Highly Efficient Uptake of TcO$_4^-$ by Imidazolium-Functionalized Wood Sawdust

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ABSTRACT: $^{99}$Tc is a radioactive fission product, mainly in the form of TcO$_4^-$, with good solubility and mobility in the environment. The development of effective and inexpensive materials to remove TcO$_4^-$ from nuclear industry wastewater or contaminated water is significant. Wood sawdust is a byproduct of the wood processing industry and is an abundant, low-cost, and sustainable material. The mesostructure of wood consists of numerous hollow cells that are joined endwise to form an interconnected channel matrix capable of rapid transfer of ions. Imidazolium-functionalized wood sawdust (IM-WS) was synthesized using natural wood sawdust by a two-step reaction. It has excellent properties of TcO$_4^-$/ReO$_4^-$ adsorption including rapid adsorption dynamics (30 s to equilibrium), good adsorption stability (pH 3–9), high selectivity (adsorption of 45.4 Re % in 1000 times excess of NO$_3^-$ ions, 76.6 Re % in 6000 times excess of SO$_4^{2-}$ ions, and 92.2 Tc % in a simulated mixed solution; after adsorption, the concentration of TcO$_4^-$ decreased to 0.056 ppb from the initial concentration of 12.09 ppb in 1000 times excess of SO$_4^{2-}$), and in particular low production costs. These characteristics give it great prospects for low-level radioactive wastewater treatment and environmental remediation.

1. INTRODUCTION

Technetium-99 ($^{99}$Tc) is produced from fission of $^{235}$U and $^{239}$Pu with a high yield (≥6.1%) in a nuclear reaction.$^{1,2}$ $^{99}$Tc has a half-life of 2.1 × 10$^5$ years and is a weak $\beta$ emitter with a maximum energy of 0.29 MeV.$^3$ When exposed to the environment, it exists as the pertechnetate anion (TcO$_4^-$). Due to the high solubility and mobility of TcO$_4^-$ underground, it needs more attention than other radionuclides.$^{5,6}$

There are two general strategies to remove pertechnetate from the environment. One is by reducing the Tc(VII)O$_4^-$ anion to less soluble technetium oxides Tc(IV)O$_2$ and then sequestering it.$^{7,8}$ Fe(II)$^9$–$^{12}$ sulfoxides, and iron sulfides$^{10,12}$ have been employed for the reduction of TcO$_4^-$, but it is difficult to prevent Tc(IV) from re-oxidation during the long geological disposal period.$^{13}$ The other effective strategy is using ion exchange, extraction, and gravity precipitation to capture TcO$_4^-$.$^{14,17}$ Ion exchange is considered to be a promising method with the advantages of easy implementation and high efficiency.$^{18}$

In the last few decades, several types of polyionic materials have been studied to dispose off TcO$_4^-$.$^{18–20}$ Ion-exchange resins show slow kinetics and poor selectivity when taking up TcO$_4^-$. Inorganic cationic materials, such as layered double hydroxides (LDHs)$^{22}$ LRHs$^{23}$ and NDTB-1,$^{19}$ are easy to synthesize but have low sorption capacity and poor selectivity toward TcO$_4^-$. The designed and synthesized cationic metal–organic frameworks (MOFs)$^{13,24,25}$ covalent organic frameworks (COFs)$^{26,27}$ nanomaterials$^{28}$ and porous organic polymers (POPs)$^{29}$ can selectively and rapidly adsorb TcO$_4^-$, but they suffer from high costs.

The recently reported imidazolium polymer SCU-CPN-1$^{30}$ and imidazolium porous organic polymer ImPOP-1$^{29}$ show excellent adsorption capacity and extraordinary selectivity to TcO$_4^-$. It is proved that the imidazolium cation is the key part for highly selective adsorption of TcO$_4^-$. Wood, a natural three-dimensional (3D) porous material, has the advantages of renewable, sustainable, and abundant resources. Due to the internal micropores and microchannels, it has more opportunities to contact pollutants in water. Wood-functionalized materials have become one of the most promising candidates for wastewater treatment. Uio-66/wood$^{31}$ Mn$_2$O$_4$/TiO$_2$/wood$^{32}$ Pd NPs/wood$^{33}$ and $\beta$-CD/WS$^{34}$ have been reported to remove organic pollutants (e.g., methylene blue, rhodamine 6G, and propranolol) from aqueous solutions. LS-C$_3$N$_4$/CWS$^{35}$ and SH-wood$^{36}$ show
excellent decontamination capability toward Pb\(^{2+}\), Cd\(^{2+}\), and Cu\(^{2+}\).

In this work, wood chips and sawdust are chosen as the matrix material due to their natural wood properties and low cost, which are byproducts of the wood processing industry.\(^3\)\(^4\) Imidazolium-functionalized wood sawdust (IM-WS) was synthesized by grafting 1,1′-(1,4-butanediyl)diimidazole groups on the cellulose of natural wood sawdust. Up to now, there have been no imidazolium-based biomass materials reported for the treatment of TcO\(_4\)\(^{−}\). The interconnected network structure in natural wood sawdust and imidazolium cations enables effective removal of TcO\(_4\)\(^{−}\).

