soluble Cs⁺ and Tl⁺. The K_d of Cs on both sorbents increased with increasing pH from 0.1 to 7.3 and was higher on FC-Cu-EDA-SAMMS than on Prussian Blue for the whole pH range. On FC-Cu-EDA-SAMMS, the K_d of Cs was above 25,000 under acidic conditions, and above 100,000 under near neutral conditions. Prussian Blue was found to be far less effective.

Capturing of Tl by FC-Cu-EDA-SAMMS was less effective than Cs, yet the K_d values for Tl were still respectable with K_d on the order of 10,000 for the entire pH range. Once again, FC-Cu-EDA-SAMMS was more effective than Prussian Blue for Tl capture. The higher K_d values indicate that FC-Cu-EDA-SAMMS is more effective than Prussian Blue at capturing Cs and Tl, in seawater, and under both acidic and alkaline conditions.

3.1.2. The effect of competing ions

The adsorption of target species on a sorbent can be greatly influenced by the presence of other ions present in natural waters that may compete for the binding sites. The effect of other common and transition metal ions present in seawater on the adsorption of Cs and Tl on FC-Cu-EDA-SAMMS and Prussian Blue was evaluated. These competing metals were both naturally occurring and spiked to the seawater (types and concentrations were listed in Table 2). Table 2 summarizes the distribution coefficients of Cs and Tl along with other competing metals. Even with the very high concentration of other competing metals, the FC-Cu-EDA-SAMMS could still capture Cs and Tl very effectively ($K_d \sim 10^4$ – 10^5) as explained in the previous section. On FC-Cu-EDA-SAMMS, no other metals tested appear to compete well with Cs and Tl, with a few exceptions including Cu, and Zn. The two metal ions appeared to bind well with FC-Cu-EDA-SAMMS at near neutral pH, but did not inhibit the material from binding Cs. On the other hand, with Prussian Blue the competition by other metal ions appeared to be more severe, especially that by Zn starting from pH 6.3 and Cu starting from pH 0.1. The high K_d values of Cs and Tl on FC-Cu-EDA-SAMMS also suggest that other common cations (e.g., Na, Mg, Ca, and K) present in very large excess of Cs and Tl did not affect the binding of Cs and Tl on the SAMMS material, which in turn indicated strong affinity between large monovalent cations (Cs and Tl) and SAMMS.

3.1.3. Matrix effect

The composition of the matrix can have a significant impact on the performance of a sorbent material due to the presence of competing ions, complexing anions, dissolved organic matter and suspended colloids. Therefore, it is important to evaluate potential sorbent materials in matrices that accurately represent those conditions under which it will likely be employed. For applications in environmental, industrial waste and nuclear waste remediation,

Table 2
Distribution coefficients (K_d , mL/g) for adsorption of various cations on FC-Cu-EDA-SAMMS and Prussian Blue (PB) in seawater.

Competing metal	Concentration (ppm)	Sorbent	pH 0.1	pH 2.1	pH 3.4	pH 6.3	pH 7.3
Cs(I)	0.5	SAMMS	26000	46000	75000	110000	140000
		PB	680	770	950	17000	52000
Tl(I)	0.5	SAMMS	8300	12000	14000	14000	14000
		PB	450	280	550	4500	8600
Na(I)	4500	SAMMS	0	19	0	14	0
		PB	0	1	4	16	8
Mg(II)	1000	SAMMS	0	15	0	10	5
		PB	0	0	13	11	4
Ca(II)	200	SAMMS	0	13	2	10	0
		PB	0	0	26	0	0
K(I)	100	SAMMS	0	0	0	8	0
		PB	0	0	23	18	19
Se(IV)	1	SAMMS	8	0	120	110	140
		PB	0	29	230	450	490
Mn(II)	0.5	SAMMS	0	0	16	68	270
		PB	0	1	19	910	4100
Fe(III)	0.5	SAMMS	26	26	3300	1400	520
		PB	0	0	0	1700	0
Cu(II)	0.5	SAMMS	0	0	4200	14000	6500
		PB	6800	14000	20000	610000	560000
Zn(II)	0.5	SAMMS	0	0	2200	19000	79000
		PB	0	29	110	260000	81000
Mo(VI)	0.5	SAMMS	61	130	220	41	17
		PB	170	110	660	170	95

Measured in pH-adjusted filtered seawater, S/L of 1.0 g/L.

