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

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ABSTRACT

^{99}Tc, ^{129}I and ^{137}Cs are among the radionuclide contaminants of serious concerns in the environment and in various waste streams. Immobilizing these radionuclides, especially the two anions, $^{99}TcO_4^-$ and $^{129}I^-$, has been especially challenging. The objective of this study was to conduct a laboratory survey for cost-effective and highly capable sorbents for $^{99}TcO_4^-$, $^{129}I^-$ and $^{137}Cs^+$ removal from contaminant aqueous and sediment systems. Two organoclays, OCB and OCM, demonstrated not only large capacities for TcO_4^- ($K_d > 1\times10^5$ mL/g), I^- ($K_d \geq 1\times10^4$ mL/g), and Cs^+ ($K_d > 1\times10^3$ mL/g), but also bound the radionuclides in a largely irreversible manner, except significant I^- desorption was measured at reduced pH values from the organoclay OCB. Activated carbon GAC 830 was effective at sorbing Tc ($K_d > 1\times10^5$ mL/g) and I ($K_d = 6.9\times10^3$ mL/g), while a surfactant-modified chabazite was effective for both Tc ($K_d > 2.5\times10^4$ mL/g) and Cs ($K_d > 6.5\times10^3$ mL/g) removal. A modified zeolite Y sorbent was effective for Tc removal ($K_d > 2.3\times10^5$ mL/g), while AgS was only effective for iodine. In addition, natural illite, natural chabazite, surfactant-modified clinoptilolite, and Th-SAMMS were especially selective for Cs. These low-cost and high capacity sorbents may provide a sustainable and cost-effective resolution to the treatment of nuclear waste and environmental remediation.

Keywords: Technetium, Iodine, Cesium, Organoclays, Sorbents

1. Introduction

^{99}Tc and ^{129}I are two of the three most common risk drivers (along ^{14}C) in low-level and high-level nuclear waste disposal sites and among the most common environmental radiological contaminants. The inventory of Tc- and I-bearing nuclear wastes continues to increase [1, 2], driven by 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 is a long-lived radionuclide contaminant ($t_{1/2}$ = 0.22 Myr) and very mobile in groundwater due to its tendency to exist as the anionic species, TcO_4^-, which sorbs very little or not at all to sediment minerals [3]. The fate and

mobility of ^{129}I in environmental systems is especially complex owing to its tendency to exist in several different oxidation states (I^-, IO_3^-, and organo-I), and its tendency to form strong covalent bonds with even trace concentrations of natural organic matter [4]. Sorption of iodine species appears to be controlled largely by soil organic matter, and to a lesser extent, by sediment pH, Eh, Fe and Al oxide contents. The biogeochemical behaviors of TcO_4^- [3] and I^-/IO_3^- species [4] in natural environments have been reviewed.

The sorption and reductive stabilization of TcO_4^- in tank wastes have been reviewed [5], but the remediation of TcO_4^- in contaminated groundwater and sediments is very different. TcO_4^- is not immobilized by most of common mineral or inorganic sorbents due to its near zero sorption [6-8]. Some previously tested TcO_4^- sorbents that showed promise included activated carbon [9], stannous apatite [10], and stibnite [11]. Anion exchange resins with a quaternary amine (e.g., Dowex SRB-OH) have been used to remove Tc contaminants from high pH raffinate [7]. However, the anion exchange resins with a quaternary amine had a modest TcO_4^- loading capacity from these important waste streams, indicating they would become completely ineffective in the presence of competing anions (e.g., nitrate) that exist at several orders of magnitude greater concentrations than the TcO_4^-. More recently, chemical reduction has been studied extensively to reduce TcO_4^- concentrations using supported zero valent iron [12], aqueous Fe^{2+} [13], Fe^{2+}-bearing clays [14], Fe^{2+}-sorbed Al (hydr)oxide [15], Fe^{2+}-sorbed goethite [16], Fe^{2+}-bearing sediments [17], sediment-associated biogenic Fe^{2+} [18], hydrogen sulfide [19], amorphous Fe sulfide (FeS) [20], and Fe_3S_4 [21]. Microbial reduction [22-24] and photoreduction of TcO_4^- by nano-size metal oxides [25] have also been reported. However, even if TcO_4^- is immobilized to more reducing and stable $TcO_2 \bullet 1.6H_2O$, its solubility is about 1.5×10^{-8} M in groundwater (17,000 pCi/L; pH 3.5 to 8.5), which greatly exceeds the EPA's maximum contaminant levels (MCL) of 900 pCi/L (5×10^{-10} M Tc). Thus, some researchers have proposed technologies for not only reducing Tc(VII), but also to subsequently encapsulate the Tc^{4+} into goethite [26] and into SnO_2 using stannous chloride as a reducing agent [27]. However, both of these technologies would be difficult to implement in the field.