Herein, we evaluated the removal capability of IM-WS for TcO\(_4\)\(^{−}\)/ReO\(_4\)\(^{−}\) by a batch adsorption experiment. In most experiments, ReO\(_4\)\(^{−}\) was used as the surrogate of radioactive TcO\(_4\)\(^{−}\) given their almost identical charge densities and similar chemical behaviors.\(^1\)\(^6\)

### 2. RESULTS AND DISCUSSION

#### 2.1. Synthesis and Characterization of IM-WS

Wood sawdust or wood chips, a natural material, are cheap and mechanically stable and can be processed into different shapes and sizes. The cellulose of wood sawdust (about 40–45\%) has a large number of modifiable hydroxyl groups, which makes it a good graft matrix material.

The imidazolium-functionalized wood sawdust was synthesized by a two-step reaction, shown as Scheme 1. Natural wood sawdust reacted with chloroacetyl chloride to form esterification products, which via quaternization with 1,1′-(1,4-butanediyl)diimidazole afforded the final product. It can be seen from Figure 1a that the modified sawdust becomes smaller due to stirring for a long time.

The successful grafting of the imidazolium cation is confirmed by elemental analysis, scanning electron microscopy (SEM), energy-dispersive spectrometry (EDS), and Fourier transform infrared spectroscopy (FT-IR). Elemental analysis reveals a nitrogen content of 2.59 wt % (Table S1), corresponding to 0.27 mmol g\(^{−1}\) imidazolium cation in IM-WS. Scanning electron microscopy (SEM) images of IM-WS (Figure 1b,c) show that the sawn-off vessel channels and micropores are well maintained after functionalization. The sawn-off vessel channels, the micropores, the natural 3D structure of wood sawdust, and grafted imidazolium make IM-WS an ideal material for ion exchange. The energy-dispersive spectrometry (EDS) mappings of IM-WS exhibit distribution of Cl and N elements throughout the material (Figure 1d). In contrast, there are no chlorine and nitrogen in natural wood sawdust (Figure S1). The elemental distribution mappings prove that the cellulose is grafted with the imidazolium cation uniformly.

On comparison of the FT-IR spectra of IM-WS with those of natural wood sawdust (WS), many new peaks appear (Figure 2). The peak at 1753 cm\(^{−1}\) is attributed to the C=O stretching vibrations of the −COO− bond. The characteristic absorption peak of the imidazolium cation appears at 1100 cm\(^{−1}\). The peaks at 1568 and 1627 cm\(^{−1}\) correspond to the vibration of the imidazole ring skeleton. The peak at 2963 cm\(^{−1}\) is attributed to the C−H stretching vibrations of −CH\(_2−\) bonds of 1,1′-(1,4-butanediyl)diimidazole. All of these findings indicate the successful synthesis of IM-WS.
2.2. ReO$_4^-$/TcO$_4^-$ Adsorption. 2.2.1. Sorption Kinetics. To evaluate the IM-WS adsorption performance toward TcO$_4^-$, a series of adsorption experiments were carried out. IM-WS (10 mg) was added to 5 mL of an aqueous solution containing 100 ppm ReO$_4^-$ in the designed time for studying the sorption kinetics of IM-WS. As shown in Figure 3a, the adsorption achieved equilibrium within 30 s. The distribution coefficient ($K_d$) was calculated using the following equation

$$K_d = \frac{C_0 - C_e}{C_e} \frac{V}{m}$$

where $C_0$ and $C_e$ are the concentrations of ReO$_4^-$ solution (mg L$^{-1}$) initially and at equilibrium, respectively, $m$ is the mass of the absorbent (g), and $V$ is the volume of the solution (L). The $K_d$ value is an important parameter that can reflect the affinity and selectivity of the adsorbents. The $K_d$ of IM-WS toward ReO$_4^-$ reaches an outstanding value of $3.79 \times 10^5$ mL g$^{-1}$, which is a competitive value among the materials reported so far (Table 1). The excellent adsorption rate of IM-WS on ReO$_4^-$ is conducive to the rapid reduction of pollution by radioactive Tc, making IM-WS an attractive environmental remediation material, which can effectively remove Tc released into the environment. The adsorption kinetics data are fitted with pseudo-first-order and pseudo-second-order kinetic models. On comparing the correlation coefficients ($R^2$) of these two models (Table S2), the adsorption process is more in line with the pseudo-second-order kinetic model with a high $R^2$ of 1 (Figure 3b). It can be considered that the adsorption process is chemical homogeneous adsorption.

2.2.2. Sorption Isotherm Tests. To investigate the saturated adsorption capacity of IM-WS toward ReO$_4^-$, 10 mg of IM-WS was added to 5 mL of ReO$_4^-$ aqueous solution. The initial concentrations of ReO$_4^-$ were varied from 100 to 1500 ppm. The adsorption isotherm data were fitted with the Langmuir and Freundlich sorption isotherm models. As shown in Figure 4a,b, the Langmuir model fits the equilibrium adsorption process well with a high correlation coefficient $R^2$ of 0.9994, which means that the IM-WS can take up ReO$_4^-$ efficiently by monolayer adsorption. The theoretical sorption capacity $q_{max}$ (201.2 mg g$^{-1}$) calculated by the Langmuir model is very close to the experimental value of 200.1 mg g$^{-1}$.

