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Pertechnetate (TcO_4^-) sequestration from groundwater by cost-effective organoclays and granular activated carbon under oxic environmental conditions

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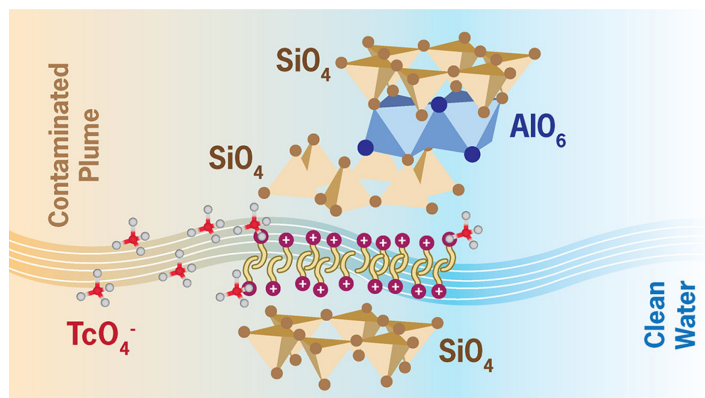
ABSTRACT

Technetium-99 (^{99}Tc) is a major risk driver at nuclear power plants and several US Department of Energy (DOE) sites. Pertechnetate (TcO_4^-), the most common chemical form present in liquid nuclear waste and the environment, displays limited adsorption onto sediments, making it highly mobile and difficult to immobilize. In this work, inexpensive organoclays and granular activated carbon (GAC) were investigated for TcO_4^- sequestration from artificial groundwater (AGW).

The Tc adsorption capacities were 15 mg/g for organoclays and 25 mg/g for GAC from pH 3–12 AGW under oxic conditions. Competitive NO_3^- at two orders of magnitude greater concentration than TcO_4^- reduced the Tc adsorption capacity by only 9–25%. In addition, the adsorbed Tc was effectively desorbed by KI, but not Na_2SO_4 , and the regenerated sorbents retained their Tc removal capacity. X-ray absorption spectroscopy demonstrated that the Tc species bound to the

organoclays and GAC was Tc(VII) (i.e., TcO_4^-), rather than Tc(IV). Thus, the inexpensive organoclays and GAC are highly effective at sequestering ^{99}Tc in its naturally existing TcO_4^- without requiring costly reductive systems, which may provide a practical solution for removing $^{99}\text{TcO}_4^-$ from environmental systems.

TOC



Keywords: Pertechnetate, Organoclays, Granular activated carbon, Synchrotron XANES and EXAFS

1. Introduction

Technetium-99 (^{99}Tc), a long-lived low-energy beta emitter, is a major fission product generated during nuclear power production. Technetium has been inadvertently introduced into the environment from leaks at waste storage facilities and currently is a key risk driver at several US Department of Energy (DOE) sites [1]. The most common chemical form of Tc in liquid nuclear wastes and the environment is pertechnetate (TcO_4^-) [1, 2]. It displays limited adsorption

on common sediment minerals [3-5], making it highly mobile. As the stockpile of ^{99}Tc -bearing nuclear waste continues to increase due to nuclear energy production, novel and practical sequestration technologies are needed to reduce the potential contamination of the environment and the threat to living organisms.

There are currently two general approaches for TcO_4^- immobilization from waste: adsorption and reductive precipitation. Strong base resins with quaternary amines (e.g., Dowex SRB-OH) have been used to remove Tc [6]; however, these expensive resins possess a modest TcO_4^- loading capacity from raffinate waste streams due to strong competition from other anions (e.g., NO_3^- and HCO_3^-) that are typically several orders of magnitude higher in concentration than TcO_4^- [7]. Granular activated carbon (GAC; Nuchar WV-G) from West Virginia Pulp and Paper was evaluated for TcO_4^- removal from groundwater, but the available data demonstrated that its adsorption capacity was low [8]. For high TcO_4^- waste streams, reductant materials (i.e., Fe sulfides [9, 10], layered potassium metal sulfides [11], tin-apatite [12], adsorbed or structural Fe(II) [13-17], zero valent iron [18]), and reducing bacteria [9, 10, 19] can chemically reduce Tc(VII) to sparingly soluble Tc(IV). However, the solubility of the precipitated reduction product, $\text{Tc(IV)O}_2 \cdot 1.6\text{H}_2\text{O}$, is still relatively high (i.e., 1.5×10^{-8} M) in groundwater [20, 21], greatly exceeding the EPA's maximum contaminant level (MCL) of 5×10^{-10} M Tc. In addition, $\text{Tc(IV)O}_2 \cdot 1.6\text{H}_2\text{O}$ is readily re-oxidized to Tc(VII) and re-mobilized under most environmental conditions [22-25].

In addition, several other approaches have also been investigated for TcO_4^- stabilization. TcO_4^- was reported to immobilize into goethite structure through reductive co-precipitation so that its leachability was significantly decreased [15]. Pertechnetate (TcO_4^-) can be reduced to form a sulfide phase (e.g., Tc_2S_7 or TcS_2) through high temperature reduction by H_2S [26],

amorphous iron sulfide [27], and nano zero-valent iron (ZVI) transformed by abiotic sulfide [28]. Although low solubility Tc sulfide phases are plausible for Tc sequestration and stabilization [29, 30], significant transformation of TcS_2 to TcO_2 after 120 h of oxidation has been observed [31], and such methods are largely impractical for field remediation applications. In addition, perrhenate (ReO_4^-), as a surrogate of TcO_4^- , was also reported to incorporate into sodalite structure as a potential waste form for TcO_4^- immobilization [32, 33].

In our previous work, organoclays and GAC were shown to have high adsorption coefficients (K_d) for removing TcO_4^- , iodide (I^-) and cesium (Cs^+) from artificial groundwater (AGW) under oxic test conditions [34]. The objectives of this study were to: 1) quantify the adsorption capacities of the organoclays and GAC for sequestering TcO_4^- from AGW under oxic conditions using batch adsorption experiments, 2) evaluate the effects of pH and ionic strength on the Tc adsorption capacity, and the Tc desorption and resorption behavior, 3) identify the chemical speciation of the adsorbed Tc using Tc K-edge X-ray absorption near structure (XANES), and 4) elucidate the molecular mechanisms responsible for Tc binding with the organoclays and GAC using Tc K-edge extended X-ray absorption fine structure (EXAFS) spectroscopy.