Selection and testing of sorbents (also commonly referred to as "getters") for ^{129}I in tank wastes have been reviewed [28]. However, under common groundwater conditions (e.g., near neutral or alkaline pH), dissolved iodine can exist as I^-, I_2, organo-I, or IO_3^-. IO_3^-, and to a much lesser extent, I^-, are sorbed by soils and some oxide / sulfide minerals [4]. The adsorption behaviors of IO_3^- and I^- are appreciably different. IO_3^- sorption onto soils and mineral surface is much stronger than I^-, but the sorption mechanisms are not completely understood [4]. Some metal oxide colloids [29] and a mixture of activated carbon and chabazite zeolite [30] have been demonstrated to remove ^{137}Cs and ^{129}I simultaneously. Ozone sparging of groundwater was proposed to promote the oxidation of iodide to volatile elemental iodine [31]. There has never been a remediation of a contaminated radioiodine plume, but a technology demonstration is presently underway, in which AgCl particles were injected to the flow path of a ^{129}I plume. The concept was to promote the *in situ* formation of the sparingly soluble precipitate, AgI [32]. ^{129}I groundwater concentrations decreased by 55% (from about 69 to 31 pCi/L; MCL = 1 pCi/L ^{99}Tc) in one of the four monitoring wells, the other three wells did not show a decrease in ^{129}I concentrations. The lack of response in the latter three wells was attributed to potentially poor well location and to the presence of about 66% of the ^{129}I as IO_3^- or organo-I species that would be minimally impacted by this technology. Although other geomaterials (e.g., smectite, layer metal hydroxide, and zeolite) [33], impregnated activated carbons [34], microwave irradiated

hydrotalcites [35], bacteriogenic iron oxides [36] have been tried for the removal of ^{129}I, there are no proven sorbent technologies that can effectively remediate radioiodine contaminants in groundwater, especially in the presence of large amounts of stable iodine, ^{127}I.

^{137}Cs is a major radionuclide in spent nuclear fuel reprocessing, primarily due to its high fission yield. Radiocesium isotopes are commonly the most important risk drivers immediately after a nuclear accident, such as those that occurred at Chernobyl and Fukushima [37]. Furthermore, it is of interest because it is one of the leading candidate radionuclides for use in a hypothetical weapon-of-mass-effect [37]. Cs^+ forms few inorganic or organic complexes in natural systems due to its low hydration energy and large ionic radius. The illite mineral, with wedged-shaped edge sites, has long been known to selectively and nearly irreversibly sorb Cs [38]. Since then, other Cs-sorbent materials have been investigated, including various clays and their modified derivatives [39-47], zeolites [48-51], ferrocyanides-based sorbents [52, 53], Ti and Zr hydroxophosphates [54], crystalline silicotitanate [55], layered metal sulfide $K_{2x}Mn_xSn_{3-x}S_6$ [56], Zr vanadate [57], and ammonium molybdophosphate composites [58-62]. Other inexpensive materials, such as humic acids [63], coal ash fly [64], and bauxite wastes [65] have also been tried and demonstrated for Cs sequestration. A comprehensive review on Cs remediation technologies has been provided by Whicker et al. [37].

However, there are not many demonstrated technologies for the effective removal of anionic radioactive contaminants such TcO_4^- and I^-/IO_3^-, which is further compromised by their frequent co-existing with other radioactive contaminants (e.g., Cs) in liquid nuclear waste, spent fuel processing solution, and the contaminated groundwater and sediment. The objective of this study was to screen-test a variety of existing sorbent materials that have low cost and may be potentially effective for the removal of aqueous Tc (added as $^{99}TcO_4^-$), I (added as $^{129}I^-$) and Cs (added as $^{137}Cs^+$). Many of the sorbents used in this screening are presently being used for other non-radiological contaminants, and as such, the objective was to evaluate whether these environmentally friendly sorbents could be used to remediate the targeted radionuclides. Importantly, the scope of this study was not to conduct measurements and experiments to elucidate the sorption mechanism. Such costly and time consuming experimentation is presently being conducted on only a selective few of these better-performing sorbents.

2. Materials and methods

2.1 Sorbent materials

A total of 27 sorbents were selected to be evaluated for $^{99}TcO_4^-$, $^{129}I^-$, and $^{139}Cs^+$ removal from the aqueous phases. The tested sequestration agents included: 1) activated carbon (824-BC and GAC 830), 2) apatite (mineral and fish bone), 3) biopolymers (xanthan and chitosan), 4) clay minerals (illite), 5) organoclays (OCB and MRM), 6) sulfide (AgS), 7) self-assembled monolayer on mesoporous silica (Th-SAMMS), and 8) zeolites (chabazite, modified chabazite, clinoptilolite, and zeolite Y). These sorbents were selected because of their expected low cost and high capacity for the Tc, I and Cs removal in low-level nuclear waste streams and contaminated groundwater. More detailed information of the selected sorbents is given in Table 1. Among them, a variety of Herschelite series sorbents were described and applied to removal of Co, Ni, Se, Sb, Tc, I, Cs and Sr from aqueous media [66, 67]; while organoclay OCM was

patented for removal of Hg/As from water [68] and organoclay OCB was used as a sequester agent for active cap remediation of metals and organic contaminant [69].