2.2.3. Adsorption Mechanism Study. The adsorption process of IM-WS toward Re was studied by determining the composition of the material after adsorption. Typically, 30 mg of IM-WS was added to 15 mL of an aqueous solution containing 1500 ppm ReO$_4^-$, whose pH was adjusted to 7. The mixture was stirred at 25 °C for 12 h, and then the Re-loaded

Table 1. Comparison of the Distribution Coefficient ($K_d$) by Cationic Materials

| cationic materials                             | $K_d$ (mL g$^{-1}$) | solid/liquid ratio (g L$^{-1}$) | ref |
|-----------------------------------------------|---------------------|---------------------------------|-----|
| inorganic materials                           |                     |                                 |     |
| Y$_2$(OH)$_5$Cl                                | 112                 | 0.5                             | 13  |
| Yb$_3$O(OH)$_6$Cl                              | 120                 | 0.5                             | 13  |
| Mg-Al-LDH                                      | 262                 | 1                               | 24  |
| ion-exchange resins                            |                     |                                 |     |
| Purolite A-850                                 | 102                 |                                 | 37  |
| Purolite A 532E                                | $1.28 \times 10^4$  |                                 | 37  |
| MOF materials                                  |                     |                                 |     |
| SCU-100                                       | $3.3 \times 10^3$   | 1                               | 24  |
| SCU-101                                       | $7.5 \times 10^3$   |                                 | 38  |
| SCU-102                                       | $5.6 \times 10^3$   | 10                              | 39  |
| SCU-103                                       | $1.00 \times 10^4$  | 1                               | 40  |
| COF materials                                 |                     |                                 |     |
| SCU-COF-1                                     | $3.89 \times 10^3$  | 1                               | 27  |
| POP materials                                 |                     |                                 |     |
| PQA-pN(Me)2Py-Cl                               | $1.00 \times 10^4$  |                                 | 41  |
| SCU-CPN-1                                     | $6.2 \times 10^4$   | 1                               | 30  |
| IM-WS                                         | $3.79 \times 10^5$  |                                 | 2   |

Figure 3. (a) ReO$_4^-$ sorption kinetics of IM-WS under the ReO$_4^-$ initial concentration of 100 ppm with the m/V ratio at 2 g L$^{-1}$. (b) Pseudo-second-order kinetic plot for adsorption.
sample IM-WS-Re was collected, washed three times with water, and dried under vacuum.

Comparing the FT-IR spectra of IM-WS-Re with those of IM-WS (Figure 2), there is a significant new peak at 907 cm\(^{-1}\), which is attributed to the Re–O\(_{\nu3}\) asymmetric stretch. The EDS spectrum of IM-WS-Re (Figure S2) confirms the successful uptake of ReO\(_4^-\). Compared to the EDS mappings of IM-WS and IM-WS-Re (Figure 1d), we can find that the amount of Cl has an appreciable decrease after Re uptake. The X-ray photoelectron spectroscopy (XPS) analysis result (Figure 5a) confirms that the oxidation state of Re(VII) was unchanged after adsorption, indicating that the Re species in IM-WS-Re is perrhenate. On comparing the XPS results of IM-WS-Re with those of NH\(_4\)ReO\(_4\) (Figure 5c), the shifts of Re 4f\(_{5/2}\) and 4f\(_{7/2}\) are 0.17 and 0.36 eV, respectively, indicating that there are special interactions between ReO\(_4^-\) and the imidazolium cation. Combining the above results, we can confirm that the adsorption of ReO\(_4^-\) by IM-WS is an anion-exchange process.

**2.2.4. pH Effect.** ζ-Potentials of IM-WS in different pHs were studied in detail. Typically, 10 mg of IM-WS was added to 5 mL of the aqueous solution, whose pH was adjusted from 1 to 13. It was stirred for 12 h at room temperature. IM-WS was separated for the ζ-potential test. IM-WS shows a positive ζ-potential in the range of pH 1–11 (Figure 6a), indicating that the surface of the material is positively charged. As shown in Figure 6b, the adsorption capacity of IM-WS for ReO\(_4^-\) remains almost unchanged for pH 3–9 and decreases when pH > 9 and pH < 3. IM-WS has good adsorption stability over a wide pH range from 3 to 9, which is necessary for practical applications in polluted sewage treatment (pH 8.0–8.5) during nuclear accidents. The adsorption capacity decreases when pH
> 9 and pH < 3, indicating that both H⁺ and HO⁻ have an effect on the adsorption capacity.

