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Synthesis of zeolite X from waste basalt powder and its efficient adsorption of uranyl ions in solution

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Abstract: In order to make full use of waste as raw materials to prepare low-cost zeolite, develop green chemical industry and achieve the purpose of treating waste with waste. High-purity zeolite X was prepared by the alkaline fusion hydrothermal method (AFH) using waste basalt powder as raw material, and was used as an adsorbent to investigate the adsorption performance for uranium-containing wastewater. The structure, morphology, specific surface area, chemical composition, chemical bonds, characteristic functional groups and chemical states of surface elements of the samples were characterized by XRD, SEM, BET, EDS, FT-IR and XPS. zeolite X with high crystallinity and rich hydroxyl/carboxyl groups was successfully synthesized by the AFH method, and its specific surface area was as high as $623.4 \text{ m}^2 \cdot \text{g}^{-1}$. When the adsorption time (t) is 720 min, the adsorption temperature (T) is 30°C , the initial uranium (VI) concentration is (C_0) 35 mg/L, pH is 6.0, and the adsorbent dosage (m) is 5/35 mg/mL, the equilibrium adsorption capacity of zeolite X for uranyl ions is $228.4 \text{ mg} \cdot \text{g}^{-1}$. Thermodynamic results show that the adsorption process of uranyl ions by zeolite X is spontaneous and exothermic. Freundlich isotherms and quasi-second-order models are suitable to describe the adsorption process of uranyl ions by zeolite X. XPS analysis results show that -OH and -COOH play an important role in the adsorption process. At the same time, there is ion exchange between UO_2^{2+} and zeolite during the adsorption process.

Keywords: Basalt, Alkaline fusion method, zeolite X, Adsorption, Uranium-containing Wastewater.

1. Introduction

With the development of economy and society, people's demand for energy is increasing [1, 2]. As clean and low-carbon energy, nuclear energy has been particularly prominent in the background of energy conservation and emission reduction advocated by countries around the world [3-5]. Especially in Asian countries where traditional petrochemical energy sources such as coal and oil are lacking, nuclear power is given priority to develop as an emerging industry. As a major component of nuclear fuel, the demand for uranium in nuclear energy will increase

with the construction of a more technologically advanced third-generation nuclear power plant [6-8]. A large amount of uranium-containing wastewater will be produced in the process of uranium mining and smelting. If this radioactive wastewater is directly discharged into the environment, as heavy metals with both chemical toxicity and radioactive toxicity, it will cause damage to the human body in the form of chemical toxicity and radiation [9-11]. At the same time, the accumulation of uranium in the environment may change the background radiation of the environment, cause species gene distortion, and pose a potential threat to the survival and development of human beings. Therefore, it is very urgent to research the treatment of uranium-containing wastewater. At present, most uranium-containing wastewater is treated by chemical precipitation [12, 13], evaporation [14], condensation-flocculation, ion exchange, extraction [15-17], membrane permeation, electrochemistry, and adsorption [18-20]. Among the above methods, adsorption method is an important research direction for uranium-containing wastewater treatment because of its convenient operation, economy and high efficiency [21]. The key to the effectiveness of the adsorption method in treating uranium-containing wastewater lies in the selection of the adsorbent material [22-24].

Zeolite is a common micron-scale material, which is widely used in the fields of separation, catalysis, and energy depending on the good stability, mechanical properties, and suitable pore structure. However, the high raw material cost of synthetic zeolite currently limits its application to a large extent [25-27]. Basalt reserves are abundant in China, and a large amount of basalt waste powder will be produced during the mining process [28]. Using basalt waste powder as a raw material can greatly reduce the cost of synthetic zeolite and increase its potential economic value [29-32].

In this study, using waste basalt powder as the raw material, high-purity zeolite X was prepared by the alkaline fusion hydrothermal method (AFH) and used as an adsorbent for the treatment of uranium-containing wastewater. The effects of different parameters including pH, C_0 , T , m , and t on the adsorption of uranyl ions by zeolite X have

been studied. The thermodynamics and kinetics of the adsorption process have also been studied, and the adsorption mechanism was discussed.

2. Experiment

2.1 Reagents and materials

Waste basalt powder was obtained from a basalt mine in Hengyang City, Hunan Province (China). Chloroacetic acid (ClCH_2COOH), sodium hydroxide (NaOH), sodium acetate (CH_3COONa), nitric acid (HNO_3), the above reagents were analytical pure and purchased from Sinopharm Chemical Reagent Co., Ltd. (China). Arsenazo III was chemical purity and purchased from Guangzhou Jiangshun Chemical Technology Co., Ltd (China). Uranium nitrate hexahydrate ($\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) was purchased from Hubei Chushengwei Chemical Co., Ltd (China).