2. Materials and Methods

2.1 Materials

A brief description of organoclays and GAC materials used in this study is provided in Table 1 [34]. Ammonium pertechnetate (NH_4TcO_4) was purchased from Eckert & Ziegler Isotope Products, Inc. (Valencia, CA, USA), sodium nitrate (NaNO_3), sodium sulfate (Na_2SO_4) and potassium iodide (KI) were purchased from Fisher Scientific (Hampton, NH, USA), while sodium perrhenate (NaReO_4) was from Sigma-Aldrich (St. Louis, MO, USA). The chemicals

were used as received. A known amount of ammonium pertechnetate was dissolved in AGW to prepare the pertechnetate (3.2×10^{-4} M) stock solution that was used for the batch sorption experiments. The composition of the AGW solution is typical uncontaminated groundwater from the DOE Savannah River Site, Aiken, South Carolina, USA [35]. The chemical composition (in mg/L) of the AGW was Na 1.25, K 0.25, Ca 0.93, Mg 0.66, Cl 5.51, and SO₄ 0.73. It had a pH ~ 6.3, an electrical conductivity of 0.03 mS/cm, and a turbidity of 4.1 NTU [36].

2.2 Batch sorption experiments

Batch sorption experiments for obtaining the adsorption isotherms (i.e., the mass (q_e , mg/g) of Tc or Re associated with the sorbent versus the concentration remaining in solution at equilibrium) were conducted in AGW under ambient atmosphere and temperature (22 °C). For each set of experiments, a sorbent-free control was included at the initial Tc concentration for q_e calculation and to provide an indication of any Tc sorption to the reaction tube during the experiment. Approximately 0.01-0.05 grams of the sorbent and a known volume of AGW were added to 15 mL polypropylene centrifuge tubes. Then, 0.05-5 mL of the Tc stock solution were added to make a final working solution volume of 5 mL with a Tc concentration ranging from 3.2×10^{-6} M to 3.2×10^{-4} M. The suspensions were adjusted to the target pH values (Radiometer Copenhagen PHM 95 pH meter) with 1 M NaOH or 1 M HNO₃ and equilibrated on a reciprocating shaker for 6 days, although our unpublished data indicated that the sorption of TcO₄⁻ by organoclays was close to complete within 24 hours, but the reaction onto GAC was slightly slower. After equilibration, the final pH values were measured, and each suspension was filtered through a 0.2 µm pore-size nylon membrane syringe filter. The filtrate was analyzed for Tc by liquid scintillation counting (LSC) (LS 6500 Multi-Purpose Scintillation Counter, Beckman Coulter, Inc.) using Optiphase HiSafe (Perkin Elmer, Inc.) scintillation cocktail. The

LSC analyses had an uncertainty of $\pm 10\%$, but our repeatability test indicated that this uncertainty was often within $\pm 5\%$. The solid samples were air dried and collected for spectroscopic characterization. In order to evaluate the effects of NO_3^- competition on TcO_4^- removal capacity for the organoclays and GAC materials, batch experiments were conducted using 0.05 g sorbents and 5 mL of AGW with or without extra 0.1 M NaNO_3 at the initial Tc concentration of 1.2×10^{-3} M.

In addition, ReO_4^- was used as a surrogate of TcO_4^- to study desorption and resorption behavior on the organoclays and GAC. The organoclays and GAC (0.1 g) materials were first exposed to 1.2×10^{-3} M sodium perrhenate in 10 mL of AGW and equilibrated on a reciprocating shaker for 3 days. After centrifugation at 7,500 rpm for 5 minutes, the supernatant pH was measured and then filtered using a 0.2 μm pore-size nylon filter. Then, 10 mL of 0.1 M sodium sulfate solution was added to the residual sorbent and equilibrated for another 3 days. After centrifugation and filtration of the supernatant, the residual organoclay and GAC sorbents were washed four times with deionized water. Subsequently, 10 mL of a 1.2×10^{-3} M sodium perrhenate working solution prepared in AGW was added for the 3-day resorption batch experiment. After that, a similar desorption test using 1 M KI was conducted and resorption of ReO_4^- was quantified. The pH value of the suspension was measured and the suspension was separated using 0.2 μm pore-size nylon filter after each of the sequential treatments. The filtrate was acidified for preservation (2% HNO_3) and analyzed for Re by inductively coupled plasma mass spectrometry (ICP-MS; NexION 300X, Perkin Elmer, Inc.). The ICP-MS analyses had an uncertainty of $\pm 10\%$, but our repeatability test indicated that this uncertainty was often within $\pm 5\%$.

2.3 Tc K-edge XANES and EXAFS

After the batch adsorption experiments, Tc K-edge XANES and EXAFS spectra of organoclays and GAC were collected using the Sector 20-BM beamline at the Advanced Photon Source (APS) (Argonne National Lab, Argonne, IL). To do so, 50 mg of each of the air-dried powder samples was pressed into a 6.3-mm diameter disk pellet and sealed by Kapton tape. The APS sector 20-BM beam line employed a Si (111) double crystal monochromator detuned 15% for harmonic rejection. Additional harmonic rejection was provided by a Rh-coated mirror set at 2.8 mrad. Absolute energy calibration was made using a Mo foil with the edge energy of 20,000.4 eV. The APS storage ring was operated at 100 ± 5 mA during the measurements. The Tc K-edge XANES and EXAFS spectra were taken in fluorescence step-scanning mode using a 13-element Ge detector array at 90° to the beam direction, in the energy range of 20,850-22,013 eV at room temperature. The fluorescence detector had a four-layer Al foil filter to suppress the Fe fluorescence [37].

