

Highly Efficient Uptake of TcO_4^- by Imidazolium-Functionalized Wood Sawdust

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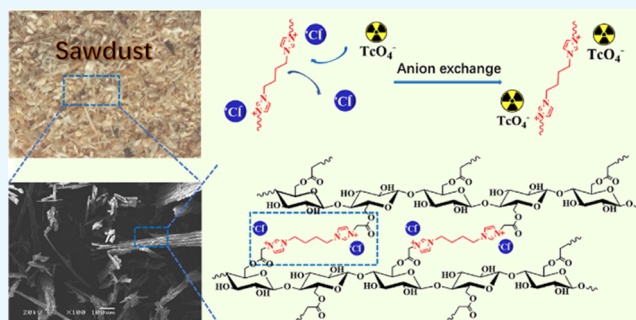


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ABSTRACT: ^{99}Tc is a radioactive fission product, mainly in the form of TcO_4^- , with good solubility and mobility in the environment. The development of effective and inexpensive materials to remove TcO_4^- from nuclear industry wastewater or contaminated 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 $\text{TcO}_4^-/\text{ReO}_4^-$ 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 ($\approx 6.1\%$) in a nuclear reaction.^{1,2} ^{99}Tc has a half-life of 2.1×10^5 years and is a weak β 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.^{4,5}

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.^{5–8} Fe(II) ,^{5–7,9} sulfides, 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^- .²¹ 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.

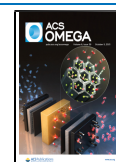
The recently reported imidazolium polymer SCU-CPN-1³⁰ and imidazolium porous organic polymer ImPOP-1²⁹ show excellent adsorption capacity and extraordinary selectivity to TcO_4^- . It is proved that the imidazolium cation is the key part for highly selective adsorption of TcO_4^- .

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 $\text{Mn}_3\text{O}_4/\text{TiO}_2/\text{wood}$,³² Pd NPs/wood,³³ and $\beta\text{-CD}/\text{WS}$ ³⁴ have been reported to remove organic pollutants (e.g., methylene blue, rhodamine 6G, and propranolol) from aqueous solutions. $\text{LS-C}_3\text{N}_4/\text{CWS}$ ³⁵ and SH-wood³⁶ show

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Scheme 1. Synthesis Route to IM-WS

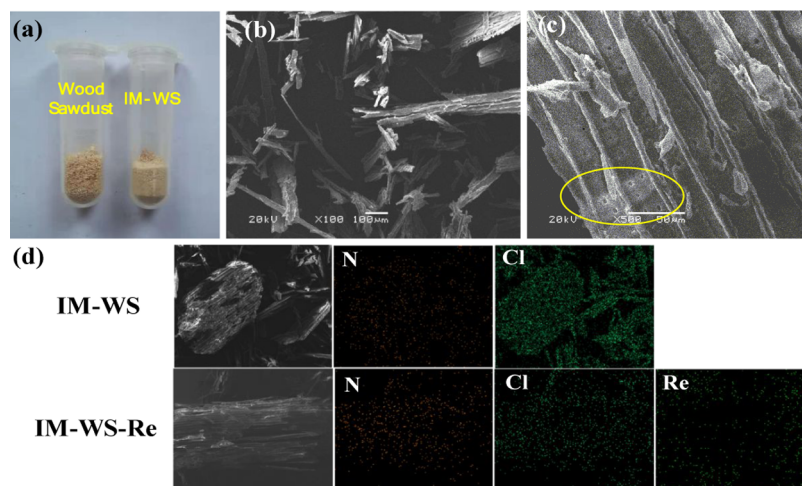
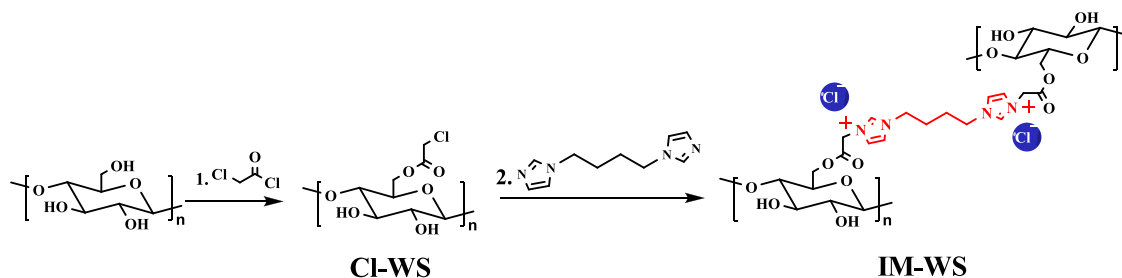