X-Max EDS instrument (Oxford) was used to analyze the element content of the sample. A Nicolet-460 Fourier Transform Infrared Spectrometer (FTIR) (Thermo Fisher Science, USA) was used to analyze the sample in the range of $4000\text{--}400\text{ cm}^{-1}$. The T6 Xinrui visible spectrophotometer (Beijing General Analytical Instrument Co., Ltd.) was used to determine the concentration of uranium in the solution. X-ray diffraction (XRD) ($K\alpha$ radiation, Cu target, Rigaku company, Japan) was performed on the sample using D/Max-RB X-ray diffractometer. A scanning electron microscope (SEM) (JSM-7500F SEM analyzer) was used to characterize the shape of the sample. X-ray fluorescence (XRF) (Axios PW4400, Holland) was used to analyze the chemical composition of Waste basalt powder.

2.2 Synthesis of zeolite X

Basalt raw material (10.0 g) and NaOH (10.0 g) were mixed uniformly in a crucible, and calcined in a muffle furnace at $560\text{ }^\circ\text{C}$ for 3 h for alkali fusion treatment. The cooled sample was ground into powder with a mortar. The powder and 50 mL of deionized water were added to a flask, and stirred for 10 h. The above mixture was put into a hydrothermal reactor lined with polytetrafluoroethylene for crystallization at $120\text{ }^\circ\text{C}$ for 12 hours, and then naturally cooled to room temperature. The crystalline product was washed to neutrality with deionized water. After washing

and filtering, the filter cake was put into a watch glass, and dried in an incubator at 60 °C for 12 h to obtain the product of zeolite X.

2.3 Adsorption experiment

2.3.1. Preparation of the uranium standard solution, buffer solution, and arsenazo III color reagent

Uranium nitrate hexahydrate (2.1091 g) was added into a 1 L volumetric flask, and deionized water was added for constant volume to 1 L to obtain 1 g·L⁻¹ uranium standard solution. Chloroacetic acid (4.7241 g) and sodium acetate (4.1055 g) was added into a 250 mL volumetric flask respectively, deionized water was added to make the volume up to 250 mL, and a chloroacetic acid-sodium acetate buffer was obtained. Arsenazo III (0.1250 g) was added into a 250 mL volumetric flask, deionized water was added to make the volume to 250 mL, then arsenazo III color reagent was obtained.

2.3.2. Adsorption process

A certain volume of uranium standard solution was added into a conical flask, a certain amount of deionized water was added to make the initial concentration of uranyl ion in the solution 35 mg·L⁻¹. Dilute nitric acid or sodium hydroxide solution was added to adjust the pH of the solution to a certain value (3.0-10.0). A certain amount of adsorbent (2-14 mg) was added. The above solution was placed in a shaker in a constant temperature water bath and shaken at a certain temperature (25-45°C) for adsorption reaction. After adsorption for a period of time (30-840 minutes), the supernatant was taken. The concentration of uranyl ions was determined by visible light spectrophotometer after filtered by 0.45 µm microporous membrane.

2.3.3. U(VI) detection methods

0.5 mL of the solution to be tested was added to a colorimetric dish, 0.5 mL of arsenazo III colorimetric agent and 5 mL of chloroacetic acid-sodium acetate were added to the solution, and the solution was left standing for 5-10 min. The absorbance was measured at 652 nm with a visible spectrophotometer.

The adsorption capacity of Zeolite X for uranyl ions (Q) and the removal rate of uranyl ions in solution (R) were calculated as follows:

$$Q = \frac{(C_0 - C_e) \times V}{m} \quad 1$$

$$R = \frac{C_0 - C_e}{C_0} \quad 2$$

Where Q is the adsorption capacity of Zeolite X for uranyl ions (mg/g), C_0 (mg/L) and C_e (mg/L) are the initial concentration and equilibrium concentration of UO_2^{2+} in the solution, respectively, and V (mL) is the volume of the solution, m (g) is the dosage of zeolite X, R is the removal rate of uranyl ions in solution.

To investigate the reusability of zeolite X, we carried out desorption experiments. The loaded UO_2^{2+} adsorbent after the above adsorption experiment was collected with a centrifuge, and the 30 mL of $2.0 \text{ mol} \cdot \text{L}^{-1}$ NaOH was carried out as the eluent to desorb UO_2^{2+} from the loaded UO_2^{2+} zeolite X adsorbent. The supernatant after each adsorption experiment uranium content was checked with the T6 Xinrui visible spectrophotometer, and repeat the above adsorption experiment.