All the collected spectra were processed and analyzed using the IFEFFIT software package including Athena and Artemis [38]. Data from multiple scans were processed using Athena by aligning and merging the spectra followed by background subtraction using the AUTOBK algorithm. Tc K-edge EXAFS data analysis was conducted on the merged and normalized spectra using Artemis. Ammonium pertechnetate was used as a reference structural model [39]. Fits to the Tc EXAFS data were made in R space (R from 1 to 4 Å) and obtained by taking the Fourier transform (FT) of $\chi(k)$ (k from 3 to 11) with a k weighting of 2.

3. Results and discussion

3.1 Capacities of organoclays and GAC for Tc sequestration

Batch adsorption experiments were conducted in order to quantify Tc removal from AGW at varying pHs by the organoclays and GAC. The mass of Tc sorbed by each sorbent (q_e , mg/g) was calculated using equations 1:

$$q_e = \frac{(C_0 - C_e) \times V}{M} \quad (1)$$

where C_0 (mg/L) is the initial Tc concentration in the control samples, C_e (mg/L) is Tc concentration remaining in the solution at equilibrium, V is the volume of the solution (mL) and M is the mass of the sorbent (g). The adsorption isotherms of Tc onto organoclay OCB (A), organoclay OCM (B) and GAC 830 (C) in AGW at varying pHs under oxic condition are shown in Fig. 1 (left panel). The Tc adsorption isotherms for OCB and OCM appear to approach their saturation; however, a sorption plateau indicative of limited retention capacity was not completely achieved for GAC 830.

The isotherm data were described using the Langmuir isotherm model (equation 2). The Langmuir model assumes that adsorption occurs as a monolayer on an energetically homogeneous surface without interaction between the adsorbates on adjacent sites:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max}} C_e + \frac{1}{K_L \times q_{\max}} \quad (2)$$

where q_e is the mass of Tc sorbed onto the sorbent at equilibrium, q_{\max} is the saturation sorption capacity, C_e is the Tc concentration in solution at equilibrium, and K_L is the Langmuir constant that is directly related to the binding site affinity. The Langmuir fits to the corresponding experimental data are shown in Fig. 1D (OCB), 1E (OCM) and 1F (GAC 830) (right panel). The Tc saturation adsorption capacities for OCB, OCM and GAC 830, together with the coefficients of determination (i.e., R^2 values) that provide a goodness of fit, are presented in Table 2. While

the adsorption isotherms for OCB and OCM were described well by the Langmuir model, the Langmuir fits to experimental adsorption isotherm data for GAC 830 were slightly poorer, as indicated by R^2 values, and the calculated saturation capacities likely provide erroneously lower estimates of total sorption capacity.

The adsorption capacities of the present organoclays and GAC for sequestering TcO_4^- or its surrogate, ReO_4^- , from aqueous media are compared with some commonly used sorbents that do not include reducing materials (Table 3). The Tc concentration, pH and the presence of other competing ions may dramatically impact Tc adsorption capacity. As a result, sorption data obtained under different experimental conditions may not be directly comparable. It is noted that an unusually high saturated adsorption capacity of 526 mg Re/g sorbent was reported for Purolite A530E to remove ReO_4^- from groundwater, even in the presence of a large excess of both NO_3^- and SO_4^{2-} [40]. More recently, several cationic metal-organic framework (MOF) and coordination polymers have been reported to show outstanding sorption capacities of up to 744 mg Re/g sorbent for ReO_4^- removal from aqueous media [41-47]. By comparison, the Tc removal capacity of the current organoclays (15 mg/g) and GAC 830 (25 mg/g) from groundwater over a broad pH range are much higher than mineral sorbents. Although their Tc removal capacities are not as high as those reported for several cationic MOFs or coordination polymers, the less expensive organoclays and GAC (~\$4-5/kg) materials may still have widespread practical applications for TcO_4^- removal from groundwater.

3.2. Effect of pH on Tc removal capacity

The effect of pH on the Tc adsorption capacities for OCB, OCM and GAC 830 can be observed in Fig. 1 and Table 2. The equilibrium pH of OCB in AGW without adjustment was

12.3, with a Tc removal capacity of 14.0 mg/g. When the pH was adjusted to 6.8, the Tc adsorption capacity (13.9 mg/g) remained nearly identical to that for the pH 12.3 AGW. The equilibrium pH of OCM in AGW without adjustment was 3.2, with the Tc removal capacity of 16.1 mg/g. When the pH was adjusted to 8.5, the Tc adsorption capacity (14.8 mg/g) was slightly, but not significantly lower than that observed at pH 3.2 in AGW. For GAC 830 in AGW at pH values of 2.9, 7.8 and 9.9, the corresponding Tc adsorption capacity varied from 28.4 to 27.9 and 23.0 mg/g, which indicated that in the AGW of pH 3-8, the Tc adsorption capacity for GAC 830 remained nearly constant, but at pH 9.9 AGW, the adsorption capacity decreased by about 20%. The decrease in sorption capacity at higher pH was presumably related to the neutralization of binding sites on GAC surfaces by OH⁻. These results demonstrated that OCB remained effective for Tc removal from pH 6.5-12.5 AGW, with the adsorption capacity of ~14 mg/g, while OCM and GAC 830 remained effective from pH 3-10 AGW, with the adsorption capacities of 15 and 25 mg Tc/g sorbent, respectively.

3.3. Effect of competitive NO₃⁻ on removal capacities

Anions (e.g., NO₃⁻, HCO₃⁻, SO₄²⁻ and PO₄³⁻) are commonly present in the contaminated environments and potentially compete for sorption sites on organoclays and GAC sorbents, potentially limiting TcO₄⁻ removal. In order to evaluate the effects of NO₃⁻ competition on TcO₄⁻ removal capacity, the organoclays and GAC were exposed to 1.2×10⁻³ M TcO₄⁻ solution in AGW in the presence or absence of 0.1 M NaNO₃. The results are shown in Fig. 2. In AGW without 0.1 M NaNO₃, the quantity of Tc adsorbed on OCB, OCM, and GAC 830 were 8.9, 11.4 and 11.5 mg Tc/g sorbent, respectively, corresponding to 0.090, 0.115 and 0.116 mmol Tc/g sorbent. The initial Tc loading (i.e., 1.2×10⁻³ M) rate was equivalent to 11.6 mg Tc/g sorbent for 100% removal. In the case of OCM and GAC in AGW there was 98 to 99% removal, but for OCB in

AGW, it was just ~78% removal, which meant that the sorbents were saturated with Tc in AGW. With the addition of 0.1 M NaNO₃ to the AGW, the capacities for removing TcO₄⁻ decreased by 9.1% for organoclay OCB, 17.5% for organoclay OCM and 25.2% for GAC 830. However, it is noted that in the 0.1 M NaNO₃ solution, the NO₃⁻ concentration was nearly 100 times higher than the Tc concentration, but the Tc removal capacities were only reduced by 10 to 25%, which meant that the organoclays and GAC selectively removed TcO₄⁻ in preference to NO₃⁻. The 10 g/L sorbent loading could not necessarily remove all TcO₄⁻ and NO₃⁻ in the 0.1 M NaNO₃ solution. The underlying chemical mechanisms controlling the high degree of selectivity for TcO₄⁻ are uncertain and clearly warrant further study.

