

Efficient separation and recovery of Re (VII) from Re/U bearing acidic solutions using aminotriazole modified cellulose microsphere adsorbents

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Research Article

Keywords: Re(VII), U(VI), Cellulose, Aminotriazole, Separation, Selectivity.

DOI: <https://doi.org/10.21203/rs.3.rs-179924/v1>

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Abstract

In this work, aminotriazole-modified microcrystalline cellulose microspheres (3-ATAR) containing an abundant nitrogen content as promising adsorbent was prepared via a radiation grafting method for the selective recovery ReO_4^- in the presence of UO_2^{2+} in acidic solution. A series of batch and column adsorption experiments including monocomponent and binary systems, were designed for evaluating the adsorption and separation performance of Re (VII) onto 3-ATAR. The 3-ATAR exhibited a good adsorption capacity (max $146.4 \text{ mg}\cdot\text{g}^{-1}$) of Re(VII) and a rapid adsorption rate, with equilibrium time of 45 min. In binary solution, the high selectivity coefficients ($\beta_{\text{Re}/\text{M}}$) indicated that 3-ATAR could separate and recover Re(VII) from U(VI) and other metal ions (Cu(II), Cr(III), Ni(II), Zn(II)). In particular, it was found that the adsorption of Re was almost unaffected in U/Re-bearing solutions no matter how much the U(VI) was changed. In the column experiment, when the concentration of U(VI) was 40 times higher than that of Re(VII), 3-ATAR manifested high Re(VII) selectivity over U(VI) from a synthetic uranium ore leachate. This work demonstrated that 3-ATAR could provide an efficient, selectively, sustainable, and industrially feasible way for Re(VII) to be recovered from uranium ore leachate and other prospective sources.

1. Introduction

Rhenium, as a rare and valuable metal, with a melting point of 5869 K (third-highest), the boiling point of 5869 K (second-highest), superior, high-temperature strength, and room-temperature ductility, plays an important role in various industrial sectors, such as in nuclear, aerospace, missile, and petrochemicals (Abisheva et al. 2011; Wang and Wang 2018). However, the content of rhenium in the earth's crust is very low, and minerals containing rhenium do not form under natural conditions. According to a geological survey, rhenium occurs as an admixture in uranium-containing minerals, and solutions obtained from underground leachates of uranium ore contained rhenium at concentrations of $0.25\text{--}0.5 \text{ g}/\text{m}^3$ (Zagorodnyaya et al. 2015). Therefore, the efficient separation and recovery of Re(VII) from the underground uranium ore leachate possesses great significance from an economically sustainable development point of view.

Various methods have been applied for recovery of Re(VII), including solvent extraction (Cheema et al. 2018; Hong et al. 2020), liquid membrane (Zhang et al. 2017) and precipitation (Oymak 2019; Hong et al. 2020); however, the solvent used for solvent extraction is toxic and flammable, the liquid membrane has a low stability, and the post-processing of the precipitation method is complicated, all of which greatly restrict their further applications (Seo et al. 2012; Shan et al. 2019). Adsorption has become increasingly popular as its operation is easy, low-cost, and particularly suitable in practical situations involving low concentrations of Re(VII) (Lou et al. 2013). Recently, various kinds of adsorbents have been used to recover Re(VII), such as ordinal mesoporous silica materials (Shan et al. 2019), layered double hydroxide-based materials (LDHs) (Goh et al. 2008), metal-organic frameworks (MOFs) (Fei et al. 2011), and Ti_2CT_x MXene (Wang et al.). However, the complicated synthetic processes, high costs, and difficulties in recycling or column packing have unfortunately restrained their practical applications in large-scale

environmental and hydrometallurgical processes. Therefore, it is necessary to develop cost-effective, micron-sized adsorbents with excellent selectivity, and superior reusability for bulk processing from a practical point of view.

Cellulose is a naturally available material that is derived from various sources of plants by photosynthesis. Cellulose has been described as a cost-effective and environmentally friendly adsorbent for the recovery of precious metals due to its abundance, low cost, biocompatibility and renewability (Guo et al. 2018; Dong et al. 2020). However, due to the lack of functional groups, the adsorption capacity of natural cellulose is quite poor, limiting its widespread application. Recently, surface modification of cellulose by the introduction of desired functional groups has been used to improve the separation performance of cellulose. It is well-known that radiation-induced graft polymerization (RIGP) is an efficient strategy to modify cellulose because it is green, effective, and environmentally friendly (Dong et al. 2016, 2019).

