



Article Highly Selective Adsorption of ⁹⁹TcO₄^{-/}ReO₄⁻ by a Novel Polyamide-Functionalized Polyacrylamide Polymer Material

Ben Qin^{1,2}, Yanqin Hu², Meiying Xie^{2,3}, Liyan Xue^{2,3,4}, Chunfa Liao^{1,*} and Fan Yang^{3,4,5,*}

- ¹ Faculty of Materials, Metallurgy and Chemistry, Jiangxi University of Science and Technology, Ganzhou 341000, China
- ² Xiamen Institute of Rare Earth Materials, Haixi Institute, Chinese Academy of Sciences, Xiamen 361021, China
- ³ Fujian Province Joint Innovation Key Laboratory of Fuel and Materials in Clean Nuclear Energy System, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, China
- ⁴ Fujian Science & Technology Innovation Laboratory for Optoelectronic Information of China, Fuzhou 350108, China
- ⁵ Sichuan Jcc Rare Earth Matals New Material Co., Ltd., Chengdu 610213, China
- * Correspondence: liaochfa@163.com (C.L.); fanyang2013@fjirsm.ac.cn (F.Y.)

Abstract: The treatment of radioactive wastewater is one of the major problems in the current research. With the development of nuclear energy, the efficient removal of ⁹⁹TcO₄⁻ in radioactive wastewater has attracted the attention of countries all over the world. In this study, a novel functional polyamide polymer p-(Amide)-PAM was synthesized by the two-step method. The experimental results show that p-(Amide)-PAM has good adsorptive properties for ⁹⁹TcO₄⁻/ReO₄⁻ and has good selectivity in the nitric acid system. The kinetics of the reaction of p-(Amide)-PAM with ⁹⁹TcO₄⁻/ReO₄⁻ was studied. The results show that p-(Amide)-PAM has a fast adsorption rate for ⁹⁹TcO₄⁻/ReO₄⁻, the saturated adsorption capacity reaches 346.02 mg/g, and the material has good application prospects in the removal of ⁹⁹TcO₄⁻ from radioactive wastewater.

Keywords: polyacrylamide; polyamidation; 99 TcO₄⁻ /ReO₄⁻ removal; polymer adsorption material

1. Introduction

With the advent of international "carbon peaking and carbon neutrality", advanced nuclear energy has attracted the attention of countries all over the world, but with the development of advanced nuclear energy, the treatment of technetium 99 (⁹⁹Tc) in nuclear waste has become a major problem [1,2]. A large amount of radioactive wastewater is produced in the process of nuclear waste material storage [3]. ⁹⁹Tc is the most potentially problematic radionuclide in radioactive wastewater because it decays by emitting β particles, and its half-life is as long as 2.13×10^5 years [4,5]. ⁹⁹Tc is a super hydrophilic radionuclide that mainly exists in radioactive wastewater in the form of ⁹⁹TcO₄⁻. ⁹⁹TcO₄⁻ has high water solubility (11.3 mol/L, 293.15 K) and almost no complexation properties, resulting in rapid migration in the environment and thus making it a dangerous radioactive pollutant [6,7]. Therefore, it is of great significance to remove ⁹⁹TcO₄⁻ from radioactive wastewater.

It has always been a difficult point for researchers to remove and capture $^{99}\text{TcO}_4^-$ in radioactive wastewater under the condition of strong acid, strong alkali, and a large number of anions [8]. The current research methods for removing and capturing $^{99}\text{TcO}_4^-$ in radioactive wastewater can be divided into solvent extraction and solid-phase extraction [9–12]. Compared with solvent extraction, solid phase extraction has a faster extraction rate, better reusability, simpler operation, and easier separation [13]. Therefore, solid phase extraction is a method that is widely used and studied in practice, and solid-phase extraction is a commonly used adsorbent. The most studied adsorbents are metal-organic frameworks (MOFs) and covalent organic frameworks (COFs). They have a high specific surface area and many



Citation: Qin, B.; Hu, Y.; Xie, M.; Xue, L.; Liao, C.; Yang, F. Highly Selective Adsorption of ⁹⁹TcO₄⁻/ReO₄⁻ by a Novel Polyamide-Functionalized Polyacrylamide Polymer Material. *Toxics* **2022**, *10*, 630. https://doi.org/ 10.3390/toxics10100630

Academic Editors: Yuezhou Wei, Yan Wu and Xinpeng Wang

Received: 27 September 2022 Accepted: 19 October 2022 Published: 21 October 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). pores, so they have high a saturated adsorption capacity for 99 TcO₄⁻, but they are insufficient for the treatment of 99 TcO₄⁻ in environments with high acidity and acidity [14–19]. Ion exchange resins are other polymer materials that have been widely studied. Such resins can effectively remove ${}^{99}\text{TcO}_4^-$ from radioactive wastewater by anion substitution and can maintain a good adsorption performance under highly acidic and alkaline conditions. Ion exchange resins have simple operation and a high recovery rate, but the removal efficiency and selectivity become very poor in the presence of a large number of competitive anions $(SO_4^{2-}, NO_3^{-}, Cl^{-}, etc.)$ [20,21]. Some people have also studied the removal of ⁹⁹TcO₄⁻ by natural zeolites. They modified natural zeolites with cationic surfactants to convert the negative charges of the surface framework of zeolites into positive charges, thus enhancing the affinity for 99 TcO₄⁻. However, the saturated adsorption content of 99 TcO₄⁻ on zeolites is generally low [22,23]. By aminating the functional groups of chitosan, researchers removed ⁹⁹TcO₄⁻ under high-acidity conditions, but chitosan has the same disadvantages as zeolite [24,25]. High-molecular-weight polymers are also adsorbents that can effectively remove $^{99}\text{TcO}_4{}^-$ from radioactive wastewater. Many polymers have been developed and used to remove ${}^{99}\text{TcO}_4^-$ in radioactive wastewater [26–30]. After polymers are modified by polyamidation, the polymer can selectively remove 99 TcO₄⁻ by electrostatic interaction or hydrogen bonding [28,31,32]. Polyacrylamide (PAM) is a widely used polymer that is often used in biomedicine, sewage treatment, and other fields. As an adsorbent, PAM can effectively remove anions in wastewater. Therefore, the removal of $^{99}\text{TcO}_4^-$ from radioactive wastewater using PAM is also an important research topic [33–35].