3.4. Desorption and resorption of ReO₄⁻ as a surrogate for TcO₄⁻

In order to evaluate whether these sorbents could be regenerated for reuse, ReO₄⁻ was used as a surrogate for TcO₄⁻ in a sequential five-step batch experiment: 1) sorption of ReO₄⁻ (1.2×10⁻³ M for 3 days); 2) desorption by 0.1 M Na₂SO₄ for 3 days; 3) resorption of ReO₄⁻ (1.2×10⁻³ M for 3 days); 4) desorption by 1 M KI for 3 days; and 5) resorption of ReO₄⁻ (1.2×10⁻³ M for 3 days). The quantity (q_e, mg Re/g sorbent) of residual Re associated with the sorbents was estimated after each step of the sequential treatments described above. The quantities of Re on the three sorbents in AGW after each of the five-step treatments are shown in Fig. 3.

When initially exposed to 1.2×10⁻³ M ReO₄⁻ in AGW for 3 days, the quantities of Re sorbed on OCB, OCM, and GAC 830 were 18.3, 18.9 and 18.8 mg Re/g sorbent, respectively, corresponding to 0.098, 0.102, and 0.101 mmol Re/g sorbent. In the presence of the 0.1 M Na₂SO₄ solution, the desorption rates of Re on OCB, OCM, and GAC 830 were 7.3%, 3.7% and 11.9%, respectively, which indicates that 0.1 M Na₂SO₄ solution was ineffective at desorbing Re

from these sorbents, especially for the organoclay OCM. In the third step of this sequential batch experiment, the same OCB, OCM, and GAC 830 samples were exposed to 1.2×10^{-3} M ReO_4^- in AGW for 3 days again. Additional Re sorbed on these sorbents and the resorption percentages for OCB, OCM, and GAC 830 were 14.9%, 27.2% and 51.7% of the added Re, respectively. Together with the residual Re from the previous step, the new total sorbed quantities of Re on the OCB, OCM, and GAC 830 were 20.0, 24.0, 27.4 mg Re/g sorbent, respectively, corresponding to 0.107, 0.129 and 0.147 mmol Re/g sorbent. In the presence of the 1 M KI solution, the desorption percentages of Re on OCB, OCM, and GAC 830 were 95.6%, 89.5% and 86.1%, respectively, which indicates that 1 M KI solution is effective at desorbing Re from these materials. The greater effectiveness of I^- compared to SO_4^{2-} for desorbing TcO_4^- has been previously reported [48]. Finally, the sorbents were exposed to 1.2×10^{-3} M ReO_4^- in AGW for 3 days again. Together with the residual Re from the KI extraction, the total sorbed quantities of Re on the OCB, OCM, and GAC 830 were 18.8, 21.3, 22.7 mg Re/g sorbent. These results demonstrate that the regenerated sorbents retained similar, if not slightly higher, retention capacity for Re when recycled. It is unclear if the intermediate extraction steps generate additional binding sites for Re; however, the increased Re resorption capacity may reflect accumulated errors generated during multiple batch equilibrations and repeated ICP-MS analysis.

3.5 Tc speciation and binding chemistry

The Tc K-edge XANES spectra of the sorbents after exposure to TcO_4^- in AGW are shown in Fig. 4, in comparison with the standard spectra of ammonium pertechnetate (NH_4TcO_4) and Tc(IV) oxide (i.e., TcO_2). Graphical comparison and linear combination fitting indicated that the adsorbed Tc species on these sorbents at varying pHs was TcO_4^- , rather than the reduced form of

TcO₂ [28, 37] or other non-pertechnetate species [15, 26, 28, 37, 49-51]. It is noted that the pre-edge feature for organoclay OCM at pH 8.5 looks slightly lower than the other samples.

Although this observation was not understood, the linear combination fitting and EXAFS data analysis described below indicate the presence of TcO₄⁻ species, without a detectable amount of reduced Tc species. Therefore, the inexpensive organoclays and GAC appear to sequester Tc in the natural form that generally persists in the environment, without requiring an artificial reducing environment.

Tc K-edge EXAFS spectra in k-space (A), Fourier transforms plots in magnitude (B) and in the real space component (C) of the sorbents after exposure to TcO₄⁻ in the AGW at near neutral pHs are shown in Fig. 5, with experimental data shown in solid circles, and EXAFS fits shown in colored lines. The fitted EXAFS parameters for all the sorbents, together with ammonium pertechnetate, are summarized in Table 4. The EXAFS spectrum of ammonium pertechnetate was fitted by tetrahedral Tc-O paths with Tc-O distance of 1.721 Å and fixed coordination number of 4. The EXAFS fitting of this model compound was fairly good as measured by reduced χ^2 of 13.4, but the obtained Tc-O distance was slightly longer (1.721 Å) than single crystal X-ray diffraction Tc-O distance of 1.703 Å [39]. In ammonium pertechnetate, TcO₄⁻ is bonded with NH₄⁺ through H-binding with the Tc-N distance of 4.048 Å. However, the Tc-N scattering path was not able to fit in its EXAFS spectrum because N is a poor scatterer and the EXAFS signal was too weak beyond 4 Å. Like ammonium pertechnetate, the Tc K-edge EXAFS data for the three sorbents were fitted with tetrahedral oxygen paths at a Tc-O distance of 1.718 ± 0.006 Å with a coordination number of 4.1 ± 0.3 . The EXAFS data fitting for these samples was also good as measured by the reduced χ^2 that ranged from 10 to 29. However, there was no meaningful structural information beyond the Tc-O tetrahedral shell. It is likely that TcO₄⁻ was

binding with the quaternary amine groups in organoclays or similar functional groups on GAC 830 as an outer-sphere species. The chemical bonding between the TcO_4^- species and the binding ligands was likely similar to the H-bonding observed in ammonium pertechnetate [39] and in hexaammine-cobalt(II) pertechnetate [52].