3. Results and discussion

3.1. Chemical composition of waste basalt powder

The chemical composition of the waste basalt powder used in this study was determined by XRF method. The results are shown in Table 1. It shows that the oxides of Si and Al in this raw material account for 47.89% and 18.17%, respectively. They are the basic components of silicon and aluminum needed for the synthesis of zeolite. The above explanation shows that zeolite can be prepared by using basalt powder as raw material.

[Table 1]

3.2. Characterization

The BET characterization results of the sample are listed in Table 2. It shows that the specific surface area of

synthetic zeolite X is $623.395 \text{ m}^2 \cdot \text{g}^{-1}$, indicating that zeolite X prepared from basalt has a large specific surface area and has good adsorption potential.

[Table 2]

The microstructure of zeolite X was characterized by SEM. Figure 1a is the SEM picture of zeolite X. The figure 1a indicates that the prepared zeolite X has a particle size of 1-5 μm , the crystal form is a tetrahedral structure and the crystal form is relatively complete, and the crystal surface is smooth. Figure 1b is the SEM picture of the prepared zeolite X after adsorbing uranyl ions. Figure 1b shows that the tetrahedral structure of the zeolite X has not changed significantly, but the crystal surface has become rough.

[Fig. 1]

In Figure 2, curves a is the XRD pattern of the prepared zeolite X, curves b is the XRD pattern of the prepared zeolite X adsorbing uranyl ions. As can be seen from curves a, the XRD diffraction peaks of the samples show ten characteristic diffraction peaks (111, 220, 311, 331, 533, 642, 751, 840, 664, and 931) with relatively large relative diffraction intensity at 2θ of 6.23° , 10.02° , 11.78° , 15.48° , 23.32° , 26.75° , 30.37° , 30.99° , 33.54° , and 34.16° , respectively. Compared with the standard data of JCPDS (NO. 38-0237), the characteristic diffraction peaks of the sample are narrow and sharp, without obvious impurity peaks, which indicates that the zeolite X with high purity and complete structure can be successfully prepared by alkali melting method using waste basalt powder as raw material.

Compared with curve a, curve b has two characteristic peaks (220) (311) at 2θ of 46.98° and 55.72° . Comparing the two characteristic peaks with the uranium standard card (JCPDS: 41-1422), the characteristic peak of UO_2 indicates that the prepared zeolite X successfully adsorbed uranyl ions. At the same time, at 2θ of 10.02° (220), 11.78° (311), 23.32° (533), 33.54° (664), the intensity of the characteristic peaks is reduced, which may be due to a large amount of uranium on the surface of the material, which reduces the scattering between the pore walls, the characteristic peak intensity is weakened.

[Fig. 2]

The FT-IR characterization results of samples are shown in Figure 3. Curve a is the FT-IR spectrum of the prepared zeolite X, curve b is the FT-IR spectrum of the prepared zeolite X adsorbing uranyl ions. In curve a, the characteristic peak at 3463.85 cm^{-1} corresponds to the O—H tensile vibration peak, the characteristic peak at 1635.30 cm^{-1} corresponds to the bending vibration peak of adsorbed water, the characteristic peak at 1464.23 cm^{-1} corresponds to the —COOH vibration peak, the characteristic peak at 975.56 cm^{-1} corresponds to the peak of asymmetric stretching vibration in the tetrahedron, the characteristic peak at 564.92 cm^{-1} corresponds to the vibration peak of the double six-membered ring bond. Comparing curve a and curve b in Figure 3, it can be seen that the O—H tensile vibration peak moved from 3463.85 cm^{-1} to 3452.01 cm^{-1} , and the —COOH vibration peak moved from 1464.23 cm^{-1} to 1421.30 cm^{-1} . The reason for the change in peak position may be that after zeolite X adsorbs uranyl ions, the H^+ originally bound to the active site is replaced by uranyl ions, which changes the chemical composition of zeolite X, leading to changes in the peak positions of O—H and —COOH.

[Fig. 3]

The EDS analysis results of the samples are shown in Figure 4. The figure 4 shows that the atomic percentage of O element in zeolite X is 51.36%, the atomic percentage of Al is 4.15%, and the atomic percentage of Si is 5.39%, indicating that zeolite X is mainly composed of O, Al and Si elements. After the adsorption experiment, the atomic percentage of uranium in the samples obtained reach 2.91%. Combined with the XRD analysis results, the adsorption of uranyl ions by zeolite X is confirmed.