⁹⁹TcO₄⁻ has strong radioactivity, and ReO₄⁻, which has similar physical and chemical properties, is used to replace ⁹⁹TcO₄⁻ in experiments [36]. In this study, a new type of polyamide-functionalized polyacrylamide polymer material was prepared by a two-step method, and its adsorption effect on ⁹⁹TcO₄⁻/ReO₄⁻ was studied. In a certain range of pH values, p-(Amide)-PAM has a good effect on the removal of ⁹⁹TcO₄⁻/ReO₄⁻. Under the influence of different competitive anions, p-(Amide)-PAM has excellent selectivity for ⁹⁹TcO₄⁻/ReO₄⁻. The adsorption kinetics of p-(Amide)-PAM for ⁹⁹TcO₄⁻/ReO₄⁻ was studied, and the material has a fast adsorption rate and high saturated adsorption capacity (346.02 mg/g). This study provides a new material design direction for the treatment of ⁹⁹TcO₄⁻ in radioactive wastewater.

2. Materials and Methods

2.1. Materials and Reagents

Polyacrylamide ((C_3H_5NO)_n, PAM, cationic; molecular weight 1800) was purchased from Beijing Huawei Ruike Chemical Co., Ltd, Beijing, China. Ammonium perrhenate (NH₄ReO₄, \geq 99.99%) was purchased from Shanghai Dibo Biotechnology Co., Ltd, Shanghai, China. Ethylenediamine ($C_2H_8N_2$, analytical purity) was provided by Shanghai Aladdin Limited Chemical Reagent Co., Ltd, Shanghai, China. Ammonia (NH₃·H₂O), nitric acid (HNO₃), and dimethylformamide (C_3H_7NO , DMF, 0.945 g/mL) were all analytically pure and were purchased from Sinopharm Chemical Reagent Co., Ltd, Beijing, China. The ultra-pure water (18.2 m Ω cm) used in this experiment was obtained from a Direct-Q3UV purification system (Research Water Purification Technology Co., Ltd, Xiamen City, Fujian Province, China).

2.2. Synthesis of p-(Amide)-PAM

The synthesis process of p-(Amide)-PAM is shown in Figure 1. Step 1: According to published articles, the p-(Amide)-PAM preparation process was as follows [37,38]: 4.2 g PAM was added to 30 mL of ethylenediamine at 373 K stirred and heated for 72 h, and the resulting product was washed 3 times with ethanol. Then, the resulting solid product was placed in a 353 K vacuum oven for 48 h, and the solid is named N-PAM.

Step 2: Amide acid was synthesized according to the literature [39]. The amide acid was mixed with N-PAM in 30 mL DMF. The mixture was heated and stirred at 373 K for



12 h. Then the product was washed 3 times with ethanol before dried at 353 K for 48h, resulting in a yellow solid powder named p-(Amide)-PAM.

Figure 1. Preparation flow chart of p-(Amide)-PAM.

2.3. Characterization of PAM, N-PAM, and p-(Amide)-PAM

The elemental (C, H, O, and N) contents of PAM, N-PAM, and p-(Amide)-PAM were determined by elemental analysis (Vario El Cube, Germany) and X-ray photoelectron spectroscopy (XPS, K-alpha+, U.K.). The surface morphologies of PAM, N-PAM, and p-(Amide)-PAM were observed by field emission scanning electron microscopy (Apreo S LoVac, Czech Republic). The surface functional groups in the range of 4000-500 cm⁻¹ were obtained by Fourier transform infrared spectroscopy (FT-IR, Nicolet iS 50, USA). The specific surface area and porosity of N-PAM and p-(Amide)-PAM were measured by an automatic specific surface area and porosity analyzer (Quantachrome Autosorb IQ, USA). FT-IR and XPS were used to analyze p-(Amide)-PAM before and after adsorption of ReO_4^- to explore its potential adsorption mechanism.

2.4. Batch Adsorption Experiments

The original solution of ReO_4^- with a concentration of 1000 mg/L was prepared with ammonium perrhenate, and other desired concentrations of ReO_4^- were prepared by further dilution of this solution. All adsorption experiments were carried out in 15 mL centrifuge tubes on a constant temperature shaker with a rotational speed of 250 rpm. The pH value of the solution was adjusted with 0.1 M HNO₃ and NH₃·H₂O. The initial concentration of ReO₄⁻ was 0–1000 mg/L, the contact time was 0–15 h, the pH value was 1–14, and the initial pH was 5.5. After adsorption, the liquid was filtered through a 0.22 µm nylon filter. The initial metal concentration and residual metal concentrations of the samples were determined by inductively coupled plasma optical emission spectrometry (ICP-OES, Ultima2, France).

The adsorption capacity of the adsorbent was calculated by Q_e (mg/g) and removal rate (*R*) was calculated by the following formulas (Formulas (1) and (2)):

$$Q_e = (C_0 - C_e) \times \frac{V}{m} \tag{1}$$

$$R\% = \frac{C_0 - C_e}{C_0} \times 100\%$$
 (2)

where C_0 and C_e are the initial concentration and equilibrium concentration (mg/L) of ReO₄⁻, Q_e is the adsorption capacity at equilibrium (mg/g), *V* is the volume of the aqueous phase (L), and *m* is the mass of the adsorbent (g).