4. Conclusions

The organoclays and GAC that we studied are inexpensive. However, they were demonstrated to be very effective at removing pertechnetate (TcO_4^-) from groundwater. Under oxic conditions, the adsorption capacity of TcO_4^- on the organoclays across the wide pH value range from 3 to 12 was 15 mg/g, while the adsorption capacity on GAC under the same pH conditions was 25 mg/g. The organoclays and GAC were demonstrated to be highly selective toward binding TcO_4^- in the presence of competitive anions like NO_3^- that are generally present at much higher concentrations than in groundwater and nuclear waste streams. The removal capacity of TcO_4^- was only reduced by about 20% when the NO_3^- concentration was nearly two orders of magnitude greater than TcO_4^- . After initial TcO_4^- adsorption, the sorption capacity for organoclay and GAC can be regenerated by treatment with 1 M KI to remove Tc, while 0.1 M sodium sulfate was ineffective at TcO_4^- removal. After washing, the regenerated sorbents remained effective at removing TcO_4^- from groundwater in subsequent tests.

The Tc species bound to the organoclays and GAC was the oxidized Tc(VII) (i.e., TcO_4^-), rather than its reduced Tc(IV) form. TcO_4^- likely formed adsorption complexes through H bonding with N ligands. This result is important for the practical applications of these remediation materials. Sediment minerals and synthetic materials, including anionic exchange resins, have very limited loading capacities for removing TcO_4^- from aqueous media [7].

Chemical reduction and bioreduction are among common technologies for the remediation of TcO_4^- from nuclear waste streams or highly contaminated sites. However, there are several disadvantages for such reductive technologies: 1) they require costly manipulation to create and maintain a reducing environment; 2) bioreduction requires a ready supply of electron donors (e.g., acetate, ethanol) to maintain sustained effectiveness; and 3) the reductive product, usually $\text{Tc(IV)O}_2 \cdot 1.6\text{H}_2\text{O}$, has high solubility of $\sim 1.5 \times 10^{-8}$ M in groundwater, which greatly exceeds the EPA's MCL of 5×10^{-10} M. The organoclays and GAC have a high capacity of removing TcO_4^- from groundwater under oxic condition, effectively retaining TcO_4^- without the need for reducing conditions. Therefore, the inexpensive and high-capacity organoclays and GAC materials may provide a practical solution for efficiently removing $^{99}\text{TcO}_4^-$ and other anionic contaminants from environmental systems.

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Table 1.
Brief description of organoclays and granular activated carbon used in this work

Sorbents	Acronym	Description	Manufacturer
Organoclay OCB	OCB	ClayFloc™ 750, a bentonite organoclay based flocculant impregnated with a quaternary amine	Biomin Inc., Ferndale, MI, USA
Organoclay OCM	OCM	Organoclay MRM™ clay impregnated with a quaternary amine and a sulfur-containing compound	Cetco® Remediation Technologies, Hoffman Estates, IL, USA
Granular 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, USA

Table 2.
Langmuir fit parameters (Equation 2) and associated determination coefficients (R^2) of organoclays and GAC for TcO_4^- removal from artificial groundwater at varying pHs

Sorbents	pH	Langmuir fits		
		q_{max} (mg Tc/g sorbent)	K_L (L/g)	R^2
OCB	6.8	13.9	0.058	0.992
	12.3	14.0	0.148	0.991
OCM	3.2	16.1	0.476	0.999
	8.5	14.8	0.120	0.996
GAC 830	2.9	28.4	0.137	0.955
	7.8	27.9	0.347	0.954
	9.9	23.0	0.052	0.969

Table 3.

Comparison of the current organoclay and GAC sorbents with other commonly used sorbents for TcO_4^- or ReO_4^- removal from aqueous media

Sorbent	Aqueous media	pH	Sorbate	Sorption coefficient, K_d (mL/g)	Tc or Re Sorption Capacity (mg/g)	References
Quartz	0.1 M NaCl solution	3.91-8.65	TcO_4^-	3.4 ± 3.6		[5]
Corundum		4.51-8.82		0.7 ± 0.3		
Hematite		4.13 - 9.13		5.4 ± 1.2		
Montmorillonite		4.11 - 8.43		9.0 ± 6.5		
Kaolinite		3.90 - 8.99		2.2 ± 1.4		
GAC, Nuchar WV-G	Groundwater from the Portsmouth site	6.2	TcO_4^-	2.7×10^4	1×10^{-3} ^a	[8]
Hexadecylpyridinium bentonite	Synthetic groundwater, ion strength 0.037 M	~ 7	ReO_4^-	$\sim 4 \times 10^3$	8.3	[53]
Hexadecyl trimethylammonium bentonite	Aqueous solution	5	TcO_4^-	421		[54]
Cellulose sponge with amine-containing polymers	Groundwater simulating the Portsmouth site	6.2	TcO_4^-	354	3.8×10^{-6} ^c	[6]
Trihexylamine / trimethylamine bifunctional resin	Contaminated groundwater from the Paducah site	~ 7	TcO_4^-	4.83×10^4	2.4×10^{-4} ^b	[55]
Bifunctional resin Purolite A530E	10 M Na nuclear waste simulant	>14	TcO_4^-	837		[56]
	Groundwater from Hanford Site well 299-W15-765	~ 9	TcO_4^-	1.94×10^4	1.3×10^{-2}	[57] ^d
	Solution with NO_3^- or SO_4^{2-}	~ 7	ReO_4^-		526 ^g	[40]
Metal-organic framework SCU-100	Aqueous solution		ReO_4^-		402 ^g	[41]
Metal-organic framework SCU-101	Aqueous solution		ReO_4^-		167 ^g	[42]
Metal-organic framework UiO-66- NH_3^+	Aqueous solution		ReO_4^-		118 ^g	[43]
Metal-organic framework NU-1000	Aqueous solution		ReO_4^-		127 ^g	[44]
Metal-organic framework SLUG-21	Aqueous solution		ReO_4^-		448 ^g	[45]