2.2.5. Uptake Selectivity. Considering that there are many kinds of anions in radioactive waste solutions, it is necessary to investigate the adsorption selectivity of IM-WS for TcO₄⁻. The adsorption properties of IM-WS toward ReO₄⁻ were further studied in the presence of different excesses of NO₃⁻ and SO₄²⁻. The results are shown in Figure 7a,b. It can be seen that with molar ratios of NO₃⁻/ReO₄⁻ = 1000:1 and SO₄²⁻/ReO₄⁻ = 6000:1, the removal efficiency for ReO₄⁻ can reach 45.44 and 76.57%, respectively. The result is similar to that of imidazolium-based cationic polymer materials SCU-CPN-I and ImPOP-1. The standard Gibbs energy of hydration of ReO₄⁻ is −330 kJ mol⁻¹, which is close to that of NO₃⁻ (−306 kJ mol⁻¹) but much lower than that of SO₄²⁻ (−1090 kJ mol⁻¹), which can explain the fact that NO₃⁻ has a greater competitive effect on the removal of ReO₄⁻ than SO₄²⁻. The selectivity for ReO₄⁻ in the presence of NO₃⁻ may be due to the special interactions between tetrahedral ReO₄⁻/TcO₄⁻ anions and the imidazolium cation.

When the concentration of coexisting SO₄²⁻ is 1000 times that of TcO₄⁻, after adsorption, the concentration of TcO₄⁻ decreased to 0.056 ppb from the initial concentration of 12.09 ppb (Table 2). The removal rate reached 99.54%, indicating the potential of treating trace technetium with IM-WS.

Table 2. Trace Technetium Adsorption Result

| C₀ (TcO₄⁻) (ppb) | Cₑ (TcO₄⁻) (ppb) | solid/liquid ratio (g L⁻¹) | molar ratio between SO₄²⁻ and TcO₄⁻ | removal (%) |
|------------------|------------------|--------------------------|----------------------------------|------------|
| 12.09            | 0.056            | 20                       | 1000                             | 99.54      |

2.2.6. Simulated Nuclear Wastes. The separation ability of IM-WS toward TcO₄⁻ in simulated low-level radioactive wastewater was tested. The chemical composition of simulated wastewater containing Tc is shown in Table 3. The concentrations of NO₃⁻ and Cl⁻ in the solution were more than 300 times that of TcO₄⁻/ReO₄⁻. The excess of NO₃⁻ was even more than 800 times that of TcO₄⁻/ReO₄⁻ (Table 3). The adsorption efficiency to Tc was 92.2% and to Re was 88.3% at the solid/liquid ratio of 50 g L⁻¹ (Figure 8 and Table S3). The better removal of Tc % and Re % is due to the lower Gibbs energy of hydration of TcO₄⁻ (−251 kJ mol⁻¹) and ReO₄⁻ (−330 kJ mol⁻¹) and the special interactions between tetrahedral TcO₄⁻/ReO₄⁻ anions and the imidazolium cation. These data show the excellent selectivity of IM-WS toward TcO₄⁻ and the practical application potential of IM-WS in nuclear waste treatment.

Table 3. Composition of Simulated Mixed Solution

| anions | concentration (mol L⁻¹) | anion/ReO₄⁻ molar ratio |
|--------|-------------------------|------------------------|
| TcO₄⁻ or ReO₄⁻ | 1.94 × 10⁻⁴ |                           |
| NO₃⁻       | 6.07 × 10⁻²   | 314                     |
| Cl⁻        | 6.39 × 10⁻²   | 330                     |
| NO₂⁻       | 1.69 × 10⁻¹   | 873                     |
| SO₄²⁻      | 6.64 × 10⁻⁴   | 0.0343                  |
| CO₃⁻       | 4.30 × 10⁻⁴   | 0.222                   |

3. CONCLUSIONS

We describe the application of imidazolium-functionalized natural wood sawdust as an anion-exchange material for adsorption of ReO₄⁻/TcO₄⁻. It is observed that the functionalized wood sawdust bearing imidazolium groups is a highly efficient anion-exchange material that has fast adsorption dynamics and high adsorption capacity. Anions with low charge density, such as ReO₄⁻/TcO₄⁻ or NO₃⁻, display a higher affinity toward the immobilized imidazolium species. Our work shows that natural sawdust can not only be developed into a material with the strength of the anion-exchange resin but also improve the mass transfer properties that may lead to more efficient separations. This work reports the first example of wood-functionalized materials showing application in purification of radioactive wastewater and provides a new design philosophy for biomass materials for the remediation of environment in the future.
4. EXPERIMENTAL SECTION

4.1. Materials and Chemicals. All reagents and solvents were obtained commercially and used as received. The wood sawdust was purchased from Changzhou, Jiangsu. 1,1’-(1,4-butanediyl)imidazole was synthesized according to previously reported steps.44

4.2. Adsorbent Synthesis. 4.2.1. Synthesis of CI-WS. The natural wood sawdust was washed with distilled water to remove impurities and dried. Then, wood sawdust (1.04 g), chloroacetyl chloride (5.73 mL), Na2CO3 (0.6 g), and CH2Cl2 (80 mL) were mixed and stirred at 50 °C under reflux for 3 days. The mixture was filtered, washed three times with water and methanol successively, and dried under vacuum to obtain CI-WS.

4.2.2. Synthesis of IM-WS. CI-WS (0.5 g), 1,1’-(1,4-butanediyl)imidazole (0.3628 g), and tetrahydrofuran (THF) (50 mL) were mixed and stirred at 90 °C under reflux for 3 days. The mixture was filtered, washed three times with water and methanol successively, and dried under vacuum to obtain the imidazolium-functionalized wood sawdust (IM-WS).