[Fig. 4]

3.3. Factors affecting the adsorption performance of zeolite X to uranyl ions

3.3.1. Effect of adsorbent dosage

Under the condition that the reaction temperature (T) was 30°C , the reaction time (t) was 720 min, pH was 6, and

the initial concentration of uranyl ions (C_0) was 35 mg/L, the volume of uranium-containing wastewater (V) was 35 mL, the effect of m on the adsorption of uranyl ions by zeolite X was investigated, as shown in Figure 5. R increases with the increase of m , and the change of Q is exactly the opposite to that of R , and Q decreases with the increase of m .

When m is 5.0 mg, R is 91.20% and Q is 219.07 mg·g⁻¹. When m is 11.0 mg, R is 96.49% and Q is 105.53 mg·g⁻¹. This is mainly because the content of uranyl ions in the uranyl solution is constant, with the increase of m , the number of effective adsorption active sites will increase, and R will increase. However, the number of uranyl ions adsorbed by zeolite X per unit mass decreased, which resulted in a decrease of adsorbent adsorption per unit mass. When m is 5.0 mg, the removal rate curve and the adsorption capacity curve just intersect. Although R increased with the increase of m , it was slow. Conversely, the adsorption capacity of adsorbent per unit mass decreased rapidly. From the optimal point of view, m of 5.0 mg is chosen as the optimal dosage in 35 mL uranium-containing wastewater.

[Fig. 5]

3.3.2. Effect of the initial concentration of uranyl ions

Under the condition that T was 30°C, t was 720 min, pH was 6, and m was 5 mg, V was 35 mL, the effect of C_0 on the adsorption of uranyl ions by zeolite X was investigated, the results are shown in Figure 6.

As can be seen from Figure 6, when C_0 is low, the uranyl ions in the solution are completely absorbed by the zeolite X. With the continuous increase of C_0 , the active adsorption sites on zeolite X are constantly occupied. When the uranyl ion concentration reaches 60 mg·L⁻¹, the maximum adsorption capacity of zeolite X for uranyl ions reaches 225.83 mg·g⁻¹. After investigation, the author found that the mass concentration of uranyl ions in the uranium-containing wastewater discharged from the factory to be treated was about 35mg·L⁻¹. Therefore, in the follow-up study, the uranium-containing wastewater with C_0 of 35 mg·L⁻¹ was selected as the research object.

[Fig. 6]

3.3.3. Effect of pH

Under the condition that T was 30°C, t was 720 min, C_0 was 35 mg·L⁻¹, and m was 5 mg, V was 35 mL, the effect of pH on the adsorption of uranyl ions by zeolite X was investigated, the results are shown in Figure 7. When the pH of the solution increases from 3.0 to 6.0, Q increases with the increase of pH, but Q decreases with the increase of the pH in the range of 6.0 to 10.0. This is because when the pH<4, U(VI) mainly exists in the form of UO_2^{2+} and UO_2OH^+ , and the functional groups on the surface of the zeolite X are protonated, which makes the zeolite X positively charged, and there is a strong electrostatic repulsion between the two, which weakens the adsorption force of the material. In the process of increasing the pH to 6, U(VI) will be hydrolyzed to form $\text{UO}_2(\text{OH})^+$ and $(\text{UO}_2)_3(\text{OH})_5^+$, and the positive charge on the surface of the zeolite X begins to decrease. At this time, the complexation reaction of U (VI) with the functional groups on the surface of the zeolite X. With the further increase of pH, OH^- and UO_2^{2+} can form ions with low adsorption affinity, including $[\text{UO}_2(\text{OH})_4]^{2-}$, $[(\text{UO}_2)_3(\text{OH})_7]^-$, $[\text{UO}_2\text{OH}]^+$, $(\text{UO}_2)_3(\text{OH})_5^+$, $[(\text{UO}_2)_2(\text{OH})_2]^{2+}$, $[(\text{UO}_2)_2\text{OH}]^{3+}$, $[(\text{UO}_2)_3\text{OH}]^{5+}$, which reduce the adsorption capacity of the adsorbent to uranyl ions. Hence, the solution pH of 6 was chosen as the optimal reaction condition.

[Fig. 7]

3.3.4. Effect of adsorption time

Under the condition that T was 30°C, pH was 6, C_0 was 35 mg·L⁻¹, and m was 5 mg, V was 35 mL, the effect of t on the adsorption of uranyl ions by zeolite X was investigated, the results are shown in Figure 8. Q increases rapidly with the increase of t for the first 6 h. After that, R became slower and slower. When t reaches 720 min, Q reaches equilibrium. At this time, the maximum adsorption capacity is 220.93 mg·g⁻¹, and R is 93.78%.