2.2 Radionuclide chemicals

The radionuclide stock solutions were purchased from Eckert & Ziegler Isotope Products (Valencia, CA). The stock solutions were composed of carrier-free 0.5 mCi/mL $^{99}TcO_4^-$ as NH_4TcO_4 in H_2O, 0.2 µCi/mL $^{129}I^-$ as NaI in 0.1 M NaOH, and 1.1 mCi/mL $^{137}Cs^+$ as CsCl in 0.1 M HCl. The spike solutions of 4.51×10^5 pCi/mL ^{99}Tc, 4.51×10^4 pCi/mL for ^{129}I and 2.25×10^{-3} or 2.25×10^4 pCi/mL ^{137}Cs used in these experiments were made by diluting the corresponding stock solutions with deionized water.

2.3 Contaminated sediment

In order to demonstrate the effectiveness of selected sorbents for the treatment of contaminated sediments, Tc-spiked SRS clayey sediment was selected for the batch experiment. To prepare the Tc-amended sediment, 900 g of air-dried SRS clayey sediment [70] was spiked with 120 mL Tc solution which was diluted from the 0.4 mL Tc stock solution of 5.37×10^5 pCi/mL. The sediment was wetted and mixed in a double baggie with plenty of air space. The moistened, amended sediment was then permitted to air dry and come to chemical steady state for two weeks. As a result, the sediment was targeted at the Tc dose of 234 pCi/g.

2.4 Artificial groundwater (AGW)

The AGW solution was designed to be representative of groundwater on the SRS and is based on the average groundwater composition reported in a survey of 26 wells in the surface aquifer located on the SRS [71]. Briefly, AGW has a pH of ~6.0, electrical conductivity (EC) of 0.026 mS/cm, turbidity of <1 NTU, and the following chemical composition: 1.25 mg/L Na, 0.25 mg/L K, 0.93 mg/L Ca, 0.66 mg/L Mg, 5.51 mg/L Cl, and 0.73 mg/L SO_4^{2-} [72].

2.5 Batch (Ad)sorption experiments

Batch sorption experiments were set up in 2-4 replicates at a constant concentration for each radionuclide in AGW solution under ambient temperature (22 °C). For each set of experiments, a solids-free control treatment was included in triplet. Its purpose was to determine the initial radionuclide concentration for K_d calculation (described below) and to provide an indication if any radionuclide sorption occurred onto the tube walls (no loss of radionuclide to the tube walls was noted). About 0.1 g of sorbent and 10 mL AGW solution were added into a 15 mL polypropylene centrifuge tube while exposed to air. The resulting solid concentration was 10 g/L. After spiking 0.1 mL of the stock solution, the initial radionuclide concentration in the working solution was targeted at 4.51×10^3 pCi/mL for ^{99}Tc, 451 pCi/mL for ^{129}I and 22.5 or 225 pCi/mL for ^{137}Cs. ^{129}I and ^{137}Cs were spiked together into the same batch tests, whereas ^{99}Tc was spiked into a separate set of batch tests. The suspensions were placed on a slow moving platform shaker for a 7-day equilibration period. Each suspension was then filtered using 0.2 µm nylon membrane syringe filter. After measuring pH, the filtrate was analyzed for radionuclide (Tc, I and Cs) concentrations using liquid scintillation counting (LSC; described in more detail below).

The extent of the radionuclide sorption to each sorbent was calculated using a distribution coefficient or K_d value (mL/g):

$$K_d = \frac{C_0 - C}{C} \times \frac{V}{M} \quad (1)$$

where C_0 is the radionuclide concentration at the start of the experiment (more specifically, the concentration in the no-solids control solution) (pCi/mL), C is the radionuclide concentration in the effluent after equilibration with the solids (pCi/mL), V is the volume of the solution (mL), and M is the mass of the sediment (g). For some selected sorbents, a mixture of sorbents was included in a single batch experiment to test their synergistic effect in the removal of radionuclide contaminants.

2.6 Batch desorption experiments

AGW was pH adjusted to 3 or 10, which were used as leaching solutions for the batch desorption experiment of the selected top-performance sorbents. Upon the completion of the (ad)sorption experiment described in Section 2.4, the liquids remaining in the test tubes were decant carefully. The remaining interstitial water was determined gravimetrically. Then 10 mL of AGW solution adjusted to pH-3 or pH-10 was added as a leaching solution. The suspensions were placed on a slow-moving platform shaker for additional 7-days to reach a second equilibration. After 24 hour, the suspensions were adjusted again to the targeted pH values. Each suspension was filtered using 0.2-μm Nylon membrane syringe filters. After measuring pH, the filtrate was submitted for radionuclide (^{99}Tc, ^{129}I, and ^{137}Cs) analysis using LSC. The desorption percentage was calculated based on the radionuclide mass in the desorption solution (M_D), interstitial solution (M_I; the solution remaining in the interstitial pore space after decanting the sorption solution) and associated with the solids (M_S):

