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Aqueous ^{99}Tc, ^{129}I and ^{137}Cs removal from contaminated groundwater and sediments using highly effective low-cost sorbents

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Technetium-99 (^{99}Tc), iodine-129 (^{129}I), and cesium-137 (^{137}Cs) are among the key risk-drivers for environmental cleanup. Immobilizing these radionuclides, especially TcO_4^- and I^-, has been challenging. TcO_4^- and I^- bind very weakly to most sediments, such that distribution coefficients (K_d values; radionuclide concentration ratio of solids to liquids) are typically <2 mL/g; while Cs sorbs somewhat more strongly (K_d ~ 50 mL/g). The objective of this laboratory study was to evaluate 13 cost-effective sorbents for TcO_4^-, I^-, and Cs^+ uptake from contaminated groundwater and sediments. Two organoclays sorbed large amounts of TcO_4^- ($K_d > 1 \times 10^5$ mL/g), I^- ($K_d \geq 1 \times 10^4$ mL/g), and Cs^+ ($K_d > 1 \times 10^3$ mL/g) and also demonstrated a largely irreversible binding of the radionuclides. Activated carbon GAC 830 was effective at sorbing TcO_4^- ($K_d > 1 \times 10^5$ mL/g) and I^- ($K_d = 6.9 \times 10^3$ mL/g), while a surfactant modified chabazite was effective at sorbing TcO_4^- ($K_d > 2.5 \times 10^4$ mL/g) and Cs^+ ($K_d > 6.5 \times 10^3$ mL/g). Several sorbents were effective for only one radionuclide, e.g., modified zeolite Y had TcO_4^- $K_d > 2.3 \times 10^5$ mL/g, AgS had I^- $K_d = 2.5 \times 10^4$ mL/g, and illite, chabazite, surfactant modified clinoptilolite, and thiol-SAMMS had Cs^+ $K_d > 10^3$ mL/g. These low-cost and high capacity sorbents may provide a sustainable solution for environmental remediation.

1. Introduction

Technetium-99 and iodine-129 are two of the three most common risk drivers (along with ^{14}C) in low-level and high-level waste disposal sites and among the most common environmental contaminants at DOE sites. The worldwide inventory of Tc- and I-bearing nuclear wastes continues to increase rapidly due to the demand for more electricity and the need for nuclear power as an alternative energy source that emits less CO_2 than fossil fuels. ^{99}Tc and ^{129}I can adversely enter groundwater and sediments from mismanaged wastes or through leakage from waste or spent fuel storage facilities.

Technetium-99 is a long-lived radionuclide contaminant ($t_{1/2} = 0.22$ million years) and very mobile in groundwater due to its existence dominantly as the anionic species, TcO_4^- (Icenhower et al., 2010). The TcO_4^- is not immobilized by most common minerals or inorganic sorbents because it is repulsed by their negative charge (Liang et al., 1996). The fate and mobility of ^{129}I in environmental systems is especially complex due to its existence in several oxidation states (commonly as −1 (I^-), +5 (IO_3^-), and 0 (organo-I)) and its tendency to form strong covalent bonds with natural organic matter (Kaplan et al., 2014). Adsorption behaviors of IO_3^- and I^- onto sediments and some oxide/sulfide minerals can be quite different, and the IO_3^- sorption is normally greater than I^- (Kaplan et al., 2014). Cesium-137 is a major radionuclide in spent nuclear fuel reprocessing, primarily due to its high fission yield. Radioactive Cs isotopes are commonly the most important risk drivers immediately after a nuclear accident, such as those that occurred at Chernobyl and Fukushima (Whicker et al., 2007). Cesium forms few inorganic or organic complexes in natural systems due to its hydrated nature and large ionic radius.

Various sorbents are presently being used to remove radiological and non-radiological inorganic contaminants out of groundwater (Cundy et al., 2008; Guo et al., 2006; Misaelides, 2011). Unlike for organic contaminants that can be chemically degraded or converted to less toxic compounds, the intent of inorganic contaminant sorbents is to reduce the mobility of the contaminants and to reduce their bioavailability/toxicity. Some of the more common modes of immobilization is reductive precipitation with various iron phases (Cundy et al., 2008), sorption into high surface area clays and porous zeolites (Misaelides, 2011), co-precipitation into less mobile phosphate or sulfur phases (Guo et al., 2006), and more recently, partitioning to surface modified clays or

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Table 1
Selected materials for $^{99}TcO_4^-$, $^{129}I^-$ and $^{137}Cs^+$ sorption evaluation.

Sorbents	Acronym	Description	Manufacturer
Activated carbon 824 BC	824 BC	Bone char 824 BC, Brimac Carbon, coarse granular bone charcoal (8 × 24 mesh) produced by carbonization of selected grades of animal bone	Charcoal House™ Brand, Crawford, NE
Activated carbon GAC 830	GAC 830	Norit® GAC 830, granular activated carbon produced by steam activation of select grades of coal	Norit America, Inc. (Cabot Corp.), Marshall, TX
Apatite II		Fish bone, phosphate mineral	PIMS-NW, Inc., Richland, WA
Chitosan		A biopolymer derived from crustaceans shells	AIDP, Inc., City of Industry, CA
Illite		Todd Light™ Illite, a natural clay mineral	Kentucky–Tennessee Clay Company, Nashville, TN
Organoclay OCB	OCB	ClayFloc™ 750, a bentonite organoclay based flocculant impregnated with a quaternary amine	Biomin Inc., Ferndale, MI
Organoclay OCM	OCM	Organoclay MRM™ clay impregnated with a sulfur-containing organic compound	CETCO® Remediation Technologies, Hoffman Estates, IL
Argentite (AgS)		A natural sulfide mineral	Ward's Science, Des Moines, IO
Thiol-SAMMS		Self-Assembled Monolayers on Mesoporous Silica (SAMMS) modified with thiol functionalization	Steward Environmental Solutions, Chattanooga, TN
Chabazite		Engineered Herschelite KUR-EH, a natural chabazite mineral	Kurion, Inc., Oak Ridge, TN
Surfactant modified chabazite	SM chabazite	Herschelite KUR-CH, a surfactant modified natural chabazite mineral	Kurion, Inc., Oak Ridge, TN
Surfactant modified clinoptilolite		Herschelite KUR-SMZ, a surfactant modified clinoptilolite mineral	Kurion, Inc., Oak Ridge, TN
Modified zeolite Y		CBV-780, a synthetic zeolite	Zeolyst International, Valley Forge, PA