4.3. Sorption Tests. 4.3.1. Sorption Kinetic Tests. First, 10 mg of IM-WS was added to 5 mL of an aqueous solution containing 100 ppm ReO4−; which had been adjusted to pH 7. The mixture was stirred at 25 °C for 30 s and 1, 2, 5, 10, 20, 40, 60, 90, and 120 min, respectively. Then, the samples were separated for inductively coupled plasma-optical emission spectrometry (ICP-OES) analysis. The adsorption capacity (qe, mg g−1) of IM-WS toward ReO4− at contact time t was calculated according to eq 2

\[
q_e = \frac{(C_0 - C_t)V}{m}
\]

where \(C_0\) and \(C_t\) are the concentrations of the ReO4− solution (mg L−1) initially and at time t, respectively, \(m\) is the mass of the absorbent (g), and \(V\) is the volume of the solution (L).

The pseudo-first-order and pseudo-second-order kinetic models were used to analyze the adsorption kinetic data. The linearization forms of the two models are shown in eqs 3 and 4, respectively.

Pseudo-first-order model:

\[
\ln(q_e - q_t) = \ln q_e - k_1t
\]

Pseudo-second-order model:

\[
\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{t}{q_e}
\]

4.3.2. Sorption Isotherm Tests. Briefly, 10 mg of IM-WS was added to 5 mL of ReO4− aqueous solution, which had been adjusted to pH 7. The initial concentrations of ReO4− were varied from 100 to 1500 ppm. The solution was stirred for 12 h at 25 °C. The supernatant was separated for ICP-OES analysis.

The classical Langmuir45 and Freundlich models were used to analyze the adsorption isotherm data. The linearization forms of the two models are eqs 5 and 6, respectively.

Langmuir model:

\[
\frac{C_e}{q_e} = \frac{1}{q_mK_L} + \frac{C_e}{q_m}
\]

Freundlich model:

\[
\ln q_e = \ln K_F + \frac{1}{n} \ln C_e
\]

where \(q_e\) and \(q_m\) are the adsorption capacity at equilibrium and the maximum adsorption capacity of IM-WS toward ReO4− (mg g−1), respectively. \(C_e\) is the concentration of ReO4− in the solution (mg L−1) at equilibrium. \(K_L\) (L mg−1) is the Langmuir constant related to adsorption capacity and energy. \(K_F\) and \(n\) are the Freundlich parameters related to adsorption capacity and adsorption intensity, respectively.

4.3.3. pH Effect Tests. Overall, 10 mg of IM-WS was added to 5 mL of an aqueous solution containing 200 ppm ReO4−, whose pH was adjusted from 1 to 13 using HNO3 and NaOH solutions. After being stirred for 12 h at room temperature, the resulting mixture was separated for ICP-OES analysis.

4.3.4. Uptake Selectivity Tests. Briefly, 10 mg of IM-WS was added to 5 mL of an aqueous solution containing 0.05 mM ReO4− and different concentrations of NaNO3 (0.05, 0.5, 5, and 50 mM) or Na2SO4 (0.005, 0.05, 0.5, 5, 50, and 300 mM) to test the selectivity of IM-WS toward ReO4− among the competing ions. The solution was stirred for 12 h at 25 °C, and the resulting mixture was separated for ICP-OES analysis.

4.3.5. Simulated Nuclear Wastes Tests. The simulated mixed solution was prepared as per the reported protocol.46 The concentrations of TcO4− or ReO4−, NO3−, Cl−, SO42−, and CO32− anions were 1.94 × 10−2, 6.07 × 10−2, 6.39 × 10−2, 1.69 × 10−2, 6.64 × 10−2, and 4.30 × 10−2 mol L−1, respectively (Table 1).

To test the selectivity of IM-WS toward TcO4− or ReO4−, 10, 20, 30, 40, and 50 mg of IM-WS were added to 1 mL of the above simulated nuclear waste solutions. After being stirred for 12 h, the samples were separated and Tc was monitored by liquid scintillation counting measurements.

4.3.6. Trace Technetium Adsorption Tests. For tests, 20 mg of IM-WS was added to 1 mL of an aqueous solution containing 12.09 ppb TcO4−, and the concentration of SO42− was 1000 times that of TcO4−. After being stirred for 12 h at 25 °C, the supernatant liquid was separated for ICP-MS analysis.

Safety Notes. 99Tc is a β-emitter (Eγmax = 294 keV, t1/2 = 2.10 x 105 years). All operations were carried out in radiological laboratories equipped for handling this isotope.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c03784.

Element content from EDS in WS, Cl-WS, IM-WS, and IM-WS-Re (Table S1); SEM images of WS and Cl-WS (Figure S1); EDS spectrum of IM-WS-Re (Figure S2); adsorption parameters of ReO4− by IM-WS (Table S2); and results of ReO4− sorption by IM-WS from simulated nuclear wastes (Table S3) (PDF)
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Notes
The authors declare no competing financial interest.