Some researchers reported that amine functional groups could enable the efficient separation and recovery of selectively adsorbed Re(VII) from co-existing cationic metal ions in acidic solution. For instance, Piotr Cyganowski et al reported the successful separation of Re(VII) from Mo(VI) by anion-exchange resins with 1-(3-aminopropyl)imidazole functionalities (Cyganowski et al. 2019). Heqing Tang et al reported that ReO_4^- could be selectively adsorbed onto chitosan-based ionic gel beads wrapped with methyl-trioctyl ammonium chloride in the presence of MoO_4^{2-} (Li et al. 2020). However, there are few papers concerning rhenium extraction from uranium ore leachates (Dong et al. 2020; Hua et al. 2020). It was reported that the pH of underground uranium ore leachates mainly varied between 2 and 3 (Abisheva et al. 2011). At an acidic pH, U(VI) exists predominantly as the uranyl ion (UO_2^{2+}), and Re(VII) exists as the perrhenate anion (ReO_4^-). Therefore, herein amine modified cellulose adsorbents are eagerly expected to efficiently and selectively adsorb ReO_4^- from underground uranium ore leachates, because amines are predominantly protonated at pH 2, leading to strong electrostatic interactions between the amine modified adsorbents and ReO_4^- , whereas electrostatic repulsions are formed between the adsorbents and UO_2^{2+} .

In the current work, 3-amino-1, 2, 4-triazole was used as a functional monomer to modify microcrystalline cellulose microspheres (MCCs) by RIGP. Herein, microcrystalline cellulose microspheres were chosen as a suitable adsorbent matrix for column filling because of its excellent mechanical properties, hydrophilicity, and easy functionalization (Dong et al. 2016; Yang et al. 2020). It is well-known that amino-1, 2, 4-triazole possesses a free amine functionality and an aromatic ring with good excellent chemical stability and a high nitrogen content (66.35% per mass unit). Introduction of amino-1, 2, 4-triazole to cellulose would increase the available active sites on cellulose for adsorbing Re(VI) and is expected to separate and recover Re(VII) from underground uranium ore leachate. The prepared adsorbent was characterized carefully, and its performance related to the separation of Re(VII) was investigated through batch and column experiments, including monocomponent and binary systems. In particular, in the column experiments, based on data from an uranium mine in Xinjiang, China, a synthetic U/Re bearing uranium

ore leachate was prepared to evaluate the separation performance of 3-ATAR. FTIR and XPS studies were also explored the adsorption mechanisms.

2. Material And Experiments

2.1 Materials and chemicals

Microcrystalline cellulose microspheres (MCC) with average diameter of 120 μm were obtained from Asahi Kasei Chemicals Corporation, Japan. Glyceryl methacrylate (GMA) was supplied by Sinopharm, China. 3-amino-1, 2, 4-triazole (3-ATA) was obtained from Macklin. Uranyl nitrate hexahydrate ($\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and potassium perrhenate (KReO_4) were obtained from Merck, China. N, N-dimethylformamide (DMF), ammonium hydroxide (NH_4OH), chromic chloride hexahydrate ($\text{CrCl}_2 \cdot 6\text{H}_2\text{O}$), copper chloride dehydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$), Zinc(II) chloride (ZnCl_2), nickel(II) chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$), sodium sulfate (Na_2SO_4), sodium carbonate (Na_2CO_3), sodium chloride (NaCl) were supplied from Sinopharm, China. All reagents were analytical grade and used without further purification.

2.2 Preparation of 3-ATAR

The synthesis of 3-ATAR is shown in Scheme1. Firstly, MCC-g-GMA was prepared by electron beam (EB) pre-irradiation grafting polymerization described in our previous report (Dong et al. 2019). Then, the 3-ATAR was prepared by adding 1.0 g MCC-g-GMA into 10 mL water/ethanol (v/v=3:7) solution containing 20% wt% 3-ATA. After shaking for 24 h at 80 °C. The prepared 3-ATAR was washed for purification with deionized water, and then vacuum-dried at 60 °C.