Figure 1. (a) Picture of the natural wood sawdust and IM-WS. (b) Scanning electron microscopy (SEM) image showing the microchannels of IM-WS. (c) Magnified SEM image showing numerous micropores of IM-WS. (d) Energy-dispersive spectrometry (EDS) mapping of IM-WS and IM-WS-Re.

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.³⁴ 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 $\text{TcO}_4^-/\text{ReO}_4^-$ 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.¹⁶

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 $\text{C}=\text{O}$ stretching vibrations of the $-\text{COO}-$ 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 $\text{C}-\text{H}$ stretching vibrations of $-\text{CH}_2-$ bonds of 1,1'-(1,4-butanediyl)diimidazole. All of these findings indicate the successful synthesis of IM-WS.

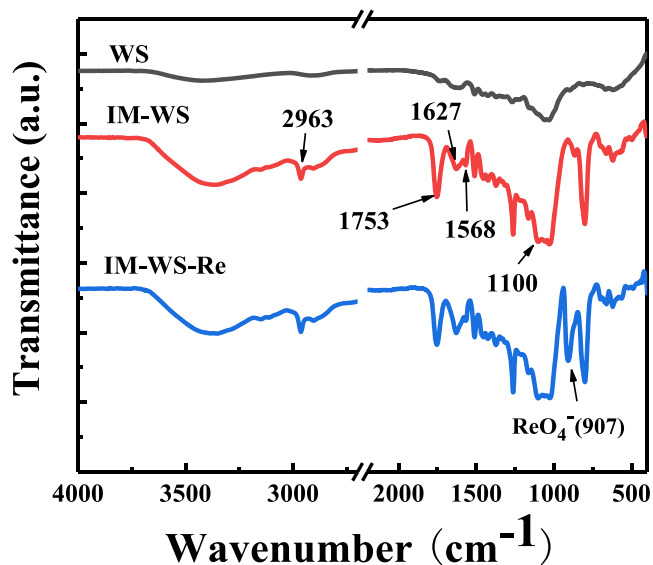


Figure 2. FT-IR spectra of WS, IM-WS, and IM-WS-Re.

2.2. $\text{ReO}_4^-/\text{TcO}_4^-$ 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

$$K_d = \left(\frac{C_0 - C_e}{C_e} \right) \frac{V}{m} \quad (1)$$

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 adsorbent (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 $3.79 \times 10^5 \text{ mL g}^{-1}$, 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

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	$\text{Y}_2(\text{OH})_5\text{Cl}$	112	0.5 13
	$\text{Yb}_3\text{O}(\text{OH})_6\text{Cl}$	120	0.5 13
	Mg-Al-LDH	262	1 24
ion-exchange resins	Purolite A-850	102	37
	Purolite A 532E	1.28×10^4	37
MOF materials	SCU-100	3.3×10^5	1 24
	SCU-101	7.5×10^5	1 38
	SCU-102	5.6×10^5	10 39
	SCU-103	$>1.00 \times 10^5$	1 40
COF materials	SCU-COF-1	3.89×10^5	1 27
POP materials	PQA- <i>p</i> N(Me) 2Py-Cl	1.00×10^7	1 41
	imidazolium-based organic polymer materials	ImPOP-1	3.2×10^5
	IM-WS	3.79×10^5	2 this work
	SCU-CPN-1	6.2×10^5	1 30