$$\%\ Radionuclide\ desorbed = \frac{M_D - M_I}{M_S} \times 100 \quad (2)$$

2.7 Batch treatment of TcO_4^--contaminated sediment

The objective of this experiment was to evaluate the impact of sorbent concentration on radionuclide uptake from Tc-amended sediment (as described above). Duplicated batch tests were established by combining 20-g dry weight sediment, 20 mL of 5 mg/L NH_4^+ (added as NH_4NO_3) in AGW solution, and 1 g, 0.1 g or 0 g of each sorbent. The final sorbent concentrations were 0, 0.5, or 5%, with respect to sediment dry weight. The no-amendment control set of sediment samples were also to permit monitoring how much radionuclide was desorbed in the aqueous phase. The suspensions were placed on a shaker for 7 day. Each suspension was filtered using 0.45 μm Nylon membrane syringe filters. After measuring pH, the filtrate was analyzed for ^{99}Tc using LSC (described below).

3. Results and discussion

3.1. Removal of Tc, I and Cs by a single sorbent

The K_d values of the sorbents for aqueous Tc, I and Cs are given in Table 2. It is noted that the Cs K_d values were obtained with the Cs working solution of 22.5 pCi/mL. Several sorbents were effective for removing multiple radionuclides. Organoclay OCB and OCM were very effective in sorbing TcO_4^- ($K_d > 1\times10^{-5}$ mL/g), I^- ($K_d \geq 1\times10^4$ mL/g), and Cs ($K_d > 1\times10^3$ mL/g) (Table 2). Activated carbon GAC 830 was very effective for Tc (K_d 1×10^5 mL/g) and I removal (K_d 6.9×10^3 mL/g), but less effective for Cs removal (K_d ~200 mL/g). Surfactant modified chabazite was effective for Tc ($K_d > 2.5\times10^4$ mL/g) and Cs ($K_d > 6.5\times10^3$ mL/g) removal, but much less effective for I removal (K_d ~120 mL/g). Some sorbents were selected for testing because of an effective removal mechanism for a specific radionuclide. For example, illite has steric edge sites that can selectively trap Cs; it had a Cs K_d value of 1.17×10^4 mL/g in edge sites. Similarly, argentite (AgS) was evaluated because it was anticipated that it would promote the formation of the sparingly soluble AgI complex; it had an I K_d value of 2.5×10^4 mL/g. Finally, several sorbents were tested for sorption of all three radionuclides, yet were only effective at taken up one of the radionuclides. For Example, engineering Herschelite or natural chabazite (K_d 4×10^4 mL/g), surfactant modified clinoptilolite (K_d 0.6×10^4 mL/g) and Th-SAMMS (K_d 0.17×10^4 mL/g) were effective for Cs, but not for Tc and I removal (Table 2).

Also listed in Table 2 are the pH values at the end of the equilibration period. No attempt was made to control the pH values in these batch suspensions, and as such, the final pH reflected the steady state pH between the pH 5.5 artificial groundwater and the sorbent. Consequently, the pH ranged from 10.5 for Organoclay OCB to 3.5 for Organoclay OCM. Given the extremely important role that pH plays in aqueous speciation and especially in surface site functionality and numbers, it is possible, perhaps likely, that different K_d values would be obtained under different pH conditions,

The K_d values of selected sorbents for Tc, I and Cs were compared with various soil types and some sorbents reported in the literature (Table 3). A ranking of the sorbents by Tc K_d values is as follows: modified zeolite Y (2.35×10^5 mL/g) ≈ activated carbon GAC 830 (1.08×10^5 mL/g ≈ Organoclay OCB (1.17×10^5 mL/g) ≈ Organoclay OCM (1.12×10^5 mL/g) > surfactant modified chabazite (2.56×10^4 mL/g). These are much larger than the K_d values of most soils [73], therefore, if placed in the presence of such soils, these sorbents would be expected to outcompete the soils for aqueous TcO_4^-. These sorbents are also more effective than previously tested sorbents including Fe filling [7], resin [74], activated carbon [9], clays and organoclays, modified apatite and chabazite [66].

A ranking of the sorbents for iodine removal by their I K_d values are as follows: Organoclay OCB (2.93×10^4 mL/g) > argentite (AgS; 2.5×10^4 mL/g) > Organoclay OCM (9.61×10^3 mL/g) > activated carbon GAC 830 (6.92×10^3 mL/g). Again, these sorbents had much greater K_d values than comparable soil K_d values [73] or previously tested I sorbents, including chalcocite and cinnabar [75].