2.3 Characterization

FTIR spectra were recorded on FTIR spectrophotometer (Bruker Tensor 207) at a resolution of 1 cm^{-1} . Scanning electron microscope (SEM) (Hitachi SU8010, Japan) was used for the morphology of dried samples. X-ray photoelectron spectroscopic (XPS) was performed on Shimadzu, Japan. The data were fitted using Casa XPS software. Inductively coupled plasma optical emission spectrometry (ICP-OES 5110, Agilent) was used for the concentration of Re(VII) and coexisting cation.

2.4 Batch adsorption experiments

A 10 mg sample of 3-ATAR was added into a 12 mL glass containing 10 mL of an aqueous Re(VII) solution, and the mixture was stirred at 160 rpm. The pH was adjusted using 0.1 M HCl or NaOH. In the monocomponent experiments, equilibrium studies conducted at 313 K and at different concentrations (20–500 $\text{mg} \cdot \text{L}^{-1}$), pH (1–12), contact times (5–180 min), co-existing anions (Cl^- , SO_4^{2-} , and CO_3^{2-}), and NaCl concentrations (0.1-1000 $\text{mmol} \cdot \text{L}^{-1}$) were systematically investigated using the batch adsorption process. Competitive adsorption experiments between Re(VII) and other representative metal ions (U(VI), Cu(II), Cr(III), Ni(II), and Zn(II)) were conducted in binary-metal systems. In addition, to further investigate the separation performance of Re(VII) from U(VI), equilibrium studies were conducted at 298 K and at

different concentrations (20 – 600 mg·L⁻¹), pH (1–10), and contact times (5–180 min). After equilibrium, the solutions were filtered, and the Re(VII) concentrations in the aqueous phase were analyzed by ICP-OES. The reported ICP data were the average of three parallel measurements.

The adsorbed capacity (q_e), distribution coefficient (K_d , mL/g), selectivity coefficients $\beta_{Re/M}$ and adsorption efficiency (E, %) for the adsorbent were calculated by Eq. (3) - (6) :

$$q_e = \frac{(C_0 - C_e)V}{m_g} \quad (3)$$

$$K_d = \frac{q_e}{C_e} \quad (4)$$

$$\beta_{Re/M} = \frac{K_{d(Re)}}{K_{d(M)}} \quad (5)$$

$$E = \frac{C_0 - C_e}{C_0} \times 100 \% \quad (6)$$

Where C_0 (mg/L) was the initial concentration of metal ions, and C_e (mg/L) were the equilibrium concentration of metal ion in the filtrate. V (L) was the volume of testing solution and m_g (g) was the weight of adsorbent.

2.5 Desorption and regeneration studies

For the regeneration experiments of 3-ATAR, 10 mg of 3-ATAR was added to 10 mL of the Re(VII) solution (20 mg·L⁻¹). After 24 h of shaking, the solid and liquid were separated, and the Re(VII)-loaded 3-ATAR was regenerated in 5% NH₄OH. After 24 h of shaking, the regenerated 3-ATAR was collected, and was reused by washing with deionized water three times for the next cycle. This adsorption–desorption process was repeated five times.

2.6 Column experiments

The column adsorption experiments were conducted in a plastic column with an inner diameter of 5 mm and a bed height of 60 mm. The column was filled with 3-ATAR (approximately 0.55g). The velocity of space (SV) was regulated at 20 h⁻¹. According to data from an uranium mine in Xinjiang, 20 mg/L and 500 µg/L were selected as the initial concentrations of U(VI) and Re(VII), respectively. After the adsorption saturation, the desorption experiments was conducted using 5% NH₄OH solution to elute the Re(VII) adsorbed onto 3-ATAR with a SV of 20 h⁻¹. Samples were obtained at regular intervals, and ICP-OES was used to analyze them.

3. Results And Discussion

3.1 Preparation and characterization

The prepared adsorbent (3-ATAR) after the ring-opening reaction was white and spherical with a diameter of approximately 300 μm . The amount of 3-ATA introduced into the adsorbents calculated by the weighing method was approximately $3.56 \text{ mmol} \cdot \text{g}^{-1}$. FTIR and SEM figures of MCC, MCC-g-GMA and 3-ATAR are discussed in detail in the supporting information S3. From these results, it was confirmed that the 3-ATA ligand was successfully anchored onto the MCC. In addition, the shape of the 3-ATAR adsorbent was comparable to commercial adsorbents, making it perfect for the processing column.