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

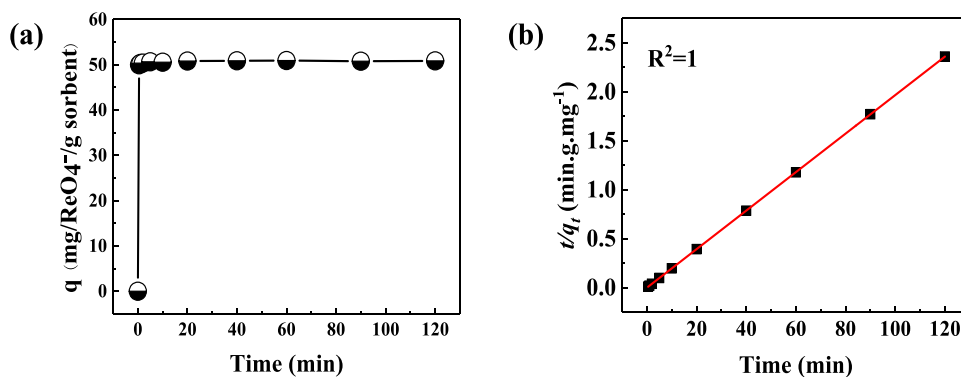


Figure 3. (a) ReO_4^- sorption kinetics of IM-WS under the ReO_4^- initial concentration of 100 ppm with the m/V ratio at 2 g L^{-1} . (b) Pseudo-second-order kinetic plot for adsorption.

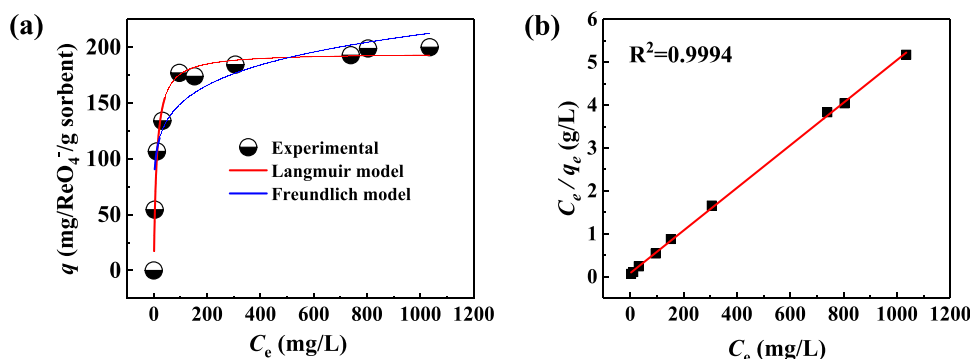


Figure 4. (a) ReO_4^- adsorption isotherm for IM-WS. (b) Linear regression by fitting the equilibrium adsorption data with the Langmuir adsorption model.

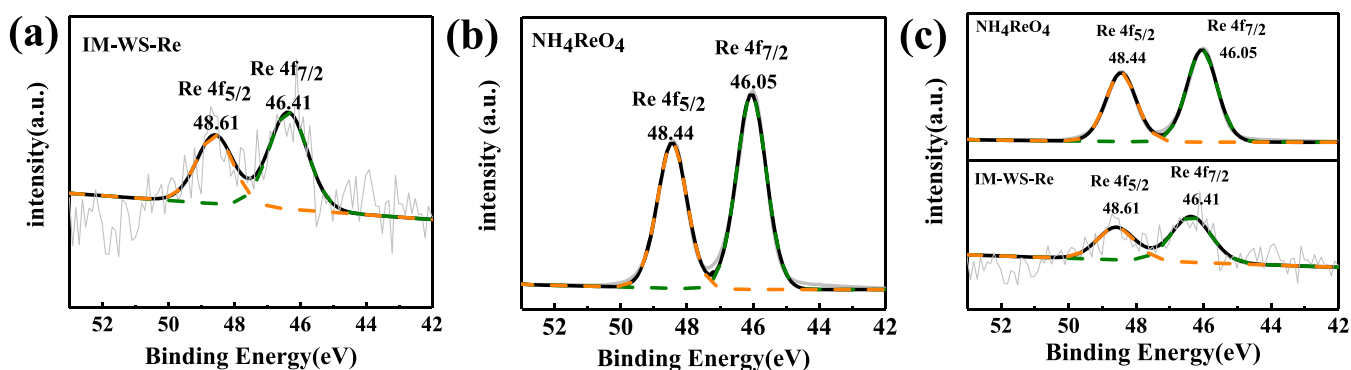


Figure 5. (a) XPS analysis of Re 4f from IM-WS-Re. (b) XPS analysis of Re 4f from NH_4ReO_4 . (c) XPS analysis of Re 4f from IM-WS-Re and NH_4ReO_4 .