The most effective sorbents for Cs were Organoclay OCB (2.8×10^3 mL/g), Organoclay OCM (1.23×10^3 mL/g), illite (IMt-2; 1.17×10^4 mL/g), Th-SAMMS (1.70×10^3 mL/g), chabazite (4.0×10^4 mL/g) and surfactant modified chabazite (6.59×10^3 mL/g). These sorbent K_d values are about the same as those previously reported for illite, mica, vermiculite [76], chabazite, potassium hexacyanofarrate modified chabazite and clinoptilolite [66].

3.2 Removal of Tc, I and Cs by mixed sorbents

In order to evaluate the synergistic effects of some top-performance sorbents for Tc, I and Cs removal from aqueous media, a batch experiment using two mixed sorbents was conducted. It is noted that the Cs concentration of the working solutions for this batch experiment was 225 pCi/mL. The K_d values of the mixed sorbents for Tc, I and Cs removal are given in Table 4. In comparison with the K_d values of each individual sorbent in Tables 2 and 3, no synergistic effects were detected. This may in part be attributed to the fact that once several of the sorbents were put in contact with targeted radionuclides, the final aqueous radionuclide concentration were at or approached the detection limit of the instrument. Consequently, there turned out to be little opportunity to observe significant additional sorption uptake in the presence of the second sorbent. Activated carbon 824 BC is not effective for Tc or I removal, when it mixed with each of organoclay OCB, organoclay OCM, chabazite and surfactant modified chabazite, the K_d value of the resulting mixture was equal to or smaller than that of the corresponding single sorbent. The reduction in K_d values in the presence of a weaker sorbent, may be attributed to the substitution of the weaker for the stronger sorbent, i.e., the total combined mass of sorbent was held constant. Similarly, when activated carbon GAC 830 was mixed with these sorbents, the K_d value of the resulting mixture was equal to or smaller than that of the higher performance component for either Tc or I removal. As shown in Table 4, the K_d value of the mixed sorbents for Cs removal is higher than the corresponding individual sorbent component. The process responsible for this synergistic effect on Cs removal is not known, but may be the result of difference in the Cs spike concentrations. The mixed sorbents had a larger Cs spike concentration than the single sorbent tests. Additional testing is warranted to evaluate this process.

3.3 Desorption of Tc, I and Cs from the sorbents

The desorption percentages of Tc, I and Cs for organoclay OCB and OCM, and of Tc for surfactant modified chabazite are given in Table 5. Tc desorption in the presence of a pH 3 or pH 10 leaching solution was <0.2% of the sorbed Tc for Organoclay OCB, Organoclay OCM, and <3% for the surfactant modified cabazite. The desorption of Cs from organolcays OCB and OCM was <4% for the pH 3 or 10 leaching solution. However, the desorption behavior of I from organoclay OCB and OCM was quite different. The desorption of iodine from oragnoclay OCM was <9% of the sorbed iodine with pH 3 or 10 leaching solution. The desorption of I from organoclay OCB depended on the leaching pH: with pH 10 leaching solution, the desorption of iodine is <1%, but with the pH 3 leaching solution (a final pH was 7.6 after 7 days), and nearly 42% of the sorbed I on organoclay OCB was desorbed. This indicated that I species sorbed on organoclay OCB is quite easily acid leachable even though its chemical speciation and bonding with the sorbent are unknown.

3.4 Treatment of Contaminated Sediments

Tc-spiked SRS clayey sediment was treated with activated carbon GAC 830, organoclay OCB and OCM, and surfactant modified chabazite, the results for these treatments are shown in Fig. 1. Without a sorbent, the aqueous Tc concentration of the control sample was 244 pCi/mL, which is close to the target Tc dosage of 234 pCi/mL. For activated carbon GAC 830, organoclay OCB and OCM, Tc concentrations of the effluents were below the Tc LSC detection limit of 2.2 pCi/mL for both 0.5% and 5% sorbent/sediment treatments. The results indicated that these sorbents effectively removed Tc contaminant from the sediment. However, Tc concentration of the effluent was 174 pCi/mL for 0.5% surfactant modified chabazite treatment, and 19.4 pCi/mL for its 5% treatment. These results indicated that surfactant modified chabazite was not as effective as activated carbon GAC 830, organoclay OCB and OCM in the treatment of Tc-contaminated sediments, in agreement with the K_d values of these sorbents (Table 2).

4. Conclusions

Organoclay OCB and OCM were very effective for removal of TcO_4^-, I^- , and Cs. The Tc sorption was nearly irreversible, the desorption of I and Cs was modest; however, decreasing pH might cause severe I desorption from organoclay OCB. The effectiveness of activated carbon GAC 830 for Tc, I and Cs removal was in the sequence of Tc > I > Cs. Surfactant modified chabazite was effective for Tc and Cs removal, but poor for I removal. In contrast, some sorbents may be more selective in the removal of specific contaminants. For example, modified zeolite Y is effective for Tc removal, but no data available for I and Cs removal, while argentite (AgS) is only effective for I removal. Illite, natural chabazite, surfactant modified clinoptilolite and Th-SAMMS are only effective for Cs removal.