Table 3
Adsorption affinity (K_d in mL/g) of Cs and Tl on FC-Cu-EDA-SAMMS and Prussian Blue in various matrices.

Matrix	Metal (ppb)	S/L (g/L)	FC-Cu-EDA-SAMMS		Prussian Blue	
			Cs	Tl	Cs	Tl
Columbia River water, pH 7.3	500	1.0	1700000	3100000	250000	1200000
Hanford groundwater, pH 7.5	500	1.0	1400000	2800000	250000	790000
Sequim Bay seawater, pH 7.4	500	1.0	240000	16000	85000	15000
0.085 M HCl, pH 1.1	50	0.2	156000	NA	5400	NA
0.2 M NaHCO ₃ , pH 8.6	50	0.2	230000	NA	73000	NA

the sorbent materials were evaluated in the three natural waters and acidic and alkaline waste stimulants. Their K_d values in these matrices for Cs and Tl are summarized in Table 3. A similar trend can be seen for both sorbents where Cs and Tl adsorption was greater in river and ground water than in seawater having the highest ionic strength. The high ionic strength appeared to negatively affect the Prussian Blue more than the FC-Cu-EDA-SAMMS. When moving toward extreme acidic (pH 1.1) and alkaline (pH 8.6) conditions, it becomes more apparent that FC-Cu-EDA-SAMMS maintains its sorption affinity for Cs (no data available for Tl) (e.g., the K_d values $\sim 10^5$, similar to that in seawater), while Prussian Blue binding affinity for Cs is significantly decreased at low pH ($K_d \sim 5400$).

3.2. Adsorption capacity

An adsorption isotherm curve is a plot between the equilibrium adsorption capacities (Q_e in mg metal ion/g sorbent, as represented in Eq. (2)) versus equilibrium solution metal concentrations (C_e in mg metal ion/L of solution). Figs. 2 and 3 show the adsorption isotherm curves of Cs and Tl, respectively. They were measured by increasing the loadings of Cs or Tl in filtered seawater (pH 7.7) onto a sorbent material (FC-Cu-EDA-SAMMS or Prussian Blue) while maintaining sorbent-to-liquid ratio of 0.1 g/L. While the K_d value (Section 3.1) indicates how effective an adsorbent is at capturing

the target metal ion at very dilute metal conditions, the adsorption capacity indicates its effectiveness at or near saturation conditions of the metal ion relative to the binding site loading of the sorbent material. Sorbent with highest K_d does not necessarily offer the

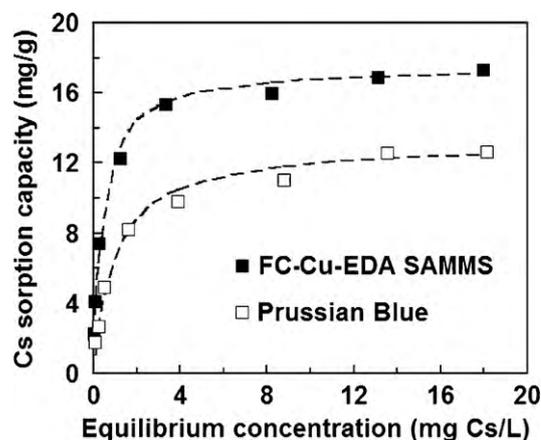


Fig. 2. Cs adsorption capacity of FC-Cu-EDA-SAMMS and Prussian Blue, measured in filtered seawater (pH 7.8), S/L of 0.1 g/L, dashed lines represent Langmuir isotherm models.

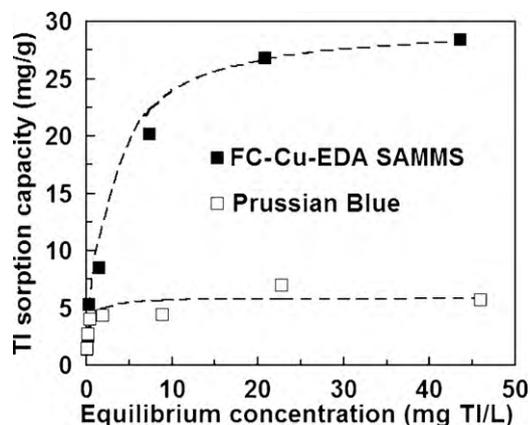


Fig. 3. TI adsorption capacity of FC-Cu-EDA-SAMMS and Prussian Blue, measured in filtered seawater (pH 7.8), S/L of 0.1 g/L, dashed lines represent Langmuir isotherm models.