The Langmuir model and Freundlich model were used to fit the isothermal adsorption data and are expressed by Formulas (3) and (4) [40]:

$$\frac{C_e}{Q_e} = \frac{1}{K_L Q_{\max}} + \frac{C_e}{Q_{\max}}$$
(3)

$$\ln Q_e = \frac{1}{n} \ln C_e + \ln K_F \tag{4}$$

where C_e refers to the concentration of ReO₄⁻ at equilibrium (mg/L), Q_{max} is the theoretical maximum adsorption capacity (mg/g), K_L is the Langmuir constant (L/mg), and K_F (mg/g (L/mg)1/n) and 1/n are Freundlich constants.

The pseudo-first-order kinetic model and pseudo-second-order kinetic model of adsorption kinetics are expressed by Formula (5) and Formula (6), respectively [41]:

$$\ln(Q_e - Q_t) = \ln(Q_e) - k_1 t \tag{5}$$

$$\frac{t}{Q_t} = \frac{t}{Q_e} + \frac{1}{k_2 Q_e^2} \tag{6}$$

where C_e refers to the concentration of ReO_4^- at equilibrium (mg/L); Q_e and Q_t are the adsorption capacity (mg/g) of ReO_4^- at equilibrium and at time *t* (min), respectively; and k_1 and k_2 are the pseudo-first-order and pseudo-second-order kinetic model constants.

3. Results and Discussion

3.1. Characterizations of PAM, N-PAM, and p-(Amide)-PAM

The scanning electron microscopy pictures of PAM (Figure 2a), N-PAM (Figure 2b), and p-(Amide)-PAM (Figure 2c) are shown in the figure and their elemental content is shown in Table 1. It can be seen from the diagram that the morphology of PAM is large particles that are relatively regular; N-PAM and p-(Amide)-PAM show irregular small particles after the reaction. By comparing the N₂ adsorption-desorption isotherms of N-PAM (Figure S1a) and p-(Amide)-PAM (Figure S1b), it can be seen that the specific surface area of p-(Amide)-PAM is 90 times higher than the specific surface area of N-PAM, and the pores of p(Amide)-PAM (Figure S1c) are microporous. Figure 2d shows the dispersion of PAM, N-PAM, and p-(Amide)-PAM in water. PAM dissolved in water and formed a hydrogel while N-PAM and p-(Amide)-PAM were insoluble in water. In the FT-IR spectrum (Figure 2e), the characteristic peaks of -NH₂ at 3345 and 3183 cm⁻¹ are greatly weakened after the reaction, indicating that most of the $-NH_2$ is involved in the reaction process. The peak at 1650 cm⁻¹ is characteristic of C=O, and the intensity of the peak of synthesized p-(Amide)-PAM increases substantially, which indicates that the functional modification of N-PAM by amide acid was successful. In the XPS wide scan spectrum of N-PAM (Figure S2a) and p-(Amide)-PAM (Figure S2b), there are N1s, C1s, and O1s spectrum. In the XPS N 1s spectrum (Figure 2f), the -NH (400.8 eV) peak of p-(Amide)-PAM is significantly increased, indicating a significant increase in the number of -NH groups on p-(Amide)-PAM. The binding energies of the modified -NH and C-N increase from 400.5 and 399.0 to 400.8 and 399.2 eV, respectively, indicating that the modification reaction took place on the amino group [42–44]. These results further indicate that the functional modification of N-PAM by amide acid was successful.

Table 1. The elemental content of PAM, N-PAM, and p-(Amide)-PAM.

Elemental	PAM	N-PAM	p-(Amide)-PAM
C [%]	45.140	42.667	39.926
H [%]	7.580	8.670	7.559
O [%]	30.577	29.696	36.562
N [%]	16.517	18.994	15.508



Figure 2. SEM images of PAM (**a**), N-PAM (**b**), and p-(Amide)-PAM (**c**); dispersion of PAM, N-PAM, and p-(Amide)-PAM in water (**d**); FT-IR spectrum of PAM, N-PAM, and p-(Amide)-PAM (**e**); and XPS N 1s spectrum of N-PAM and p-(Amide)-PAM (**f**).

3.2. Adsorption Experiment of ReO_4^- by *p*-(Amide)-PAM 3.2.1. Influence of Different Molar Reaction Ratios

The effect of the amount of amide acid on the removal of ReO_4^- in the synthesis of p-(Amide)-PAM was investigated. Five groups of samples were prepared with the molar ratios of amide acid to N-PAM of 0.5:1, 0.75:1, 1:1, 1.25:1, and 1.5:1. In Figure 3, the removal rate of ReO_4^- by the intermediate N-PAM is only 29%. The removal rate of p-(Amide)-PAM significantly improves after the functionalization of polyamides. When the molar ratio of the reaction is 0.5:1, the removal rate of ReO_4^- is the highest (up to 90%). With the increase in the amide acid molar ratio, the removal rate of ReO_4^- by p-(Amide)-PAM decreases. This may be due to the N-H functional groups of the adsorbents occupying the adsorption sites of ReO_4^- . These results show that the addition of amide acid has an effect on the removal of ReO_4^- by p-(Amide)-PAM, especially when the molar amount of amide acid is greater than that of N-PAM.