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REFERENCES

(1) Icenhower, J. P.; Qafoku, N. P.; Zachara, J. M.; Martin, W. J. The Biogeochemistry of Technetium: A Review of the Behavior of an Artificial Element in the Natural Environment. Am. J. Sci. 2010, 310, 721–752.
(2) Momoshima, N.; Sayad, M.; Yamada, M.; Takamura, M.; Kawamura, H. Global fallout levels of Tc-99 and activity ratio of Tc-99/ Cs-137 in the Pacific Ocean. J. Radioanal. Nucl. Chem. 2005, 266, 455–460.
(3) Radijovic, Jovanovic, I.; Gallagher, C. M. B.; Salcedo, R.; Lukens, W. W.; Burton-Pye, B. P.; McGregor, D.; Francesconi, L. C. Strategies for the PhotoReduction of Tc-99 Pertechnetate to Low-Valent Tc by Keggin Polyoxometalates. Eur. J. Inorg. Chem. 2020, 2020, 2133–2142.
(4) McBeth, J. M.; Lear, G.; Lloyd, J. R.; Livens, F. R.; Morris, K.; Burke, I. T. Technetium reduction and reoxidation in aquifer sediments. Geomicrobiol. J. 2007, 24, 189–197.
(5) Um, W.; Chang, H.; Icenhower, J. P.; Lukens, W. W.; Seme, R. J.; Qafoku, N.; Kukkadapu, R. K.; Westsk, J. H. Iron oxide waste form for stabilizing (TC)-Tc-99. J. Nucl. Mater. 2012, 429, 201–209.
(6) Um, W.; Chang, H. S.; Icenhower, J. P.; Lukens, W. W.; Seme, R. J.; Qafoku, N. P.; Westsk, I. J.; Buck, E. C.; Smith, S. C. Immobilization of 99-Tecnethum (VII) by Fe(II)-Goethite and Limited Reoxidation. Environ. Sci. Technol. 2011, 45, 4904–4913.
(7) Choi, J.; Um, W.; Chong, S. Development of iron phosphate ceramic waste form to immobilize radioactive waste solution. J. Nucl. Mater. 2014, 452, 16–23.
(8) Levitskaya, T. G.; Chatterjee, S.; Pence, N. K.; Romero, J.; Varga, T.; Engellard, M. H.; Du, Y. G.; Kovarik, L.; Arey, B. W.; Bowden, M. E.; Walter, E. D. Inorganic tin alumophosphate nanocomposite for reductive separation of pertechnetate. Environ. Sci.: Nano 2016, 3, 1003–1013.
(9) Bishop, M. E.; Dong, H. L.; Kukkadapu, R. K.; Liu, C. X.; Edelmann, R. E. Bioreduction of Fe-bearing clay minerals and their reactivity toward pertechnetate (Tc-99). Geochim. Cosmochim. Acta 2011, 75, 5229–5246.
(10) Liu, Y.; Terry, J.; Jurisson, S. Pertechnetate immobilization in aqueous media with hydrogen sulfide under anaerobic and aerobic environments. Radiochim. Acta 2007, 95, 717–725.
(11) Liu, Y.; Terry, J.; Jurisson, S. S. Potential interferences on the pertechnetate-sulfide immobilization reaction. Radiochim. Acta 2009, 97, 33–41.
(12) Liu, Y.; Terry, J.; Jurisson, S. Pertechnetate immobilization with amorphous iron sulfide. Radiochim. Acta 2008, 96, 823–833.
(13) Zhou, L.; Xiao, C. L.; Dai, X.; Li, J.; Gui, D. X.; Sheng, D. P.; Chen, L. H.; Zhou, R. H.; Chai, Z. F.; Albrecht-Schmitt, T. E.; Wang, S. Exceptional Perrenate/Pertechnetate Uptake and Subsequent Immobilization by a Low-Dimensional Cationic Coordination Polymer: Overcoming the Hofmeister Bias Selectivity. Environ. Sci. Technol. Lett. 2017, 4, 316–322.
(14) Custelcean, R. Urea-functionalized crystalline capsules for recognition and separation of tetrahedral oxoanions. Chem. Commun. 2013, 49, 2173–2182.
(15) Custelcean, R.; Moyer, B. A. Anion separation with metal-organic frameworks. Eur. J. Inorg. Chem. 2007, 10, 1321–1340.
(16) Darab, J. G.; Smith, P. A. Chemistry of technetium and rhenium species during low-level radioactive waste vitrification. Chem. Mater. 1996, 8, 1004–1021.
(17) Katayev, A. E.; Kolesnikov, G. V.; Sesler, J. L. Molecular recognition of perrenate and perhenate. Chem. Soc. Rev. 2009, 38, 1572–1586.
(18) Banerjee, D.; Kim, D.; Schweiger, M. J.; Kruger, A. A.; Thallapally, P. K. Removal of TcO4- ions from solution: materials and future outlook. Chem. Soc. Rev. 2016, 45, 2724–2739.