3.2 Batch experiments

3.2.1 pH studies

The Re(VII) adsorption performance of the 3-ATAR was investigated in a Re(VII) solution (20 mg L^{-1}) at different pH's (Fig. 1a). From pH 1.0 to 3.0, the adsorption capacity of Re(VII) onto 3-ATAR increased sharply to $17.35 \text{ mg} \cdot \text{g}^{-1}$ and decreased to $4.61 \text{ mg} \cdot \text{g}^{-1}$ at pH 10.0. Therefore, the optimal pH for Re(VI) adsorption onto the 3-ATAR was determined to be 3.0. The pH-dependent adsorption behavior might have been attributed to the surface charge of 3-ATAR and the Re(VII) speciation. It is known that Re(VII) exists uniformly as the negatively charged ReO_4^- in the aqueous phase, whereas the amine functionality of 3-ATAR is protonated and positively charged when the pH is less than 3.0. Therefore, the strong electrostatic attractions between Re(VII) and 3-ATAR elicited an increase in the adsorption capacity of Re(VII) onto 3-ATAR. On the other hand, the amines become deprotonated as the pH increases. Therefore, the electrostatic repulsions between ReO_4^- and 3-ATAR were enhanced, leading to a decrease in the adsorption capacity.

3.2.2 Adsorption kinetics and isotherms

The adsorption kinetics of Re(VII) onto 3-ATAR were investigated and the results are shown in Fig. 1b. The adsorption capacity at pH 3.0 increased rapidly with longer contact times. As the adsorption capacity increased peaking (16.45 mg g^{-1}) at 45 min, a rapid adsorption of Re(VII) was observed. Four different kinetic models, *i.e.* pseudo-first-order, pseudo-second-order, intraparticle diffusion and Boyd film models (detailed in Table S1) were applied to fit the adsorption kinetics in order to explore the adsorption mechanism of 3-ATAR. As shown in Table S1, the correlation coefficient (R^2) of the pseudo-second-order model was greater than 0.99, and there was a strong agreement between the theoretical values of q_e and the experimental values ($q_{e(\text{exp})}$). This indicated the existence of a chemical or strong electrostatic attraction between the 3-ATAR and Re(VII) (Li et al. 2020).

The adsorption isotherms of Re(VII) onto 3-ATAR are presented in Fig. 1c. As the initial concentration increased, the adsorption capacity of Re(VII) increased, until reaching a maximum capacity of 135.04 mg L^{-1} . The Langmuir and Freundlich models (detailed in S2) were adopted to fit the isothermal data, and the relative parameters are summarized in Table S2. The correlation coefficients (R^2) of the two models were both larger than 0.98, indicating that the isothermal data were well-fitted by the Langmuir and Freundlich models. The maximum adsorption capacity of 3-ATAR was calculated to be $146.4 \text{ mg} \cdot \text{g}^{-1}$ using the Langmuir model equation, which indicated a large adsorption capacity of 3-ATAR for Re(VII). In

addition, it is notable that the n of the 3-ATAR was 2.425, which greater than 1, suggesting the favorable and simple adsorption of Re(VII) onto 3-ATAR (Fathi et al. 2018).

3.2.3 Anion and ionic strength influence

Leachates of ore and industrial wastewaters contain different co-existing ions such as Cl^- , SO_4^{2-} , NO_3^- , which might compete with Re(VII) for adsorbing onto surface active sites. To assess the competing effect of these three anions, batch adsorption experiments of Re(VII) (0.1 mM) were performed with the addition of other anions, whose molar concentrations were 1, 5, and 10 times that of Re(VII) in binary solution. The results in Fig. 2a show that Cl^- and NO_3^- had minor effects on the adsorption of Re(VII) compared to SO_4^{2-} . Therefore, the adverse effects are ranked as follows: $\text{SO}_4^{2-} > \text{NO}_3^- > \text{Cl}^-$. As the concentration of the anions increased, the adsorption efficiency of Re(VII) slowly decreased, indicating that an ion exchange was involved in the adsorption process. In particular, the adsorption efficiency of Re(VII) surpassed 98%, even though the Cl^- and NO_3^- concentration were 10 times high than Re(VII).