3.2.2. Effect of Initial pH

The effect of p-(Amide)-PAM on ReO_4^- removal under acid-base conditions was explored. In this study, adsorption experiments under different pH conditions were performed, as shown in Figure 4. As the pH increases from 1.3 to 4.0, the removal rate of ReO_4^- by p-(Amide)-PAM gradually increases (from 4% to 80%). When the pH is in the range of 4.0 to 8.0, the removal rate of ReO_4^- by p-(Amide)-PAM gradually increases (from pH 8.0 to 11.0, the removal rate of ReO_4^- by p-(Amide)-PAM decreases gradually, and the removal rate is only 3% when the pH is 11.0. In the case of low pH, the removal rate of ReO_4^- by p-(Amide)-PAM is

low, which may be due to the high concentration of NO_3^- and the lack of protonation of -NH on p-(Amide)-PAM. As the pH increases, -NH can protonate to produce a positive charge, resulting in electrostatic interactions with ReO_4^- . In an alkaline environment, OH^- in the aqueous phase will be attracted by protonated -NH, which occupies the adsorption sites, resulting in a decline in the adsorption effect of ReO_4^- . Compared to amino triazole-modified microcrystalline cellulose microsphere and ionic liquid-MIMDIDOA, p-(Amide)-PAM can efficiently remove ReO_4^- over a wide range of pH values [42,45].



Figure 3. Removal rate of ReO_4^- by p-(Amide)-PAM generated by different reaction molar ratios. The dosage of the absorbent was 1 g/L, pH was 5.5, time was 240 min, initial concentration of ReO_4^- was 100 mg/L, and the temperature was 298.15 K.

3.2.3. Influence of Competitive Anions

There are a large number of competitive anions (NO₃⁻, Cl⁻, SO₄²⁻, etc.) in radioactive wastewater, which will adversely affect the adsorption of ReO₄⁻. As shown in Figure 5, when the molar ratio of ReO₄⁻ to competing anions is 1:1, the removal rate of ReO₄⁻ by p-(Amide)-PAM is 95.7–96.7%. When the molar ratio of ReO₄⁻ to competitive anions is 1:100, the removal rate of ReO₄⁻ by p-(Amide)-PAM still reaches 60%. The selectivity of p-(Amide)-PAM may be attributable to its hydrophobic surface and ReO₄⁻ has a relatively low hydration energy (-170 kJ/mol). Compared with other anions such as NO₃⁻ (-275 kJ/mol) and Cl⁻ (-340 kJ/mol), the hydrophobic surface of p-(Amide)-PAM more easily adsorbs ReO₄⁻. In addition, the negative charge of SO₄²⁻ (-1080 kJ/mol) is higher than that of ReO₄⁻, and SO₄²⁻ is a more favorable compound for adsorption via electrostatic interactions [28]. According to the research report of existing adsorbents, in the anionic system of SO₄²⁻ or Cl⁻, the adsorbent is more effective in removing ⁹⁹TcO₄⁻/ReO₄⁻ from radioactive wastewater, but it is interesting that in this work, the effect is better under the system of NO₃⁻.



Figure 4. The pH effect on the removal efficiency for ReO_4^- by p-(Amide)-PAM. The dosage of the absorbent was 1 g/L, time was 240 min, initial concentration of ReO_4^- was 100 mg/L, and the temperature was 298.15 K.

3.2.4. Adsorption Isotherm

In order to explore the adsorption performance, the adsorption isotherm of ReO_4^- by p-(Amide)-PAM (Figure 6a) was tested, and the adsorption isotherm data were fitted by the Langmuir model (Figure 6b, Table 2) and Freundlich model (Figure 6c, Table 2). Through the comparison of the two models, the adsorption of ReO_4^- by p-(Amide)-PAM is more consistent with the Langmuir model ($\text{R}^2 = 0.99452$), indicating that the adsorption is monolayer chemisorption on a homogeneous surface. The results show that the saturated adsorption capacity of p-(Amide)-PAM for ReO_4^- is as high as 346.02 mg/g. Compared with the reported adsorbent materials (Table 3), the saturated adsorption capacity of p-(Amide)-PAM for ReO_4^- is a high as 346.02 mg/g.

Table 2. Fitting parameters of the Langmuir model and Freundlich model.

Models	Parameters	p-(Amide)-PAM
	K _L	0.0247
Langmuir	$Q_{\rm max} ({\rm mg/g})$	346.02
	\mathbb{R}^2	0.99452
	K _F	25.319
Freundlich	п	2.28
	R ²	0.95520



Figure 5. Effect of competing anions on the removal percentage of ReO_4^- by p-(Amide)-PAM. The dosage of the absorbent was 4 g/L, pH was 5.5, time was 240 min, initial concentration of ReO_4^- was 10 mg/L, and the temperature was 298.15 K.



Figure 6. Adsorption isotherm of ReO_4^- by p-(Amide)-PAM (**a**): fitting the Langmuir model (**b**) and fitting the Freundlich model (**c**). The dosage of the absorbent was 1 g/L, pH was 5.5, time was 12 h, initial concentration of ReO_4^- was 0–1000 mg/L, and the temperature was 298.15 K.

Table 3.	Adsorption	capacity of	f ⁹⁹ TcO₄ [−]	$/ReO_4$ – by	v different adsor	ntion materials
Incie of	raborption	cupacity of	1004	, neo4 v	y annerent aabor	priori materialo.