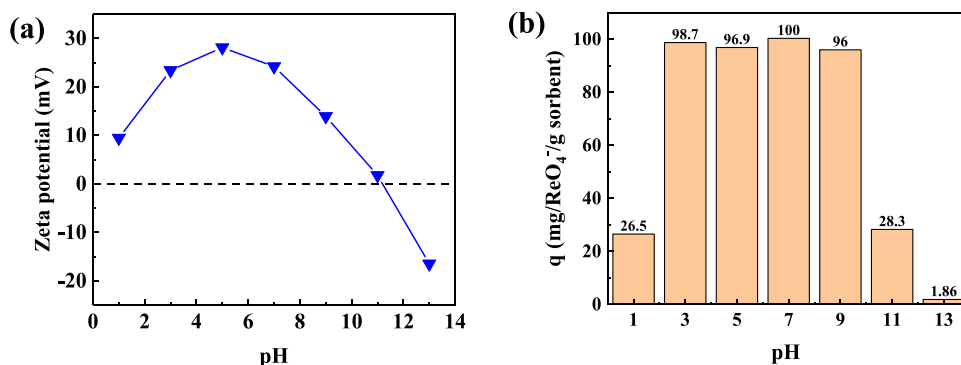


Figure 6. (a) Effect of pH on ζ -potential of IM-WS. (b) Effect of pH on the sorption properties of ReO_4^- by IM-WS.

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 $\text{Re}-\text{O}$ ν_3 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_4ReO_4 (Figure 5c), the shifts of $\text{Re } 4f_{5/2}$ 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 $\text{pH} > 9$ and $\text{pH} < 3$. 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

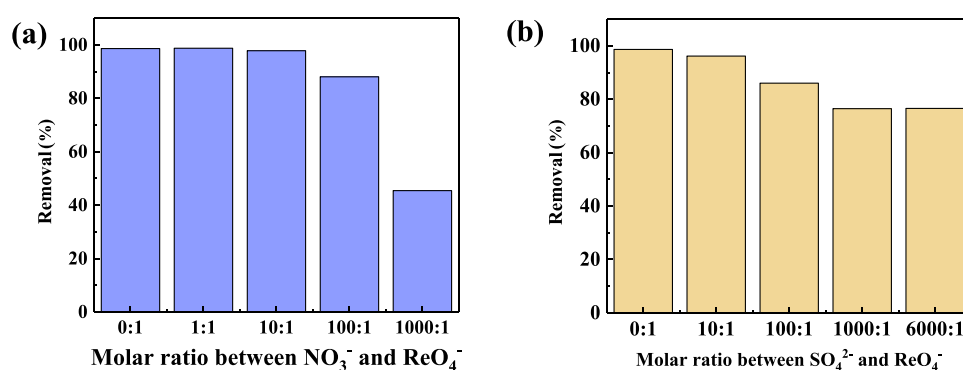


Figure 7. (a) Effect of competing NO_3^- on adsorption of ReO_4^- by IM-WS. (b) Effect of competing SO_4^{2-} on adsorption of ReO_4^- by IM-WS.

> 9 and $\text{pH} < 3$, 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 TcO_4^- . The adsorption properties of IM-WS toward ReO_4^- were further studied in the presence of different excesses of NO_3^- and SO_4^{2-} . The results are shown in Figure 7a,b. It can be seen that with molar ratios of $\text{NO}_3^-/\text{ReO}_4^- = 1000:1$ and $\text{SO}_4^{2-}/\text{ReO}_4^- = 6000:1$, the removal efficiency for ReO_4^- can reach 45.44 and 76.57%, respectively. The result is similar to that of imidazolium-based cationic polymer materials SCU-CPN-1³⁰ and ImPOP-1.²⁹ The standard Gibbs energy of hydration of ReO_4^- is -330 kJ mol^{-1} , which is close to that of NO_3^- (-306 kJ mol^{-1}) but much lower than that of SO_4^{2-} ($-1090 \text{ kJ mol}^{-1}$), which can explain the fact that NO_3^- has a greater competitive effect on the removal of ReO_4^- than SO_4^{2-} .^{15,42,43} The selectivity for ReO_4^- in the presence of NO_3^- may be due to the special interactions between tetrahedral $\text{ReO}_4^-/\text{TcO}_4^-$ anions and the imidazolium cation.