highest sorption capacity and vice versa. However, according to Eqs. (1) and (2), the K_d value can be estimated from the sorption isotherm curve while the metal concentration is very dilute (e.g., at the onset of the curve, K_d (in L/g) = Q_e/C_e).

$$Q_e = (C_o - C_e) \frac{V}{M} \quad (2)$$

Some adsorption isotherm data can be fitted to the Langmuir adsorption model, which is given by Eq. (3).

$$Q_e = \frac{Q_{\max} K_L C_e}{1 + K_L C_e} \quad (3)$$

where Q_{\max} is the adsorption capacity (mg of metal/ion/g of sorbent) when all adsorption sites are occupied, C_e is the equilibrium concentration of the metal ion, and the Langmuir constant K_L (L of solution/mg of metal ion) represents the ratio of the adsorption rate constant to the desorption rate constant. Both Cs and TI adsorption isotherm data on both materials were in agreement with the Langmuir model with an excellent fit ($R^2 > 0.99$), indicating monolayer adsorption (without precipitation) of Cs and TI ions. The maximum sorption capacities for Cs and TI estimated from the Langmuir model are listed in Table 4. Even in seawater with high ionic strength and large excess of other cations, FC-Cu-EDA-SAMMS still exhibited large maximum sorption capacities (17.1 mg Cs and 28.3 mg TI per gram of SAMMS, or equivalent to ~ 0.13 mmol of Cs or TI per gram of SAMMS), owing to chemically selective binding sites and high surface area of the mesoporous structure, while the capacities of TI and Cs on Prussian Blue were much smaller (12.5 mg Cs and 5.82 mg TI per gram of Prussian Blue). In addition to seawater, the isotherms for Cs were also measured in acid and alkaline waste simulants and the maximum sorption capacities of Cs in

Table 4
Maximum capacity of FC-Cu-EDA-SAMMS and Prussian Blue for Cs and TI as estimated by Langmuir sorption isotherm model.

Metal	Sorbent	Matrix	Max. capacity (mg/g) ^a	R ²
Cs	FC-Cu-EDA-SAMMS	Seawater, pH 7.7	17.1	0.999
Cs	Prussian Blue		12.5	0.997
TI	FC-Cu-EDA-SAMMS		28.3	0.997
TI	Prussian Blue		5.82	0.987
Cs	FC-Cu-EDA-SAMMS	0.085 M HCl, pH 1.1	21.7	0.974
Cs	Prussian Blue		2.60	0.998
Cs	FC-Cu-EDA-SAMMS	0.2 M NaHCO ₃ , pH	17.9	0.999
Cs	Prussian Blue	8.6	16.5	0.994

^a All measured with S/L of 0.1 g/L.

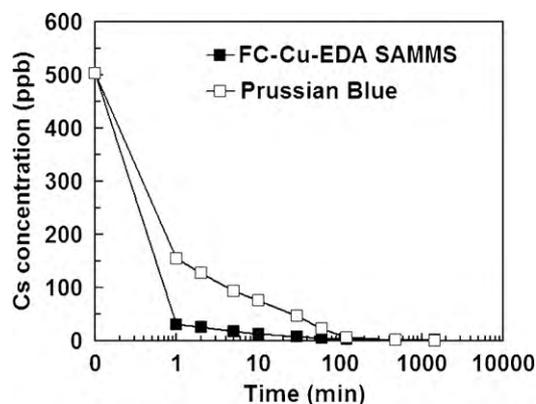


Fig. 4. Sorption kinetics of Cs from filtered seawater (pH 7.7) using FC-Cu-EDA-SAMMS and Prussian Blue, S/L of 1.0 g/L.

these two matrices are reported in Table 4. In 0.05 M NaHCO₃ used as alkaline waste simulant, FC-Cu-EDA-SAMMS has slightly higher maximum sorption capacity for Cs than Prussian Blue (17.9 versus 16.5 mg/g). However, in 0.085 M HCl used as acid waste simulant, the FC-Cu-EDA-SAMMS has eight-fold higher Cs sorption capacities than Prussian Blue. This could be that defect sites in the Prussian Blue is getting protonated, thereby reducing the number of anion equivalents inherent to the sorbent and therefore limiting the number of Cs ions that can be exchanged.