organoclays (Yariv and Cross, 2002). For example, zeolite-based sorbents have been used to remove Co, Ni, Se, Sb, Tc, I, Cs and Sr from aqueous media (Bonhomme et al., 2010; Denton and Bostick, 2011). Organoclay OCM with a sulfur-containing quaternary amine was patented for Hg and As removal from water (Wang and Abraham, 2011). Organoclay OCB has been used as a sequestering agent for active cap remediation of metals and organic contaminants (Knox et al., 2007).

The objective of this study was to evaluate several low-cost sorbents for their effectiveness to bind aqueous $^{99}TcO_4^-$, $^{129}I^-$ and $^{137}Cs^+$. Many of these sorbents have been used for other non-radioactive contaminants. Therefore the goal of this study was more specifically to evaluate whether these environmentally benign sorbents could be extended to effectively sorb TcO_4^-, I^-, and Cs^+. As such, the scope of this study was not to determine the maximum sorption capacity, sorption kinetics, or to elucidate the sorption mechanism. While these are critical criteria for full evaluation of sorbents, they are the subject of on-going experimentation.

2. Materials and methods

2.1. Sorbent materials

A variety of sorbents were evaluated for $^{99}TcO_4^-$, $^{129}I^-$, and $^{137}Cs^+$ removal from the aqueous phases (Table 1). Tested sorbent materials included: 1) activated carbons (824 BC and GAC 830), 2) apatite (fish bone), 3) biopolymer (chitosan), 4) clay mineral (illite), 5) organoclays (OCB and OCM), 6) silver sulfide (AgS), 7) thiol-functionalized self-assembled monolayer on mesoporous silica (thiol-SAMMS), and 8) zeolites (chabazite, surfactant modified chabazite, surfactant clinoptilolite, and modified zeolite Y). These sorbents were tested because of their low cost (except for thiol-SAMMS) and expected high capacity to sorb $^{99}TcO_4^-$, $^{129}I^-$, and/or $^{137}Cs^+$ from low-level nuclear waste streams and contaminated groundwater.

2.2. Radionuclide chemicals

The radionuclide stock solutions were purchased from Eckert & Ziegler Isotope Products (Valencia, CA). The as-received stock solutions were 1.85×10^4 kBq/mL NH_4TcO_4 in H_2O, 7.4 kBq/mL NaI in 0.1 M NaOH, and 4.07×10^4 kBq/mL CsCl in 0.1 M HCl. The ^{99}Tc stock solution was diluted with deionized water to create an 18.5 kBq/mL ^{99}Tc spike solution. The ^{129}I stock solution was diluted with 0.1 M NaOH to create an 1.85 kBq/mL ^{129}I spike solution. The ^{137}Cs stock solution was diluted with 0.1 M HCl to create a 0.204 or 2.04 kBq/mL ^{137}Cs spike solution.

2.3. Contaminated sediment

To demonstrate the effectiveness of selected sorbents for the treatment of contaminated sediments, Tc-amended Savannah River Site (SRS) clayey sediment was selected to perform a proof-of-concept experiment. The SRS sediment has the following properties (Kaplan, 2010): pH 4.55 (measured for a suspension of 50 g sediment in 50 mL deionized water), 57% sand, 41% silt, 2% clay (pipette method), 1.2% organic matter (CHOS Niko Analyzer), 1.1 cmol/kg cation exchange capacity (un-buffered NH_4Cl exchange), 1.6 cmol/kg anion exchange capacity (un-buffered NH_4Cl exchange), 15.3 m^2/g surface area (BET analyzer), and a clay-size mineralogy composed primarily of kaolinite, goethite, hematite, and quartz (based on XRD). To prepare the ^{99}Tc-amended sediment, 0.4 mL of 1.99×10^4 Bq/mL ^{99}Tc solution was added to 120 mL deionized water, which was then added to 900 g of the air-dried SRS sediment described above. The moistened sediment was mixed by shaking in a double baggie with plenty of air space. The Tc-spiked sediment was then air dried for two weeks to promote Tc and sediment contact. The sediment had a final ^{99}Tc concentration of 8.66 Bq/g, a concentration well within the range of values reported in contaminated sites on the SRS (Denham et al., 2004).

2.4. Artificial groundwater (AGW)

An artificial groundwater (AGW) solution was used in the batch sorption studies. Its chemical composition is based on the average groundwater composition reported in a survey of 26 uncontaminated wells located on the SRS. The AGW had a pH of ~6.0, electrical conductivity of 0.026 mS/cm, turbidity of <1 NTU, and the following