When the concentration of coexisting SO_4^{2-} is 1000 times that of TcO_4^- , after adsorption, the concentration of TcO_4^- 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

C_0 (TcO_4^-) (ppb)	C_e (TcO_4^-) (ppb)	solid/liquid ratio (g L^{-1})	molar ratio between SO_4^{2-} and TcO_4^-	removal (%)
12.09	0.056	20	1000	99.54

2.2.6. Simulated Nuclear Wastes. The separation ability of IM-WS toward TcO_4^- in simulated low-level radioactive wastewater was tested. The chemical composition of simulated wastewater containing Tc is shown in Table 3. The concentrations of NO_3^- and Cl^- in the solution were more

Table 3. Composition of Simulated Mixed Solution

anions	concentration (mol L^{-1})	anion/ ReO_4^- molar ratio
TcO_4^- or ReO_4^-	1.94×10^{-4}	
NO_3^-	6.07×10^{-2}	314
Cl^-	6.39×10^{-2}	330
NO_2^-	1.69×10^{-1}	873
SO_4^{2-}	6.64×10^{-6}	0.0343
CO_3^{2-}	4.30×10^{-5}	0.222

than 300 times that of $\text{TcO}_4^-/\text{ReO}_4^-$. The excess of NO_2^- was even more than 800 times that of $\text{TcO}_4^-/\text{ReO}_4^-$ (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

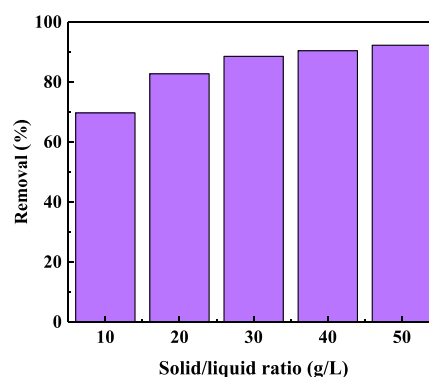


Figure 8. (a) Removal of TcO_4^- in simulated nuclear wastes with different solid/liquid ratios.

S3). The better removal of Tc % and Re % is due to the lower Gibbs energy of hydration of TcO_4^- (-251 kJ mol^{-1}) and ReO_4^- (-330 kJ mol^{-1}) and the special interactions between tetrahedral $\text{TcO}_4^-/\text{ReO}_4^-$ anions and the imidazolium cation. These data show the excellent selectivity of IM-WS toward TcO_4^- and the practical application potential of IM-WS in nuclear waste treatment.

3. CONCLUSIONS

We describe the application of imidazolium-functionalized natural wood sawdust as an anion-exchange material for adsorption of $\text{ReO}_4^-/\text{TcO}_4^-$. 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 $\text{ReO}_4^-/\text{TcO}_4^-$ or NO_3^- , 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)diimidazole 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)diimidazole (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, successively. Then, the samples were separated for inductively coupled plasma-optical emission spectrometry (ICP-OES) analysis. The adsorption capacity (q_t , mg g⁻¹) of IM-WS toward ReO₄⁻ at contact time t was calculated according to eq 2

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (2)$$

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 adsorbent (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:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

Pseudo-second-order model:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

where q_e and q_t represent the adsorption capacity of ReO₄⁻ (mg g⁻¹) at equilibrium and at contact time t (min), respectively, and k_1 (min⁻¹) and k_2 (g mg⁻¹ min⁻¹) are the rate constants of the pseudo-first-order and pseudo-second-order equations, respectively.

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:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad (5)$$

Freundlich model:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (6)$$

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⁻, NO₂⁻, SO₄²⁻, and CO₃²⁻ anions were 1.94 × 10⁻⁴, 6.07 × 10⁻², 6.39 × 10⁻², 1.69 × 10⁻¹, 6.64 × 10⁻⁶, and 4.30 × 10⁻⁵ 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 β-emitter ($E_{\max} = 294$ keV, $t_{1/2} = 2 \times 10^5$ years). All operations were carried out in radiochemical 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, CI-WS, IM-WS, and IM-WS-Re (Table S1); SEM images of WS and CI-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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