Cationic crystalline coordination polymer SBN	Aqueous solution		ReO ₄ ⁻		585 ^g	[46]
Cationic crystalline coordination polymer SCU-CPN-1	Aqueous solution		ReO ₄ ⁻		744 ^g	[47]
Organoclay OCB	Groundwater simulating Savannah River Sites	12.3	TcO ₄ ⁻	1.17×10 ⁵	14.0	This work and [34] ^e
Organoclay OCM		3.2		1.12×10 ⁵	16.1	
GAC 830		7.8		1.08×10 ⁵	27.9	
^a This was estimated using 16,000 pCi/g. The isotherm was linear and the saturation capacity was not reported.						
^b This was estimated using 2.4 nmol/g. The isotherm was linear and the saturation capacity was not reported.						
^c This was estimated using 60 pCi/g. The isotherm was linear and the saturation capacity was not reported.						
^d This was desorption K _d value of spent resin obtained from leach test at solid-solution ratio of 1:1. The Tc sorption load on the spent resin was estimated based on the leached Tc concentration of 42 pCi/g, which is <0.02% of the total Tc loaded. The saturation capacity was not reported.						
^e The sorption coefficient numbers were cited from [34].						
^g The Re capacity values were converted from the ReO ₄ ⁻ capacity values reported in the original references.						

Table 4.

Tc K-edge EXAFS fitting data for Tc species onto organoclays and GAC 830

Samples ^a	pH	Scattering path	Interatomic distance (Å)	Coordination number	Debye–Waller factor, σ^2 (Å ²)	E ₀ (eV)	R-factor	Reduced χ^2
OCB	6.8	Tc-O	1.713 ± 0.005	4.4 ± 0.3	0.0015 ± 0.0008	6.4 ± 1.2	0.0130	26.7
	12.3	Tc-O	1.720 ± 0.003	4.1 ± 0.2	0.0015 ± 0.0005	9.5 ± 0.6	0.0045	29.3
OCM	3.2	Tc-O	1.712 ± 0.007	4.1 ± 0.2	0.0015	5.6 ± 1.4	0.0201	18.0
	8.5	Tc-O	1.724 ± 0.003	3.8 ± 0.2	0.0013 ± 0.0005	9.1 ± 0.7	0.0058	9.9
GAC 830	2.9	Tc-O	1.723 ± 0.003	4.1 ± 0.2	0.0013 ± 0.0005	9.2 ± 0.6	0.0047	13.1
	7.8	Tc-O	1.724 ± 0.003	4.2 ± 0.2	0.0014 ± 0.0005	9.1 ± 0.7	0.0055	10.4
	9.9	Tc-O	1.716 ± 0.006	4.4 ± 0.3	0.0015 ± 0.0008	9.3 ± 1.1	0.0128	14.4
Ammonium pertechnetate	EXAFS	Tc-O	1.721 ± 0.003	4.3 ± 0.3	0.0016 ± 0.0004	8.7 ± 0.6	0.0039	13.4
	X-ray structure [39]	Tc-O	1.703	4				

^a Amplitude was set to 1.