3.3. Adsorption kinetics

The sorption kinetics of Cs on FC-Cu-EDA-SAMMS and Prussian Blue is shown in Fig. 4, and that of TI in Fig. 5. All were measured in filtered seawater (pH 7.7), which was spiked with both Cs and TI at 0.5 ppm (each) and at a sorbent-to-liquid ratio of 1.0 g/L. The adsorption rate of both Cs and TI was more rapid on FC-Cu-EDA-SAMMS than on Prussian Blue. Specifically, Fig. 4 shows that over 95 wt% of Cs was removed after 2 min with SAMMS, while only 75 wt% was removed with Prussian Blue; in fact it took about 60 min to achieve the 95 wt% of Cs removal with Prussian Blue. The adsorption rate for TI was somewhat slower than Cs on both materials, which may be due to the larger size of TI, or possibly because it is a “softer” cation. However, as seen in Fig. 5, SAMMS still outperformed Prussian Blue by achieving 85 wt% of TI removal after 2 min, while Prussian Blue achieved only 40 wt% of TI removal.

In Prussian Blue, the pore structure arises directly from the molecular dimensions of the building blocks used to make it. As a result, the pores are small, and diffusion through them is

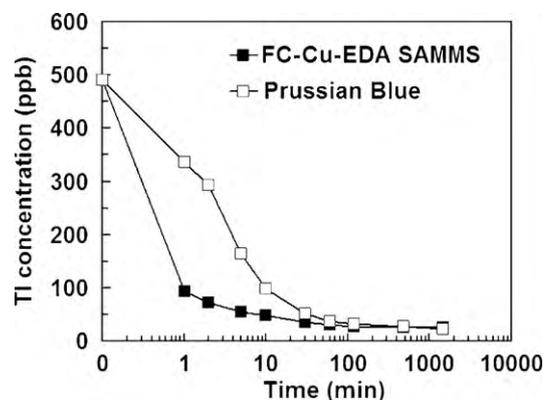


Fig. 5. Sorption kinetics of TI from filtered seawater (pH 7.7) using FC-Cu-EDA-SAMMS and Prussian Blue, S/L of 1.0 g/L.

slower than would be experienced in a mesoporous architecture like SAMMS. In addition, the ferrocyanide Cs sorbents (including Prussian Blue) work because the Cs adduct is insoluble, suggesting that once the Cs is bound to a site in Prussian Blue, it does not move from that site. This binding event occupies pore volume, making the pore even smaller, and restricting diffusion even more (and perhaps even shutting it down entirely). Thus a binding event in Prussian Blue will have an impact on the ability of neighboring binding sites to bind Cs ions. This inherent limitation of Prussian Blue will negatively impact both capacity and kinetics for the capture of Cs. On the other hand, SAMMS is built on a mesoporous silica with pore diameter of several dozen Angstroms, and the binding sites are all at the interface and readily accessible to solution-borne species. With the larger pores of SAMMS, diffusion is faster, allowing the binding chemistry to take place more rapidly. Also, binding Cs at one ferrocyanide site has virtually no impact on the Cs binding at an adjacent site as a result of their site isolation. This allows virtually all of the ferrocyanide sites of SAMMS to bind Cs, and to do it very quickly, resulting in larger capacity and faster adsorption rate than those on Prussian Blue as evidenced by the data in Sections 3.2 and 3.3.

For capturing of Cs and Tl, which are normally present at very dilute levels in the natural waters and nuclear wastes, the most important performance measures are K_d and adsorption rate (since the adsorption must overcome mass transfer limitation of metal ions especially at dilute metal conditions). The maximum adsorption capacity is a less important measure since at dilute metal conditions the sorbents normally operate at far below saturation capacity (granted that the materials are selective for the target metals and not saturated by the non-target metals like FC-Cu-EDA-SAMMS). Besides insoluble Prussian Blue, other outstanding sorbent materials for Cs according to their K_d values are Tin(IV) phosphate (K_d of 200,000 mL/g, measured in a groundwater simulant (pH ~3.5) containing 100 ppm Ca, 10 ppm Mg, 15 ppm Na, and 6 ppm Cs [27]) and calix [4] arene impregnated zeolite (K_d of 27,630 mL/g, measured in water (pH 5.0) containing 464 ppm K [28]). The K_d values are very comparable to our materials (K_d of 140,000 mL/g, measured in seawater (pH 7.3) containing 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, Tl, and Mo). However, SAMMS is superior in term of adsorption rate; to achieve such equilibrium K_d values, the contact time required for the Tin(IV) phosphate was 5 days and for the calix [4] arene impregnated zeolite was 6 h, while SAMMS material reached equilibrium K_d within 5 min.