Adsorbent	Adsorption Capacity (mg/g)	References
p-(Amide)-PAM	346.02	This work
GO-DEADIBA	140.82	[32]
SCU-100	541	[15]
SCU-101	217	[46]
SCU-102	291	[17]
SCU-103	318	[47]
Ag-TPPE	251	[19]
ZJU-X6	507	[18]
3-ATAR	146.4	[42]
DNOA-GO-CS	90.33	[25]
CSN	222	[48]
SCU-CPN-4	437	[30]

3.2.5. Adsorption Kinetics

The adsorption properties were further explored, and the adsorption kinetics of ReO₄⁻ by p-(Amide)-PAM were determined (Figure 7a); the data were fitted by a pseudo-firstorder kinetic model (Figure 7b, Table 4) and pseudo-second-order kinetic model (Figure 7c, Table 4). Figure 7a shows that the adsorption rate is fast during the initial stage of adsorption, more than 80% of ReO_4^- is adsorbed in approximately 60 s, and adsorption equilibrium is gradually reached after 120 s. In the first stage, the rapid adsorption process is mainly controlled by physical diffusion, and ReO_4^- quickly occupies the effective adsorption sites. The slow adsorption in the second stage mainly depends on chemical adsorption, which continues until the adsorption equilibrium is reached. Comparing the pseudofirst-order kinetic model and the pseudo-second-order kinetic model, the adsorption of ReO₄⁻ by p-(Amide)-PAM is more consistent with the pseudo-second-order kinetic model, which indicates that the adsorption process is controlled by chemical adsorption such as surface complexation and metal coprecipitation [49]. The adsorption rate and equilibrium time of adsorbents are important factors for evaluating the performance of adsorbents, where a fast rate and short equilibrium time correspond to a good performance. Therefore, p-(Amide)-PAM has good prospects for the removal of 99 TcO₄⁻ in radioactive wastewater.



Figure 7. Adsorption kinetics of p-(Amide)-PAM for ReO_4^- (**a**): fitting pseudo-first-order kinetic model (**b**) and fitting pseudo-second-order kinetic model (**c**). The dosage of the absorbent was 1 g/L, pH was 5.5, time was 0–240 min, initial concentration of ReO_4^- was 300 mg/L, and the temperature was 298.15 K.

|--|

Models	Parameters	p-(Amide)-PAM
	k_1	0.01037
Pseudo-first-order	$Q_{e1}(mg/g)$	13.279
	R^2	0.49508
	<i>k</i> ₂	0.0116
Pseudo-second-order	$Q_{e2}(mg/g)$	228.311
	R^2	0.99998

3.3. Sorption Mechanism

The sorption mechanism of ReO_4^- by p-(Amide)-PAM was studied by XPS and FT-IR. The comparison of the FT-IR spectra (Figure 8a) before and after the adsorption of ReO_4^- by p-(Amide)-PAM shows a new peak at 903 cm⁻¹ after adsorption, which corresponds to the stretching vibration of Re-O formed by electrostatic interactions between ReO_4^- and protonated -NH groups [25,27]. Comparing the XPS (Figure 8b) patterns before and after the adsorption of ReO_4^- by p-(Amide)-PAM, the peaks of Re $4f_{5/2}$ (47.8 eV) and Re $4f_{7/2}$ (45.4 eV) in Re 4f of p-(Amide)-PAM@Re (Figure 8c) are visible, which indicates that the removed ReO_4^- still exists in the form of ions. In the N 1s pattern of p-(Amide)-PAM@Re (Figure 8d), the binding energies of -NH (400.2 eV) and C-N (399.3 eV) have changed, indicating electrostatic interactions between amino groups and ReO_4^- after protonation.



Figure 8. FT-IR spectra (**a**) and XPS wide scan spectrum (**b**) of p-(Amide)-PAM and p-(Amide)-PAM@Re; XPS Re 4f spectrum (**c**) and XPS N 1s spectrum (**d**) of p-(Amide)-PAM@Re.

4. Conclusions

In this study, the polymer material p-(Amide)-PAM with polyamide functionalization was successfully synthesized. The results show that p-(Amide)-PAM has good selective adsorption properties for ⁹⁹TcO₄⁻ / ReO₄⁻. The removal of ⁹⁹TcO₄⁻ / ReO₄⁻ by p-(Amide)-PAM has a relatively wide pH window (3.0-8.0) and maintains an excellent adsorption performance. P-(Amide)-PAM maintains good selectivity in environments with a large number of competitive anions (NO₃⁻, Cl⁻, SO₄²⁻), and was best under the NO₃⁻ system. P-(Amide)-PAM has a fast adsorption rate (adsorption equilibrium after 120 s) and high saturated adsorption capacity (346.02 mg/g) for ⁹⁹TcO₄⁻ / ReO₄⁻. The predominant ⁹⁹TcO₄⁻ / ReO₄⁻ sorption mechanism by p-(Amide)-PAM was the electrostatic interaction of amino groups with ⁹⁹TcO₄⁻ / ReO₄. These results all indicate that p-(Amide)-PAM has good application prospects in the rapid and deep removal of ⁹⁹TcO₄⁻ / ReO₄⁻ from radioactive wastewater.

Supplementary Materials: The following supporting information can be downloaded at: https:// www.mdpi.com/article/10.3390/toxics10100630/s1, Figure S1a: N₂ adsorption-desorption isotherms of the N-PAM, Figure S1b: N₂ adsorption-desorption isotherms of the p-(Amide)-PAM, Figure S1c: pore size distribution of N-PAM and p-(Amide)-PAM; Figure S2a: XPS wide scan spectrum of N-PAM, Figure S2b: XPS wide scan spectrum of p-(Amide)-PAM.