Ionic strength studies were conducive to understanding the adsorption mechanism (Yu et al. 2016). Therefore, a series of Re-bearing solutions (the concentration of Re(VII) was 0.1 mmol/L) containing different NaCl concentrations (0.1, 1, 10, 100, and 1000 mmol/L) were prepared to investigate the effect of the ionic strength on the adsorption of Re(VII) onto 3-ATAR. As shown in Fig. 2b, the adsorption efficiency of Re(VII) decreased by 15% when the Cl^- concentration was 1 mol L^{-1} , suggesting that Cl^- competed weakly with Re(VII) for the active sites. These results corroborated that the existence of an electrostatic adsorption mechanism in the adsorption process (Chen et al. 2018).

3.2.4 Desorption and regeneration

The recyclability of adsorbents is important for the separation and recovery of metal ions from an aqueous solution. Ammonium hydroxide (5% w/v) as an eluent was selected to study the recyclability of 3-ATAR, and the adsorption-desorption cycles were repeated five times. As shown in Fig. 3, 3-ATAR could be recycled by 5% NH_4OH five times with a marginal decrease in the adsorption efficiency. The results highlighted the long-term stability of 3-ATAR and indicated that 3-ATAR is potentially an ideal adsorption material for adsorbing Re(VII).

3.2.5 Competitive adsorption in binary system

Table 1
The selectivity coefficients (β) of Re(VII) over other metal of 3-ATAR

Molar Concentration Ratio	$\beta_{\text{Re/U}}$	$\beta_{\text{Re/Cu}}$	$\beta_{\text{Re/Cr}}$	$\beta_{\text{Re/Ni}}$	$\beta_{\text{Re/Zn}}$
1:1	424.36	12.16	175.98	32.71	293.26
1:10	37.05	14.17	67.83	30.85	319.16

Competitive adsorption was investigated by evaluating the adsorption efficiency of Re(VII) from binary mixtures in the presence of U(VI), Cu(II), Cr(III), Ni(II), and Zn(II), respectively. The concentrations of the co-existing cations were 1, 10 times higher than Re(VII). As shown in Fig. 4, when the molar ratio between Re(VII) and the co-existing cations was 1:1, the adsorption efficiency of Re(VII) onto 3-ATAR was approximately 80% higher than U(VI), Cr(III), Ni(II), and Zn(II). The relatively high adsorption efficiency of Cu(II) was attributed to the ability of 3-ATA to easily form metal-ligand complexes with Cu(II) (Finšgar 2013). The selectivity coefficients ($\beta_{\text{Re/M}}$) of 3-ATAR were also calculated and are listed in Table 1. The selectivity coefficients ($\beta_{\text{Re/Cu}}$) of the 3-ATAR were in the range of 12–14, implying that the selectivity was not impaired by a large excess of Cu(II) (10-fold molar excess over Re). In addition, the high selectivity coefficients ($\beta_{\text{Re/M}}$) of U(VI), Cu(II), Cr(III), Ni(II), and Zn(II) indicated that 3-ATAR could separate and recover Re(VII) from U(VI) and other metal ions (Cu(II), Cr(III), Ni(II), Zn(II)).

3.2.6 pH studies in the U/Re binary system

To investigate the separation performance of 3-ATAR against Re(VI) from U(VI), adsorption experiments in a U/Re binary system were performed. The pH of the reaction mixture is considered the most important factor that directly impacts the adsorption behavior of metal ions (Soylak and Cay 2007). As depicted in Fig. 5, the adsorption capacity of Re(VII) onto 3-ATAR was increased with the increasing pH in acid solution, but the adsorption capacity of U(VI) could be ignored. It was reported that the predominant species of U(VI) under acidic conditions is UO_2^{2+} (Yuan et al. 2016). Therefore, the low adsorption capacity of U(VI) onto 3-ATAR was attributed to the strong electrostatic repulsions between UO_2^{2+} and 3-ATAR. Notably, the adsorption trend of Re(VII) in the U/Re binary system under acidic conditions was similar to that in the single Re(VII) system. Therefore, it was possible to separate and recover Re(VII) onto 3-ATAR from a U/Re bearing acidic solution. Since it was reported that the pH of underground uranium ore leachate was 2–3 (Abisheva et al. 2011), pH 2 was used for subsequent experiments.