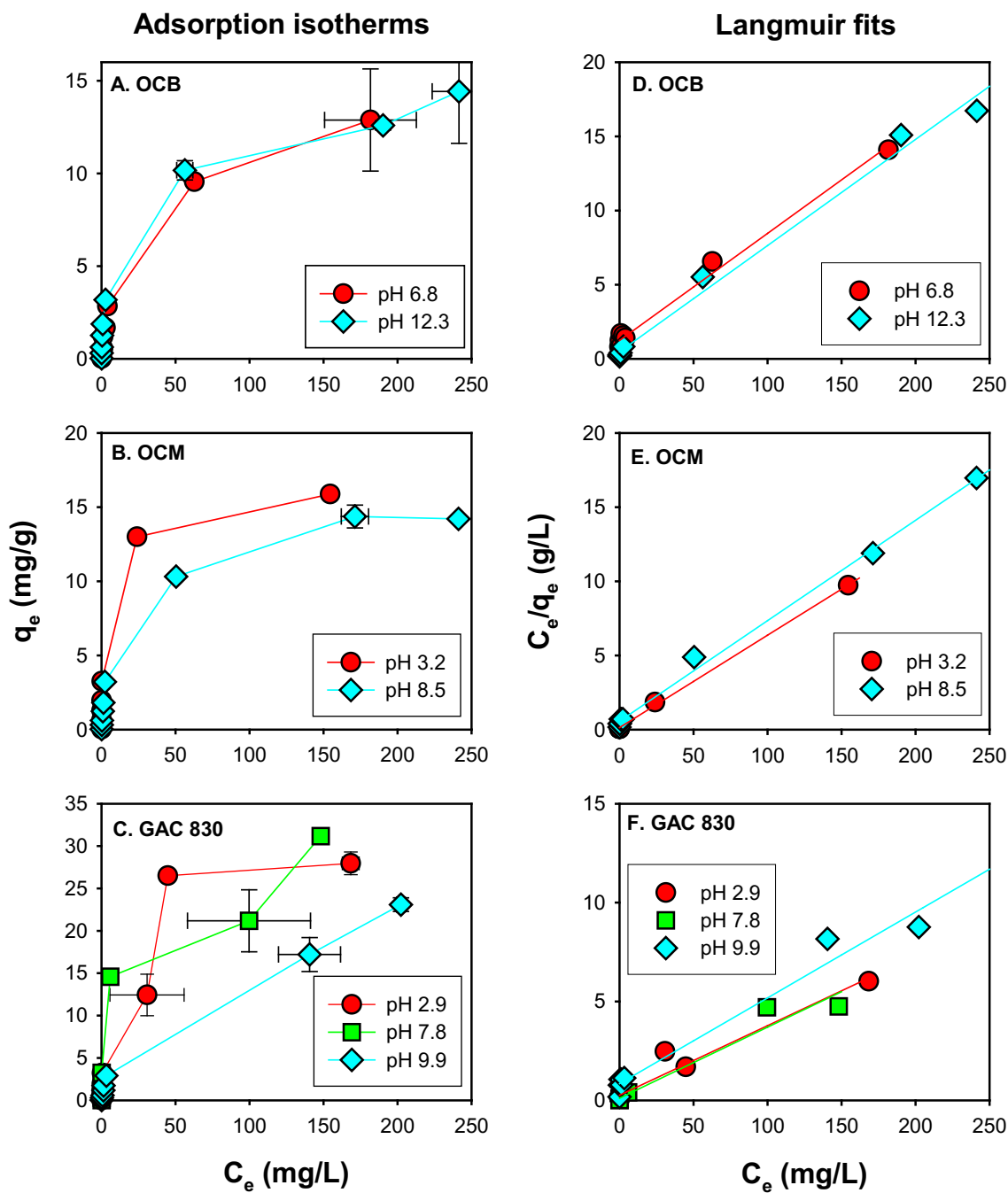


Fig. 1. Adsorption isotherms of TcO_4^- on organoclay OCB (A), organoclay OCM (B) and GAC 830 (C) in AGW under varying pHs and oxidic conditions. The Langmuir fits to the corresponding experimental data of OCB (D), OCM (E) and GAC 830 (F) are also shown.

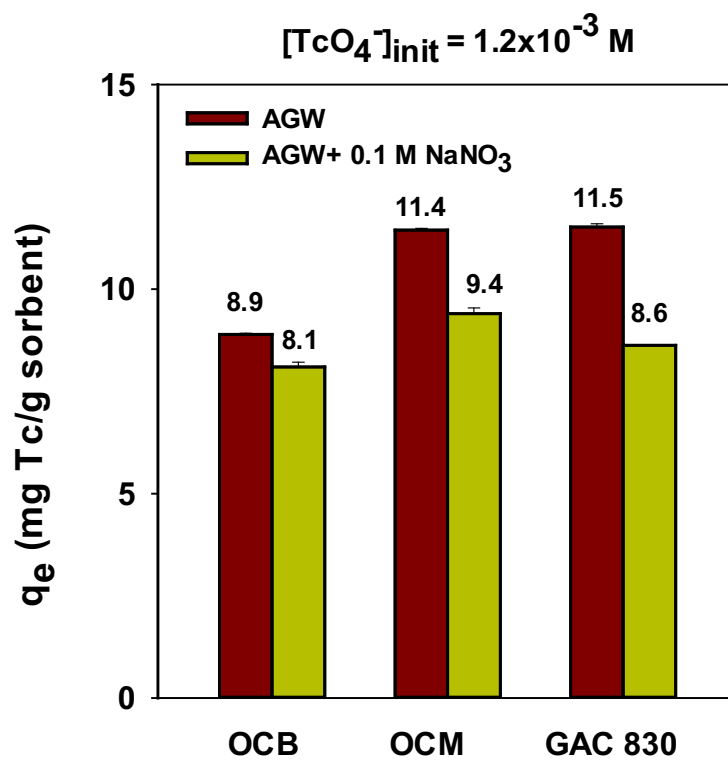


Fig. 2. Effects of nitrate on TcO_4^- removal from AGW at pH 8 - 9 by organoclays OCB, OCM, and GAC 830.

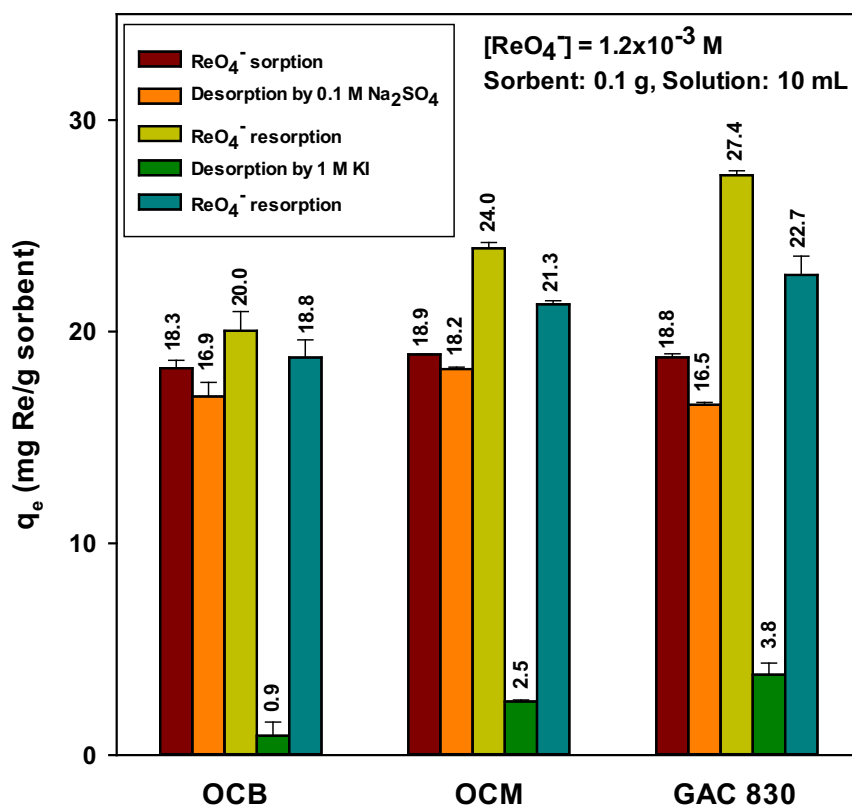


Fig. 3. Desorption and resorption of ReO₄⁻ on organoclays (OCB and OCM) and GAC 830 in artificial groundwater (AGW). The quantity (q_e , mg/g) of Re on the sorbents were obtained after each step of the sequential treatments. For example, the q_e data from each of the resorption steps included the quantities of both residual and newly sorbed Re.