3.4. Material stability

There are several methods to determine sorbent stability after exposure to seawater for prolonged periods of time. One of them is to monitor the dissolved amount of elements such as Si, Fe and Cu for FC-Cu-EDA-SAMMS and Fe for Prussian Blue. Fig. 6 shows leaching of Fe and Cu from FC-Cu-EDA-SAMMS and Fe from Prussian Blue. The leachate of Fe from FC-Cu-EDA-SAMMS was only ~0.4 mg/g after 24 h, while that from Prussian Blue was as high as 2.6 mg/g after 8 h and 4.6 mg/g after 24 h. There was also a small amount of Cu leachate from FC-Cu-EDA-SAMMS (~0.1–0.2 mg/g) within 24 h, which if needed can be reduced by prewashing of the material prior to use. It should be noted that there was also a gradual Si leaching (up to 6.8 mg/g after 24 h) from SAMMS. This might be due to leaching of small amounts of residual polysiloxane left behind from the synthesis, rather than the decomposition of monolayers, which is felt to be less likely due to the strong covalent bonding between the organosilane anchor and the silica substrate, as well as the high degree of cross-linking between the organosilanes.

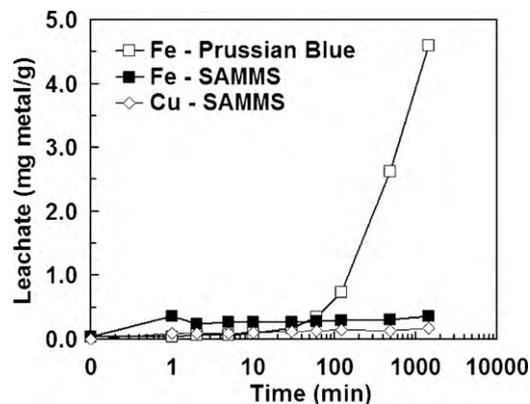


Fig. 6. The dissolved Cu and Fe from FC-Cu-EDA-SAMMS and dissolved Fe from Prussian Blue as a function of contacting time between the material and seawater (pH 7.7), S/L of 1.0 g/L.

3.5. Potential use of SAMMS in medicine

It is worth noting that in the matrix effect study, 0.085 M HCl (pH 1.1) and 0.2 M NaHCO₃ (pH 8.6) not only served as waste simulants, but they have also been used as gastric fluid [29] and intestinal fluid simulants [30,31]. The fact that Cs and Tl bind FC-Cu-EDA-SAMMS more favorably and less negatively affected by matrices (pH, competing metals, ionic strength) than do Prussian Blue suggests that the FC-Cu-EDA-SAMMS may be used in the same manner with Prussian Blue (i.e., oral drug for limiting gut absorption of Cs and Tl), but capable of providing better therapeutic results. In addition, FC-Cu-EDA-SAMMS appears to be stable chemically and can be made on silica substrate approved by FDA for food additives, suggesting that the material might be safer for use in humans. Lastly, SAMMS can be attached with various organic groups, and the cocktail of SAMMS mixture is hence being investigated for preventing gut absorption of multiple radionuclides that may be encountered as components of dirty bombs. Among them are cobalt, strontium, polonium, cesium, and iodine, which absorb in adults' gastrointestinal tract for 10%, 30%, 50%, 100%, and 100%, respectively [32]. Results will be reported in due course.

4. Conclusion

The FC-Cu-EDA-SAMMS was superior to insoluble Prussian Blue for capturing of Cs and Tl in all aspects investigated, including adsorption affinity, adsorption capacity, adsorption rate, and material stability. In addition, SAMMS also had broader working pHs. The binding of Cs and Tl on SAMMS was less interfered by other competing metal ions and less negatively affected by solution matrices.

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