3.2.7 Adsorption kinetics and isotherms in the U/Re binary system

The effect of contact time on the ability for 3-ATAR to separate Re(VII) from the U/Re binary system was evaluated, and the results are presented in Fig. 6a. The adsorption capacity of Re(VII) was quickly increased and reached equilibrium after approximately 45 min. This phenomenon could be due to the abundance of active sites on the 3-ATAR surface. On the other hand, the adsorption capacity of U(VI) onto 3-ATAR was negligible under these conditions. Besides, the high $\beta_{\text{Re/U}}$ (917.54) manifested a high adsorption selectivity of 3-ATAR for Re(VII) compared to U(VI).

To evaluate the adsorption capacity of Re(VII) onto 3-ATAR in the presence of U(VI), adsorption isotherms were carried out over a wide initial concentration range of 20–600 mg/L. As seen in Fig. 6b, the adsorption capacity of Re(VII) onto 3-ATAR increased markedly with the increasing equilibrium concentration of Re(VI), and reached a maximum of $183.54 \text{ mg}\cdot\text{g}^{-1}$. On the other hand, the adsorption capacity of U(VI) was negligible in the low initial U(VI) concentration range of 20 – 150 mg/L. However, when the initial U(VI) concentration was greater than 150 mg/L, the adsorption capacity of U(VI) slowly increased and reached a maximum of $27.33 \text{ mg}\cdot\text{g}^{-1}$. This might have been attributed to the partial chelation of partial uranyl ions by 3-ATAR at high concentrations of U(VI). To evaluate the maximum adsorption capacities of Re(VII) onto 3-ATAR, two adsorption isotherms, the Langmuir and Freundlich models, were applied and the relative parameters are presented in Table 2. According to the results of Langmuir model, the maximum adsorption capacity of 3-ATAR was 266.6 mg g^{-1} .

Table 2
Isotherm parameters for the Re (VII) on 3-ATAR

	Langmuir model			Freundlich model		
	$q_e(\text{mg g}^{-1})$	$k_1(\text{L mg}^{-1})$	R^2	$k_2 / (\text{mg/g})/(\text{mg/l})^{1/n}$	n	R^2
3-ATAR	266.6	0.005468	0.9979	4.387	1.556	0.9885

3.3 Column experiments

The increased content of rhenium has been found in uranium ore (Chekmarev et al. 2004; Abisheva et al. 2011). Raw uranium material may also be a new source of rhenium. Most studies have focused on the recovery of Re(VII) from solutions of pure Re(VII), but few studies have concentrated on the recovery of Re(VII) from U/Re-bearing solutions. In this experiment, based on the data from sandstone type uranium deposits by the Xinjiang CNNC Tianshan Uranium Industry Company, the content of rhenium in underground uranium ore leachate was $0.28 \sim 0.5 \text{ mg/L}$ at pH 2 (Hua 2017). The synthetic leachate of U/Re-bearing uranium ore was prepared using 20 mg/L U(VI) and 0.5 mg/L Re(VII) at pH 2 to evaluate the separation performance of 3-ATAR for practical applications. As shown in Fig. 7a, it can be concluded that 3-ATAR possessed high Re selectivity over U(VI) by comparing the breakthrough curves for Re(VII) and U(VI). The breakthrough for Re(VII) occurred at 555 BV, while the breakthrough for U(VI) occurred immediately. In addition, the adsorption saturation point of Re(VII) onto 3-ATAR did not occur until 2180 BV, and the corresponding saturation adsorption capacity was $1189.18 \text{ }\mu\text{g/g}$ at $\text{SV } 20 \text{ h}^{-1}$.

The desorption experiments were carried out using 5% ammonium hydroxide as the eluent. As shown in Fig. 7b, the Re(VII) was eluted from 3-ATAR, producing a Re(VII)-rich solution containing 13.09 mg/L Re(VII), which was higher than the feed concentrations ($0.5 \text{ mg}\cdot\text{L}^{-1}$). In summary, 3-ATAR might be used as an effective adsorbent for Re(VII) recovery from uranium ore leachate at low concentration.

3.4 Interaction mechanisms

3.4.1. FT-IR analysis

The FT-IR spectra of 3-ATAR and 3-ATAR-Re are presented in Fig. 8a. It is evident that the absorption peaks at 912 cm^{-1} belonged to the Re-O bond in ReO_4^- (Xiong et al. 2017), indicating that ReO_4^- was successfully adsorbed onto 3-ATAR. A shift of the O-H/N-H stretching vibrations to lower frequencies were observed, while the other characteristic adsorption peaks of 3-ATAR remained unchanged, demonstrating the formation of ion pairs between ReO_4^- and the protonated amines of 3-ATAR (Li et al. 2018).