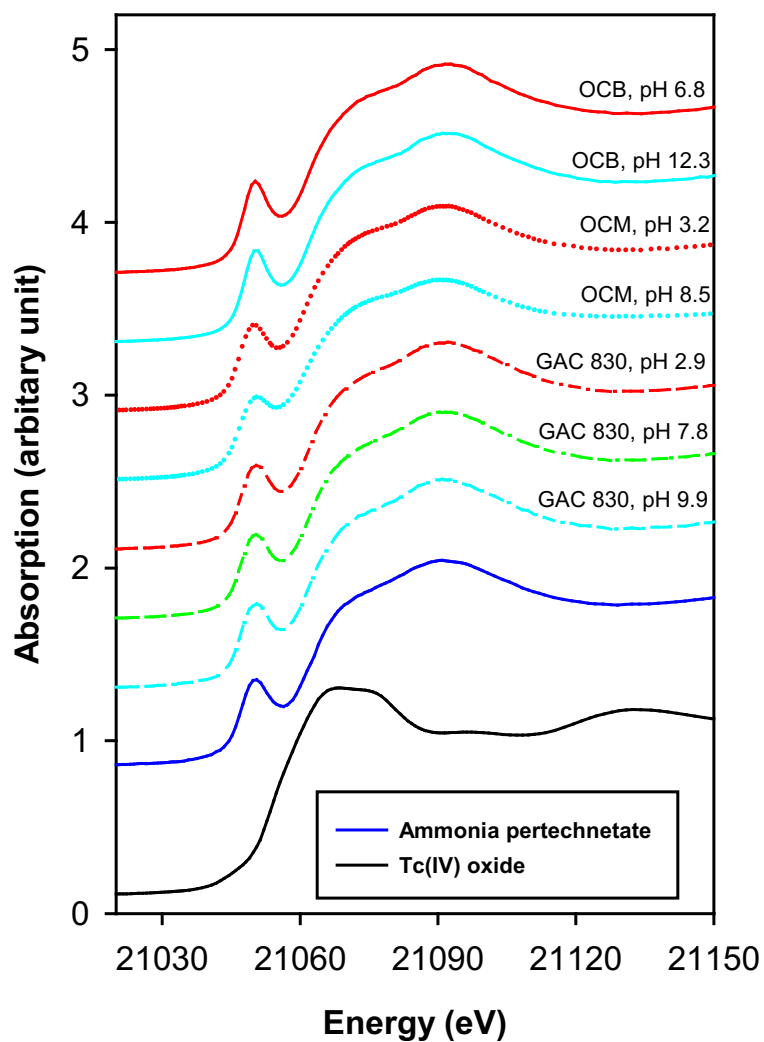


Fig. 4. Tc K-edge XANES spectra of organoclays and GAC after exposed to TcO_4^- in AGW at different pHs, in comparison with those of two model compounds, ammonium pertechnetate and Tc(IV) oxide.

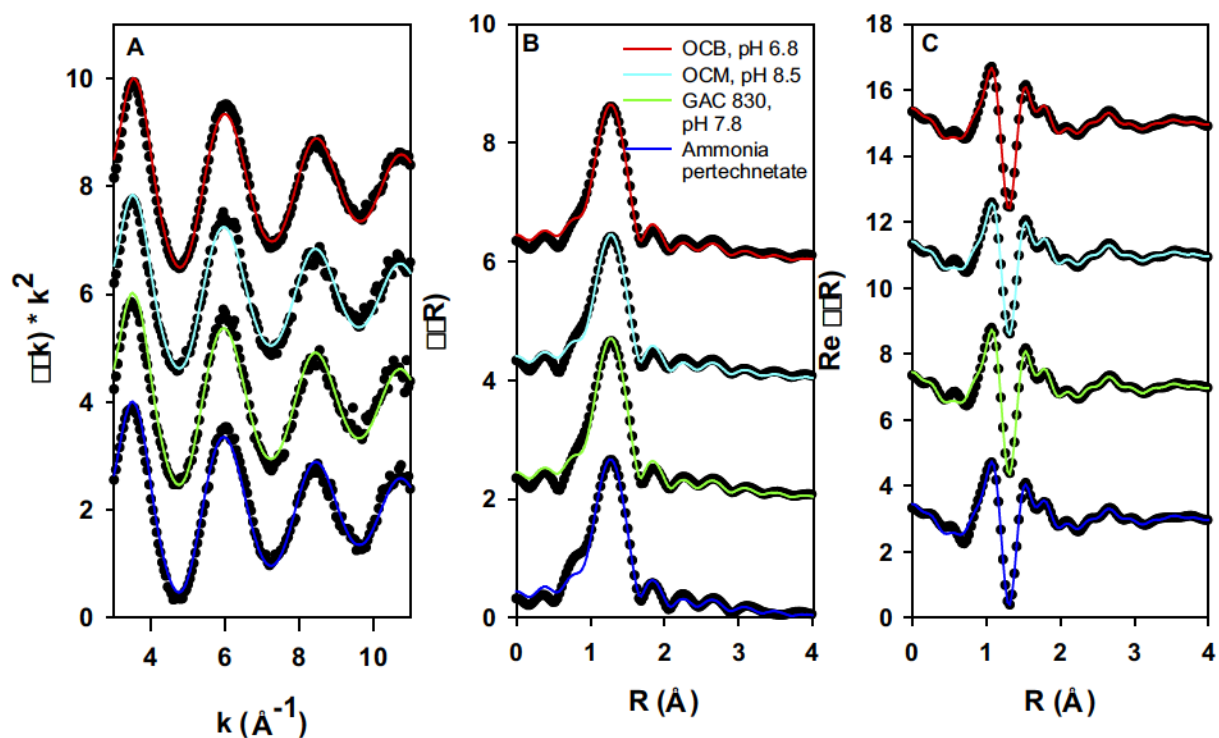


Fig. 5. Tc K-edge EXAFS spectra in k-space (A), Fourier transform plots in magnitude (B) and in the real space component (C) of organoclays (OCB and OCM) and GAC 830 after exposed to TcO_4^- in AGW with the equilibrium pHs of 6.8-8.5, in comparison with the EXAFS spectra of ammonium pertechnetate.