These sorbents not only showed high K_d values in the removal of aqueous radionuclide contaminants like Tc, I and Cs, but also are cost effective. The effectiveness of these sorbents for Tc, I and Cs removal were just evaluated at the specific pH. The study to quantify their actual capacity, to determine the geochemical conditions where they are effective, and to evaluate the sorption mechanisms using spectroscopic and sequential extraction is under way. Such experiments will permit evaluating the sorbents for use at a specific site or designing engineered systems. These highly effective, low-cost sorbent materials can be potentially applied to removing radionuclide contaminants, such as TcO_4^-, I^- and Cs^+, selectively or collectively from low-level nuclear wastes, contaminated groundwater and sediments.

Acknowledgements

This work was supported by Department of Energy, Environmental Management. Work was conducted at the Savannah River National Laboratory (SRNL) under the U.S. Department of Energy Contract DE-AC09-96SR18500. The SRNL Laboratory Director's Research and Development (LDRD) funding is more specifically appreciated for supporting this research work.

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Table list

Table 1. Materials evaluated for $^{99}TcO_4^-$, $^{129}I^-$ and $^{137}Cs^+$ sorption

Table 2. ^{99}Tc, ^{129}I and ^{137}Cs K_d (mL/g) values of sorbent suspension in artificial groundwater (AGW)

Table 3. Comparison of ^{99}Tc, ^{129}I and ^{137}Cs K_d (mL/g) values of sorbents to literature K_d values of natural geological materials and sorbents previously evaluated.

Table 4. ^{99}Tc , ^{129}I and ^{137}Cs K_d values (mL/g) of mixed sorbents.

Table 5. Desorption (%) of ^{99}Tc, ^{129}I and ^{137}Cs from sorbents in pH-adjusted groundwater

Figure list

Fig. 1. Performance of selected sorbents for the treatment of Tc-contaminated SRS clayey sediment. Sorbent treatments: 1 = Activated carbon GAC 830; 2 = Organoclay OCB; 3 = Organoclay OCM; 4 = Surfactant modified chabazite.

Table 1

Materials evaluated for $^{99}TcO_4^-$, $^{129}I^-$ and $^{137}Cs^+$ sorption.

Sorbent Type	Product Name / Description	Manufacturer
Activated carbon	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
	Norit® GAC 830 / Granular activated carbon produced by steam activation of select grades of coal	Norit America, Inc. (Cabot Corp.), Marshall, TX
Apatite II	Phosphate mineral, fish bone	PIMS-NW, Richland, WA
Biopolymer	Chitosan / derived from crustaceans shells	AIDP, City of Industry, CA
Clay minerals	Todd Light™ Illite / natural mineral	Kentucky-Tennessee Clay Company, Nashville, TN
Organoclay	ClayFloc™ 750 / bentonite organoclay based flocculant	Biomin Inc., Ferndale, MI
	Organoclay MRM™ / sulfur-impregnated organophilic clay	CETCO® Remediation Technologies, Hoffman Estates, IL
Mesoporous silica	Self-Assembled Monolayers on Mesoporous Silica (SAMMS) / modified with thiol functionalization (Th-SAMMS)	Steward Environmental Solutions, Chattanooga, TN
Sulfide	Argentite – natural mineral	Ward's Science, DesMoines, IO
Zeolite	Engineered Herschelite, KUR-EH / chabazite natural mineral	Kurion, Inc., Oak Ridge, TN
	Surfactant modified Herschelite, KUR-CH / surfactant modified chabazite mineral	Kurion, Inc., Oak Ridge, TN
	Modified zeolite Y, CBV-780 / synthetic chemical	Zeolyst International Valley Forge, PA

Table 2

^{99}Tc, ^{129}I and ^{137}Cs K_d (mL/g) values of sorbent suspension in groundwater

Sorbents	Tc K_d	I K_d	Cs K_d
SRS sediment - reference	0.6-1.8	0.3-0.9	10-50
Activated carbon 824 BC	120 ± 41	12 ± 5	21 ± 13
Activated carbon GAC 830	$>1.08 \pm 0.03\times10^5$	$>6.92 \pm 0.22\times10^3$	192 ± 50
Apatite II	223 ± 8	N/A	N/A
Chitosan	54 ± 6	88 ± 1	134
Illite (IMt-2)	N/A	N/A	$>1.17 \pm 0.39\times10^4$
Organoclay OCB	$>1.17 \pm 0.07\times10^5$	$>9.61 \pm 0.63\times10^3$	$>2.80 \pm 0.57\times10^3$
Organoclay OCM	$>1.12 \pm 0.01\times10^5$	$>2.93 \pm 0.04\times10^4$	$>1.23 \pm 0.11\times10^3$
Argentite (AgS)	N/A	$>2.5\times10^4$	N/A
Th-SAMMS	14 ± 0	7 ± 3	$>1.70 \pm 0.16\times10^3$
Engineered Herschelite (KUR-EH)	0 ± 5	0 ± 2	$>4.0\times10^4$
Zeofume (Engineered Herschelite fines)	0 ± 0	0 ± 2	$>8.63\times10^3$
Surfactant-modified Chabazite	$>2.56 \pm 0.11\times10^4$	122 ± 13	$>6.59\times10^3$
Surfactant-modified clinoptilolite (KUR-SMZ)	247 ± 59	6 ± 7	$>6.09\times10^3$
Modified zeolite Y	$>2.35 \pm 0.01\times10^5$	N/A	N/A

Table 3.