3.4.2. XPS analysis

XPS analysis was performed to further explore the adsorption mechanism. As shown in Fig. 8b, after the adsorption of Re(VII), 3-ATAR-Re not only displayed the signals of C 1s, N 1s, and O 1s signals but also a new Re 4f signal (45.56eV), indicating the adsorption of Re(VII) onto 3-ATAR.

As shown in Fig. 8c, the N1s peaks of 3-ATAR were deconvoluted into two peaks: imine nitrogen (C = N) in the triazole ring and/or nitrogen atoms of the deprotonated triazole ring (399.42 eV), imino group (N-H) (401.14 eV) (Pagacz-Kostrzewa et al. 2019). In acid solution, the C = N and N-H of 3-ATAR were protonated, providing abundant adsorption sites that would interact with ReO_4^- via electrostatic attraction. In addition, the Re 4f spectrum of 3-ATAR-Re shown in Fig. 8d, could be divided into two peaks at 45.45 eV (Re 4f $_{7/2}$), and 48.08 eV (Re 4f $_{5/2}$), respectively. The binding energy of the Re 4f $_{7/2}$ and 4f $_{5/2}$ peaks were low compared to the Re 4f $_{7/2}$ (46.5 eV) and 4f $_{5/2}$ (48.9 eV) peaks of the KReO_4 powders, respectively (Li et al. 2020). This phenomenon was attributed to the change in formation from $\text{K}^+\cdot\text{ReO}_4^-$ to $\text{NH}^+\cdot\text{ReO}_4^-$. The adsorption mechanism of Re(VII) onto the 3-ATAR could be mainly attributed to electrostatic attractions between the protonated NH of 3-ATAR and the Re(VII) based on the findings of FTIR and XPS (Lou et al. 2018).

4. Conclusion

To separate and recover Re(VII) from the uranium ore leachate, aminotriazole-functionalized cellulose microspheres were employed and studied. The 3-ATAR exhibited a high adsorption capacity ($146.4\text{ mg}\cdot\text{g}^{-1}$), fast adsorption rate (45 min), and high selectivity in the presence U(VI), Cu(II), Cr(III), Ni(II), and Zn(II). In particular, it was found that the presence of U(VI) demonstrated a negligible inhibitory effect on the adsorption of Re(VII) no matter how much the state of U(VI) changed. In the column experiments, 3-ATAR possessed superior Re selectivity over U(VI) even though the concentration of U(VI) (20 mg/L) was 50-fold higher than Re(VII) (500 $\mu\text{g/L}$). With a marginal decrease in adsorption efficiency, 3-ATAR could be recycled by 5 % NH_4OH up to five times. The adsorption mechanism of Re(VII) was determined to consist of electrostatic attractions between the protonated NH of 3-ATAR and Re(VII). In summary, this work demonstrated that 3-ATAR could provide an efficient, selective, sustainable, and industrially feasible way for Re(VII) to be recovered in practical applications.

Declarations

Ethics approval and Consent to participate

Not applicable.

Consent for publication

Not applicable.

Availability of data and materials

All data generated or analyzed during this study are included in this published article and its supplementary information files.

Declaration of competing interest

The authors declare that they have no competing interests

Funding

This work was supported by the National Natural Science Foundation of China (11875138, 11905070). This work was also supported by a grant from the nuclear energy development project titled as technology for the mining and metallurgy of associated uranium resources-on the demonstration of uranium co-mining in Bayan Ura (Inner Mongolia) of state administration of science, Technology and Industry for National Defense, PRC.

Authors' contributions

Di Wen: Conceptualization, Data curation, Writing – original draft, Methodology. **Rong Hua:** Investigation, Funding acquisition. **Zhen Dong:** Formal analysis, Funding acquisition. **Kangjun Xie:** Methodology. **Wei Qi:** Formal analysis. **Long Zhao:** Writing – review & editing, Funding acquisition, Supervision. All authors read and approved the final manuscript.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (11875138, 11905070). This work was also supported by a grant from the nuclear energy development project titled as technology for the mining and metallurgy of associated uranium resources-on the demonstration of uranium co-mining in Bayan Ura (Inner Mongolia) of state administration of science, Technology and Industry for National Defense, PRC.

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