Author Contributions: Conceptualization: B.Q. and F.Y.; methodology and writing—review and editing, F.Y. and C.L.; writing—original draft preparation, validation and formal analysis, B.Q. and Y.H.; data curation, B.Q. and M.X.; visualization, M.X. and L.X.; supervision, F.Y. and C.L.; All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by The National Key Research and Development Program of China (No. 2019YFC0605000); the independent deployment project of Ganjiang Innovation Research Institute of Chinese Academy of Sciences (No. E055A002); The key deployment project of the Chinese Academy of Sciences (No. ZDRW-CN-2021-3); the independent deployment project of Fujian Science & Technology Innovation Laboratory for Optoelectronic Information of China (No. 2021ZZ109); Supported by the Fund of Science and Technology on Reactor Fuel and Materials Laboratory (No. STRFML-2021-07).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

References

- 1. Zheng, K.; Zhang, F.; Xu, Z.; Feng, J.; Chen, X. Research on the Prospect of Nuclear Power Development in Mid-and-Long Term. *IOP Conf. Ser. Earth Environ. Sci.* 2020, 546, 022028. [CrossRef]
- Zhan, L.; Bo, Y.; Lin, T.; Fan, Z. Development and outlook of advanced nuclear energy technology. *Energy Strategy Rev.* 2021, 34, 100630. [CrossRef]
- 3. Zhang, X.; Ping, G.; Liu, Y. Decontamination of radioactive wastewater: State of the art and challenges forward. *Chemosphere* **2018**, 215, 543–553. [CrossRef] [PubMed]
- 4. Gephart, R.E. A short history of waste management at the Hanford Site. *Phys. Chem. Earth Parts A/B/C* 2010, 35, 298–306. [CrossRef]
- Smirnov, I.V.; Karavan, M.D.; Logunov, M.V.; Tananaev, I.G.; Myasoedov, B.F. Extraction of Radionuclides from Alkaline and Carbonate Media. *Radiochemistry* 2018, 60, 470–487. [CrossRef]
- Zhou, X.; Ye, G.-A.; Zhang, H.; Li, L.; Luo, F.; Meng, Z. Chemical behavior of neptunium in the presence of technetium in nitric acid media. *Radiochim. Acta* 2014, 102, 111–116. [CrossRef]
- Lee, M.S.; Um, W.; Wang, G.; Kruger, A.A.; Lukens, W.W.; Rousseau, R.; Glezakou, V.A. Impeding ⁹⁹Tc(IV) mobility in novel waste forms. *Nat. Commun.* 2016, 7, 12067. [CrossRef]
- Li, J.; Dai, X.; Zhu, L.; Xu, C.; Zhang, D.; Silver, M.A.; Li, P.; Chen, L.; Li, Y.; Zuo, D.; et al. ⁹⁹TcO₄⁻ remediation by a cationic polymeric network. *Nat. Commun.* 2018, *9*, 3007. [CrossRef]
- 9. Shu, X.; Xu, Y.; Liu, L.; Fan, Y.; Zhuang, X.; Huang, C.; Chen, S.; Zheng, C.; Jin, Y.; Xia, C. Synthesis of new carbazole derivative extractants and study on extraction of perrhenate/pertechnetate. *Polyhedron* **2022**, *214*, 115641. [CrossRef]
- Patra, K.; Sengupta, A.; Boda, A.; Ali, M.; Mittal, V.K.; Valsala, T.P.; Kaushik, C.P. Mechanism unravelling for highly efficient and selective ⁹⁹TcO₄⁻ sequestration utilising crown ether based solvent system from nuclear liquid waste: Experimental and computational investigations. *RSC Adv.* 2022, *12*, 3216–3226. [CrossRef]
- Wang, X.; Ding, S.; Wang, Z.; Song, L.; Yang, X.; Xiao, Q.; Xu, H.; Wang, J.; Shen, Z.; Wang, H. A H-Bonding and Electrostatic Interaction Combined Strategy for TcO₄⁻ Separation by a Nitrotriacetate-Derived Amine–Amide Extractant. *Inorg. Chem.* 2021, 60, 10899–10908. [CrossRef] [PubMed]
- 12. Fiskum, S.K.; Thompson, C.J.; Riley, R.G. Preconcentration and analysis of strontium-90 and technetium-99 from Hanford groundwater using solid phase extraction. *J. Radioanal. Nucl. Chem.* **2000**, 245, 261–272. [CrossRef]
- 13. Kameo, Y.; Katayama, A.; Hoshi, A.; Haraga, T.; Nakashima, M. Simple determination of ⁹⁹Tc in radioactive waste using Tc extraction disk and imaging plates. *Appl. Radiat. Isot.* **2010**, *68*, 139–143. [CrossRef] [PubMed]
- Wang, Y.; Lan, J.; Yang, X.; Zhong, S.; Yuan, L.; Li, J.; Peng, J.; Chai, Z.; Gibson, J.K.; Zhai, M.; et al. Superhydrophobic Phosphonium Modified Robust 3D Covalent Organic Framework for Preferential Trapping of Charge Dispersed Oxoanionic Pollutants. *Adv. Funct. Mater.* 2022, 32, 2205222. [CrossRef]