(19) Wang, S. A.; Alekseev, E. V.; Juan, D. W.; Casey, W. H.; Phillips, B. L.; Depmeier, W.; Albrecht-Schmitt, T. E. A Supertetrahedral Cationic Framework That Removes TcO4- from Solution. Angew. Chem., Int. Ed. 2010, 49, 1057–1060.
(20) Goh, K. H.; Lim, T. T.; Dong, Z. Application of layered double hydroxides for removal of oxyanions: A review. Water Res. 2008, 42, 1343–1368.
(21) Wilmarth, W. R.; Lumetta, G. J.; Johnson, M. E.; Poirier, M. R.; Thompson, M. C.; Sugis, P. C.; Machara, N. P. Review: Waste-Pretreatment Technologies for Remediation of Legacy Defense Nuclear Waste. Solvent Extr. Ion Exch. 2011, 29, 1–48.
(22) Wang, Y. F.; Gao, H. Z. Compositional and structural control on anion sorption capability of layered double hydroxides (LDHs). J. Colloid Interface Sci. 2006, 301, 19–26.
(23) Gándara, F.; Perles, J.; Snejko, N.; Iglesias, M.; Gomez-Lor, B.; Gutierrez-Puebla, E.; Monge, M. A. Layered rare-earth hydroxides for removal of oxyanions: a class of pillared crystalline compounds for intercalation chemistry. Angew. Chem., Int. Ed. 2006, 45, 7998–8001.
(24) Sheng, D. P.; Zhu, L.; Xu, C.; Xiao, C. L.; Wang, Y. L.; Wang, Y. X.; Chen, L. H.; Duiw, J.; Chen, J.; Chai, Z. F.; Albrecht-Schmitt, T. E.; Wang, S. A. Efficient and Selective Uptake of TcO4- by a Cationic Metal-Organic Framework Material with Open Ag+ Sites. Environ. Sci. Technol. 2017, 51, 3471–3479.
(25) Fei, H. H.; Bresler, M. R.; Oliver, S. R. J. A New Paradigm for Anion Trapping in High Capacity and Selectivity: Crystal-to-Crystal Transformation of Cationic Materials. J. Am. Chem. Soc. 2011, 133, 11110–11113.
(26) Liu, X.; Peng, H.; Liu, X.; Li, Q.; Zhang, N.; Mao, L.; Qiu, M.; Hu, B.; Yang, H.; Wang, X. Orderly Porous Covalent Organic Frameworks-based Materials: Superior Adsorbents for Pollutants Removal from Aqueous Solutions. Innovation 2021, 2, No. 100076.
(27) He, L. W.; Liu, S. T.; Chen, L.; Dai, X.; Li, J.; Zhang, M. X.; Ma, F. Y.; Zhang, C.; Yang, Z. X.; Zhou, R. H.; Chai, Z. F.; Wang, S. Exceptional Perrenate/Pertechnetate Uptake by a radiation-resistant cationic covalent organic framework: a combined radiological experiment and molecular dynamics simulation study. Chem. Sci. 2019, 10, 4303–4305.
(28) Wang, X. X.; Chen, L.; Wang, L.; Fan, Q. H.; Pan, D. Q.; Li, J. X.; Chi, F. T.; Xie, Y.; Yu, S. J.; Xiao, C. L.; Luo, F.; Wang, J.; Wang, X. L.; Chen, C. L.; Wu, W. S.; Shi, W. Q.; Wang, S.; Wang, X. K.
Synthesis of novel nanomaterials and their application in efficient removal of radionuclides. Sci. China: Chem. 2019, 62, 933–967.
(29) Liu, Z. W.; Han, B. H. Evaluation of an Imidazolium-Based Porous Organic Polymer as Radioactive Waste Scavenger. Environ. Sci. Technol. 2020, 54, 216–224.
(30) Li, J.; Dai, X.; Zhu, L.; Xu, C.; Zhang, D.; Silver, M. A.; Li, P.; Chen, L.; Li, Y.; Zuo, D.; Zhang, H.; Xiao, C.; Chen, J.; Diwu, J.; Farha, O. K.; Albrecht-Schmitt, T. E.; Chai, Z.; Wang, S. 99TcO4(-) remediation by a cationic polymeric network. Nat. Commun. 2018, 9, No. 3007.
(31) Guo, R. X.; Cai, X. H.; Liu, H. W.; Yang, Z.; Meng, Y. J.; Chen, F.; Li, Y.; Li, W. In Situ Growth of Metal-Organic Frameworks in Three-Dimensional Aligned Lumen Arrays of Wood for Rapid and Highly Efficient Organic Pollutant Removal. Environ. Sci. Technol. 2019, 53, 2703–2712.
(32) Liu, G. G.; Chen, D. Y.; Liu, R. K.; Yu, Z. Y.; Jiang, J. L.; Liu, Y.; Hu, J. B.; Chang, S. S. Antifouling Wood Matrix with Natural Water Transfer and Microreaction Channels for Water Treatment. ACS Sustainable Chem. Eng. 2019, 7, 6782–6791.
(33) Chen, F. J.; Gong, A. S.; Zhu, M. W.; Chen, G.; Lacey, S. D.; Jiang, F.; Li, Y. F.; Wang, Y. B.; Dai, J. Q.; Yao, Y. G.; Song, J. W.; Liu, B. Y.; Fu, K.; Das, S.; Hu, L. B. Mesoporous, Three-Dimensional Wood Membrane Decorated with Nanoparticles for Highly Efficient Water Treatment. ACS Nano 2017, 11, 4275–4282.