Comparison of ^{99}Tc, ^{129}I and ^{137}Cs K_d (mL/g) values of sorbents to literature K_d values of natural geological materials and sorbents previously evaluated.

This work		Literature		
Sorbents	K_d (mL/g)	Sorbents	K_d (mL/g)	Ref.
^{99}Tc				
Activated carbon GAC 830	$>1.08\times10^5$	Sandy soil	0.01-16	[73]
Organoclay OCB	$>1.17\times10^5$	Silt soil	0.01-0.4	[73]
Organoclay OCM	$>1.12\times10^5$	Clay soil	1.16-1.32	[73]
Surfactant modified chabazite (MC)	$>2.56\times10^4$	Organic soil	0.02-340	[73]
Modified zeolite Y	$>2.35\times10^5$	Fe filling	$<2.7\times10^3$	[7]
		Resin Bio-Rad AG-OH	1.36×10^3	[74]
		Activated carbon	$>1.0\times10^4$	[9]
		Lockit clay[a]	6.07×10^4	[66]
		Modified Lockit[a]	6.37×10^4	[66]
		CTMA apatite[a]	1.52×10^4	[66]
		CTMA chabazite[a]	2.17×10^3	[66]
^{129}I				
Activated carbon GAC 830	$>6.92\times10^3$	Sandy soil	0.04-81	[73]
Organoclay OCB	$>2.93\times10^4$	Silt soil	0.1-43	[73]
Organoclay OCM	$>9.61\times10^3$	Clay soil	0.2-29	[73]
Argentite (AgS)	$>2.5\times10^4$	Organic soil	1.4-368	[73]
		Chalcocite	1.38×10^3	[75]
		Cinnabar	3.08×10^3	[75]
^{137}Cs				
Organoclay OCB	$>2.80\times10^3$	Illite	$6.3\text{-}8.3\times10^3$	[76]
Organoclay OCM	$>1.23\times10^3$	Mica	$3.2\text{-}3.4\times10^3$	[76]
Illite (IMt-2)	$>1.17\times10^4$	Kaolinite	240-290	[76]
Th-SAMMS	$>1.70\times10^3$	Vermiculite	$5.7\text{-}6.7\times10^3$	[76]
Chabazite	$>4.0\times10^4$	Chabazite[b]	1.5×10^3	[66]
Surfactant modified chabazite (MC)	$>6.59\times10^3$	Clinoptilolite[b]	570	[66]
		KCCF-chabazite[b]	1.26×10^4	[66]
		KCCF-clinoptilolite[b]	0.94×10^4	[66]

[a] Initial Tc spike = 5.27×10^3 pCi/mL (1pCi/mL = 2.22 dpm/mL), CTMA= a proprietary surfactant
[b] Initial Cs spike = 9 mg/L, KCCF = potassium hexacyanoferrate

Table 4.
^{99}Tc , ^{129}I and ^{137}Cs K_d values (mL/g) of mixed sorbents.

Sorbent 1	Sorbent 2	Ratio	Batch for Tc spiking		Batch for I and Cs co-spiking		
			pH	Tc K_d (mL/g)	pH	I K_d (mL/g)	Cs K_d (mL/g)
Activated carbon 824 BC	Organoclay OCB	1:1	9.9	$1.064 \pm 0.002\times10^5$	9.9	$9.63 \pm 0.69\times10^3$	$1.13 \pm 0.11\times10^3$
	Organoclay OCM	1:1	8.7	$1.18 \pm 0.03\times10^4$	8.2	$1.54 \pm 0.12\times10^3$	1,201 ± 5
	Chabazite	1:1	9.4	23 ± 11	9.2	4 ± 1	$5.98 \pm 3.58\times10^4$
	Surfactant modified chabazite	1:1	9.2	$2.02 \pm 0.22\times10^3$	9.1	92 ± 5	$3.70 \pm 0.29\times10^4$
Activated carbon GAC 830	Organoclay OCB	1:1	9.0	$1.08 \pm 0.02\times10^5$	9.4	$1.10 \pm 0.01\times10^4$	977 ± 32
	Organoclay OCM	1:1	6.2	$1.07 \pm 0.02\times10^5$	8.3	$1.08 \pm 0.06\times10^4$	$1.17 \pm 0.07\times10^3$
	Chabazite	3:7	7.3	$1.055 \pm 0.002\times10^5$	7.0	$1.17 \pm 0.40\times10^4$	$3.35 \pm 0.09\times10^4$
	Chabazite	1:1	7.2	$0.68 \pm 0.53\times10^5$	7.0	2,381 ± 5	$3.21 \pm 0.16\times10^4$
	Chabazite	7:3	7.2	$1.08 \pm 0.03\times10^5$	6.9	4.0×10^4	3.41×10^4
	Surfactant modified chabazite	1:1	7.5	$1.08 \pm 0.01\times10^5$	7.6	$4.55 \pm 0.73\times10^3$	$4.18 \pm 0.29\times10^4$
Organoclay OCM	Chabazite	1:1	4.4	$2.82 \pm 0.53\times10^4$	4.4	$4.03 \pm 0.08\times10^3$	$2.54 \pm 3.33\times10^4$
	Surfactant modified chabazite	1:1	4.4	$1.071 \pm 0.004\times10^5$	4.3	$5.32 \pm 0.41\times10^3$	$4.59 \pm 0.81\times10^4$