- Sheng, D.; Zhu, L.; Xu, C.; Xiao, C.; Wang, Y.; Wang, Y.; Chen, L.; Diwu, J.; Chen, J.; Chai, Z.; et al. Efficient and Selective Uptake of TcO₄⁻ by a Cationic Metal-Organic Framework Material with Open Ag⁺ Sites. *Environ. Sci. Technol.* 2017, 51, 3471–3479. [CrossRef]
- 16. Hao, M.; Chen, Z.; Yang, H.; Waterhouse, G.I.N.; Ma, S.; Wang, X. Pyridinium salt-based covalent organic framework with well-defined nanochannels for efficient and selective capture of aqueous ⁹⁹TcO₄⁻. *Sci. Bull.* **2022**, *67*, 924–932. [CrossRef]
- Sheng, D.; Zhu, L.; Dai, X.; Xu, C.; Li, P.; Pearce, C.I.; Xiao, C.; Chen, J.; Zhou, R.; Duan, T.; et al. Successful Decontamination of ⁹⁹TcO₄ ⁻ in Groundwater at Legacy Nuclear Sites by a Cationic Metal-Organic Framework with Hydrophobic Pockets. *Angew. Chem. Int. Ed. Engl.* 2019, *58*, 4968–4972. [CrossRef]
- Kang, K.; Shen, N.; Wang, Y.; Li, L.; Zhang, M.; Zhang, X.; Lei, L.; Miao, X.; Wang, S.; Xiao, C. Efficient sequestration of radioactive ⁹⁹TcO₄⁻ by a rare 3-fold interlocking cationic metal-organic framework: A combined batch experiments, pair distribution function, and crystallographic investigation. *Chem. Eng. J.* 2022, 427, 130942. [CrossRef]
- Kang, K.; Liu, S.; Zhang, M.; Li, L.; Liu, C.; Lei, L.; Dai, X.; Xu, C.; Xiao, C. Fast Room-Temperature Synthesis of an Extremely Alkaline-Resistant Cationic Metal-Organic Framework for Sequestering TcO₄⁻ with Exceptional Selectivity. *Adv. Funct. Mater.* 2022, 1–12. [CrossRef]
- 20. Li, J.; Zhu, L.; Xiao, C.; Chen, L.; Chai, Z.; Wang, S. Efficient uptake of perthenate/pertechnenate from aqueous solutions by the bifunctional anion-exchange resin. *Radiochim. Acta* 2018, *106*, 581–591. [CrossRef]
- 21. Fu, L.; Zu, J.; He, L.; Gu, E.; Wang, H. An adsorption study of ⁹⁹Tc using nanoscale zero-valent iron supported on D001 resin. *Front. Energy* **2019**, *14*, 11–17. [CrossRef]
- Milićević, S.; Matović, L.; Petrović, D.; Đukić, A.; Milošević, V.; Đokić, D.; Kumrić, K. Surfactant modification and adsorption properties of clinoptilolite for the removal of pertechnetate from aqueous solutions. *J. Radioanal. Nucl. Chem.* 2016, 310, 805–815. [CrossRef]
- Dickson, J.; Conroy, N.A.; Xie, Y.; Powell, B.A.; Seaman, J.C.; Boyanov, M.I.; Kemner, K.M.; Kaplan, D.I. Surfactant-modified siliceous zeolite Y for pertechnetate remediation. *Chem. Eng. J.* 2020, 402, 126268. [CrossRef]
- 24. Xiong, Y.; Song, Y.; Tong, Q.; Zhang, P.; Wang, Y.; Lou, Z.; Zhang, F.; Shan, W. Adsorption-controlled preparation of anionic imprinted amino-functionalization chitosan for recognizing rhenium(VII). *Sep. Purif. Technol.* **2017**, 177, 142–151. [CrossRef]
- Zhang, H.; Yang, F.; Lu, C.; Du, C.; Bai, R.; Zeng, X.; Zhao, Z.; Cai, C.; Li, J. Effective decontamination of ⁹⁹TcO₄⁻/ReO₄⁻ from Hanford low-activity waste by functionalized graphene oxide-chitosan sponges. *Environ. Chem. Lett.* 2020, *18*, 1379–1388. [CrossRef]
- 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. [CrossRef]
- 27. Hu, Q.-H.; Jiang, W.; Liang, R.-P.; Lin, S.; Qiu, J.-D. Synthesis of imidazolium-based cationic organic polymer for highly efficient and selective removal of ReO₄⁻/TcO₄⁻. *Chem. Eng. J.* **2021**, *419*, 129546. [CrossRef]
- Huang, Y.; Ding, M.; Ding, J.; Kang, J.; Yan, Z.; Zhao, P.; Zhou, X.; Jin, Y.; Chen, S.; Xia, C. Targeted synthesis of a high-stability cationic porous aromatic framework for highly efficient remediation of ⁹⁹TcO₄⁻. *Chem. Eng. J.* 2022, 435, 134785. [CrossRef]
- 29. Han, D.; Li, X.; Cui, Y.; Yang, X.; Chen, X.; Xu, L.; Peng, J.; Li, J.; Zhai, M. Polymeric ionic liquid gels composed of hydrophilic and hydrophobic units for high adsorption selectivity of perrhenate. *RSC Adv.* **2018**, *8*, 9311–9319. [CrossRef]
- Li, J.; Li, B.; Shen, N.; Chen, L.; Guo, Q.; Chen, L.; He, L.; Dai, X.; Chai, Z.; Wang, S. Task-Specific Tailored Cationic Polymeric Network with High Base-Resistance for Unprecedented ⁹⁹TcO₄⁻ Cleanup from Alkaline Nuclear Waste. ACS Cent. Sci. 2021, 7, 1441–1450. [CrossRef]
- 31. Sarri, S.; Misaelides, P.; Zamboulis, D.; Gaona, X.; Altmaier, M.; Geckeis, H. Rhenium(VII) and technetium(VII) separation from aqueous solutions using a polyethylenimine-epichlorohydrin resin. *J. Radioanal. Nucl. Chem.* **2015**, 307, 681–689. [CrossRef]
- 32. Xiong, Y.; Cui, X.; Zhang, P.; Wang, Y.; Lou, Z.; Shan, W. Improving Re(VII) Adsorption on Diisobutylamine-Functionalized Graphene Oxide. *ACS Sustain. Chem. Eng.* **2016**, *5*, 1010–1018. [CrossRef]
- 33. Mo, L.; Zhang, S.; Qi, F.; Huang, A. Highly stable cellulose nanofiber/polyacrylamide aerogel via in-situ physical/chemical double crosslinking for highly efficient Cu(II) ions removal. *Int. J. Biol. Macromol.* **2022**, 209, 1922–1932. [CrossRef]
- Xiong, B.; Loss, R.D.; Shields, D.; Pawlik, T.; Hochreiter, R.; Zydney, A.L.; Kumar, M. Polyacrylamide degradation and its implications in environmental systems. *Npj Clean Water* 2018, 1, 17. [CrossRef]
- 35. Tuzikov, A.; Chinarev, A.; Shilova, N.; Gordeeva, E.; Galanina, O.; Ovchinnikova, T.; Schaefer, M.; Bovin, N. 40 years of glyco-polyacrylamide in glycobiology. *Glycoconj. J.* **2021**, *38*, 89–100. [CrossRef]
- 36. Farrell, D.; Gloe, K.; Gloe, K.; Goretzki, G.; Mckee, V.; Nelson, J.; Nieuwenhuyzen, M.; Pál, I.; Stephan, H.; Town, R.M.; et al. Towards promising oxoanion extractants: Azacages and open-chain counterparts. *Dalton Trans.* **2003**, 2003, 1961–1968. [CrossRef]
- Tamami, B.; Fadavi, A. Amino group immobilized on polyacrylamide: An efficient heterogeneous catalyst for the Knoevenagel reaction in solvent-free and aqueous media. *Catal. Commun.* 2005, *6*, 747–751. [CrossRef]
- Zare, M.A.; Husain, S.W.; Tehrani, M.S.; Azar, P.A. Pentaazatetraethylene supported polyacrylamide (PAA-N5) as a novel adsorbent for the efficient removal of industrial dyes from aqueous solutions: Adsorption isotherms and kinetics. *Mon. Fur Chem. Chem. Mon.* 2016, 148, 191–197. [CrossRef]
- Baba, Y.; Kubota, F.; Kamiya, N.; Goto, M. Development of Novel Extractants with Amino Acid Structure for Efficient Separation of Nickel and Cobalt from Manganese Ions. *Ind. Eng. Chem. Res.* 2014, 53, 812–818. [CrossRef]