(34) Guo, R. X.; Liu, H. W.; Yang, K.; Wang, S. T.; Sun, P. P.; Gao, H.; Wang, B. D.; Chen, F. J. beta-Cyclodextrin Polymerized in Cross-Flowing Channels of Biomass Sawdust for Rapid and Highly Efficient Pharmaceutical Pollutants Removal from Water. ACS Appl. Mater. Interfaces 2020, 12, 32817–32826.
(35) Gu, Y.; Ye, M. X.; Wang, Y. C.; Li, H. M.; Zhang, H. M.; Wang, G. Z.; Zhang, Y. X.; Zhao, H. J. Lignosulfonate functionalized g-C3N4/carbonized wood sponge for highly efficient heavy metal ion scavenging. J. Mater. Chem. A 2020, 8, 12687–12698.
(36) Yang, Z.; Liu, H. W.; Li, J.; Yang, K.; Zhang, Z. Z.; Chen, F. J.; Wang, B. D. High-Throughput Metal Trap: Sulphydryl-Functionalized Wood Membrane Stacks for Rapid and Highly Efficient Heavy Metal Ion Removal. ACS Appl. Mater. Interfaces 2020, 12, 15002–15011.
(37) Bonnensen, P. V.; Brown, G. M.; Alexandratos, S. D.; Bovaux, L. B.; Presley, D. J.; Patel, V.; Ober, R.; Moyer, B. A. Development of bifunctional anion-exchange resins with improved selectivity and sorptive kinetics for pertechnetate: Batch-equilibrium experiments. Environ. Sci. Technol. 2000, 34, 3761–3768.
(38) Zhu, L.; Sheng, D. P.; Xu, C.; Dai, X.; Silver, M. A.; Li, J.; Li, P.; Wang, Y. X.; Wang, Y. L.; Chen, L. H.; Xiao, C. L.; Chen, J.; Zhou, R. H.; Zhang, C.; Farha, O. K.; Chai, Z. F.; Albrecht-Schmitt, T. E.; Wang, S. Identifying the Recognition Site for Selective Trapping of (TcO4-)-Tc-99 in a Hydrolitically Stable and Radiation Resistant Cationic Metal-Organic Framework. J. Am. Chem. Soc. 2017, 139, 14873–14876.
(39) Sheng, D. P.; Zhu, L.; Dai, X.; Xu, C.; Li, P.; Pearce, C. I.; Xiao, C. L.; Chen, J.; Zhou, R. H.; Duan, T.; Farha, O. K.; Chai, Z. F.; Wang, S. Successful Decontamination of (TcO4-)-Tc-99 in Groundwater at Legacy Nuclear Sites by a Cationic Metal-Organic Framework with Hydrophobic Pockets. Angew. Chem., Int. Ed. 2019, 58, 4968–4972.
(40) Shen, N.; Yang, Z.; Liu, S.; Dai, X.; Xiao, C.; Taylor-Pashow, K.; Li, D.; Yang, C.; Li, J.; Zhang, Y.; Zhang, M.; Zhou, R.; Chai, Z.; Wang, S. 99TcO4(-) removal from legacy defense nuclear waste by an alkaline-stable 2D cationic metal organic framework. Nat. Commun. 2020, 11, No. 5571.
(41) Sun, Q.; Zhu, L.; Aguila, B.; Thallapally, P. K.; Xu, C.; Chen, J.; Wang, S.; Rogers, D.; Ma, S. Optimizing radionuclide sequestration in anion nanotrips with record pertechnetate sorption. Nat. Commun. 2019, 10, No. 1646.
(42) Xiao, C. L.; Khayambashi, A.; Wang, S. Separation and Remediation of (TcO4-)-Tc-99 from Aqueous Solutions. Chem. Mater. 2019, 31, 3863–3877.
(43) Dickson, J. O.; Harsh, J. B.; Lukens, W. W.; Pierce, E. M. Perrhenate incorporation into binary mixed sodalites: The role of anion size and implications for technetium-99 sequestration. Chem. Geol. 2015, 395, 138–143.
(44) Daneshvar, N.; Nasiri, M.; Shirzad, M.; Langarudi, M. S. N.; Shirini, F.; Tajik, H. The introduction of two new imidazole-based bis-dicationic Bronsted acidic ionic liquids and comparison of their catalytic activity in the synthesis of barbituric acid derivatives. New J. Chem. 2018, 42, 9744–9756.
(45) Langmuir, I. The Adsorption of Gases on Plane Surfaces of Glass, Mica and Platinum. J. Am. Chem. Soc. 1918, 40, 1361–1403.
(46) Wang, S. A.; Yu, P.; Purse, B. A.; Orta, M. J.; Diwu, J.; Casey, W. H.; Phillips, B. L.; Alekseev, E. V.; Depmeier, W.; Hobbs, D. T.; Albrecht-Schmitt, T. E. Selectivity, Kinetics, and Efficiency of Reversible Anion Exchange with TcO4- in a Supertetrahedral Cationic Framework. Adv. Funct. Mater. 2012, 22, 2241–2250.