Table 5

Desorption (%) of ^{99}Tc, ^{129}I and ^{137}Cs from sorbents in pH-adjusted groundwater

	Tc desorption		I and Cs Desorption	
	Final pH		Final pH	
Sorbents	**Leachate pH**	**% Tc**	**% I**	**% Cs**
Organoclay OCB	3	0.2	41.8	3.9
	10	0.1	0.9	3.0
Organoclay OCM	3	0.1	8.5	3.6
	10	0.1	7.6	3.5
Surfactant modified chabazite	3	2.7		
	10	1.0		

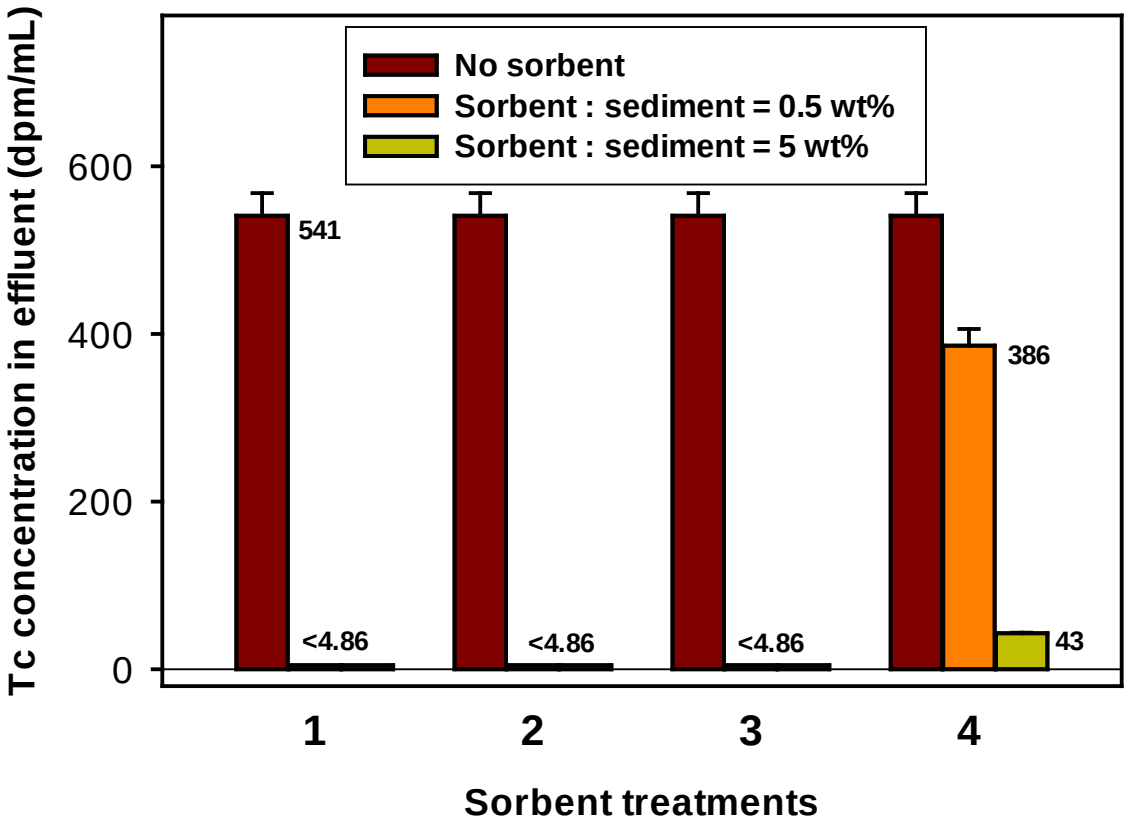

Fig. 1. Performance of selected sorbents for the treatment of Tc-contaminated SRS clayey sediment. Sorbent treatments: 1 = Activated carbon GAC 830; 2 = Organoclay OCB; 3 = Organoclay OCM; 4 = Surfactant modified chabazite.