- 40. Wang, Y.; Zheng, K.; Jiao, Z.; Zhan, W.; Ge, S.; Ning, S.; Fang, S.; Ruan, X. Simultaneous Removal of Cu²⁺, Cd²⁺ and Pb²⁺ by Modified Wheat Straw Biochar from Aqueous Solution: Preparation, Characterization and Adsorption Mechanism. *Toxics* **2022**, *10*, 316. [CrossRef]
- 41. Lin, W.; Zhao, Z.; Yang, F.; Liu, Z.; Tan, F.; Xie, M.; Ma, Y.; Meng, L. Promising priority separation of europium from lanthanide by novel DGA-functionalized metal organic frameworks. *Miner. Eng.* **2021**, *164*, 106831. [CrossRef]
- Wen, D.; Hua, R.; Dong, Z.; Xie, K.; Qi, W.; Zhao, L. Efficient separation and recovery of Re(VII) from Re/U bearing acidic solutions using aminotriazole modified cellulose microsphere adsorbents. *Environ. Sci. Pollut. Res. Int.* 2021, 28, 52225–52235. [CrossRef]
- Zhang, W.; Wang, S.; Ji, J.; Li, Y.; Zhang, G.; Zhang, F.; Fan, X. Primary and tertiary amines bifunctional graphene oxide for cooperative catalysis. *Nanoscale* 2013, 5, 6030–6033. [CrossRef]
- 44. Ding, M.; Chen, L.; Xu, Y.; Chen, B.; Ding, J.; Wu, R.; Huang, C.; He, Y.; Jin, Y.; Xia, C. Efficient capture of Tc/Re(VII, IV) by a viologen-based organic polymer containing tetraaza macrocycles. *Chem. Eng. J.* **2020**, *380*, 122581. [CrossRef]
- 45. Huang, Y.; Li, X.; Wu, F.; Yang, S.; Dong, F.; Zhi, X.; Chen, X.; Tian, G.; Shen, Y. A Novel Functionalized Ionic Liquid for Highly Selective Extraction of TcO₄⁻. *Inorg. Chem.* **2022**, *61*, 10609–10617. [CrossRef]
- 46. Zhu, L.; Sheng, D.; Xu, C.; Dai, X.; Silver, M.A.; Li, J.; Li, P.; Wang, Y.; Wang, Y.; Chen, L.; et al. Identifying the Recognition Site for Selective Trapping of ⁹⁹TcO₄⁻ in a Hydrolytically Stable and Radiation Resistant Cationic Metal-Organic Framework. *J. Am. Chem. Soc.* 2017, 139, 14873–14876. [CrossRef]
- 47. Shen, N.; Yang, Z.; Liu, S.; Dai, X.; Xiao, C.; Taylor-Pashow, K.; Li, D.; Yang, C.; Li, J.; Zhang, Y.; et al. ⁹⁹TcO₄⁻⁻ removal from legacy defense nuclear waste by an alkaline-stable 2D cationic metal organic framework. *Nat. Commun.* **2020**, *11*, 5571. [CrossRef]
- 48. Li, W.; Dong, X.; Zhu, L.; Tang, H. Highly selective separation of Re(VII) from Mo(VI) by using biomaterial-based ionic gel adsorbents: Extractive adsorption enrichment of Re and surface blocking of Mo. *Chem. Eng. J.* **2020**, *387*, 124078. [CrossRef]
- 49. Xia, Y.; Li, Y.; Xu, Y. Adsorption of Pb(II) and Cr(VI) from Aqueous Solution by Synthetic Allophane Suspension: Isotherm, Kinetics, and Mechanisms. *Toxics* **2022**, *10*, 291. [CrossRef]