[Fig. 8]

3.3.5. Effects of temperature

Under the condition that t was 720 min, pH was 6, C_0 was 35 mg·L⁻¹, and m was 5 mg, V was 35 mL, the effect

of T on the adsorption of uranyl ions by zeolite X was investigated, the results are shown in Figure 9. As can be seen from Figure 9, when T is 25-30 °C, Q increases with the increase of T . When T is 30 °C, R is 90.69% and Q is 222.18 mg·g⁻¹. After that, with the further increase of T , Q and R decreased rapidly. Hence, 30 °C were chosen as the optimal reaction temperature.

[Fig. 9]

3.4. Adsorption thermodynamics

The thermodynamic parameters are calculated by formulas (3) - (5).

$$K_d = \frac{Q_e}{C_e} \quad 3$$

$$\Delta G = -RT \ln K_d \quad 4$$

$$\ln K_d = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad 5$$

Where: Q_e is the adsorption capacity at equilibrium, mg·g⁻¹. K_d is the adsorption distribution coefficient, L/mg. C_e is the mass concentration at equilibrium, mg·L⁻¹. T is the thermodynamic temperature, K. R is the ideal gas constant, 8.314 J·(mol·K)⁻¹. ΔH is the change in enthalpy, kJ·mol⁻¹. ΔG is the Gibbs free energy, kJ·mol⁻¹. ΔS is the change in entropy, J·(mol·K)⁻¹.

$\ln K_d$ is used to plot $1/T$. The slope and intercept are $\Delta H/R$ and $\Delta S/R$ respectively. The result is shown in Figure 10 and Table 3. $\Delta H < 0$ and $\Delta S < 0$, indicating that the reaction is a process of exothermic and entropy reduction. As the reaction temperature increases, ΔG gradually increases, indicating that lowering the temperature can increase the removal effect of zeolite X on uranyl ions.

[Fig. 10]

[Table 3]

3.5. Adsorption kinetics

The quasi-first-order kinetic equation (Equation (6)) and the quasi-second-order kinetic equation (Equation (7))

were used to fit the experimental data. The results are shown in Figures 11 and Table 4.

$$\lg(Q_e - Q) = \lg Q_e - \left(\frac{K_1}{2.303} \right) t \quad 6$$

$$\frac{t}{Q} = \frac{1}{K_2 Q_e^2} + \frac{t}{Q_e} \quad 7$$

Where, Q_e and Q are the adsorption capacity at the time of adsorption equilibrium and time t , ($\text{mg} \cdot \text{g}^{-1}$), K_1 (min^{-1}) and K_2 ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$) are the two kinetic reaction constants, respectively.

It shows that the fitting degree of the quasi-first-order kinetic equation (R_1^2) is 0.7239, the fitting degree of the quasi-second-order kinetic equation (R_2^2) is 0.9967, $R_2^2 > R_1^2$, and the theoretical value Q_e obtained by the quasi-second kinetic model is very close to the actual value q_e . The results show that the adsorption of uranyl ions by zeolite X is more in line with the quasi-second-order kinetic model, indicating that the adsorption and removal process of uranyl ions by zeolite X is mainly controlled by chemical adsorption.

[Fig. 11]

[Table 4]

3.6. Adsorption isotherm

Langmuir, Freundlich and Dubinin-Radushkevich isothermal models were used to analyze the experimental data.

Langmuir adsorption isotherm:
$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad 8$$

Freundlich adsorption isotherm:
$$\ln q_e = \ln K_F - \frac{1}{n} \ln C_e \quad 9$$

Dubinin-Radushkevich (D-R) adsorption isotherm:

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \quad 10$$

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad 11$$

$$E = \frac{1}{(-2\beta)^{\frac{1}{2}}} \quad 12$$

Where, q_e represents the adsorption capacity of zeolite X to uranyl ions at equilibrium adsorption, ($\text{mg}\cdot\text{g}^{-1}$). C_e is the concentration of uranyl ions in the solution at adsorption equilibrium, ($\text{mg}\cdot\text{L}^{-1}$). q_m is the maximal adsorption capacity of zeolite X to uranyl ions, ($\text{mg}\cdot\text{g}^{-1}$). K_L is the Langmuir constant, ($\text{L}\cdot\text{mg}^{-1}$). K_F is the Freundlich constant. the value of $1/n$ indicates the strength of adsorption. β represents the activity constant. R is the ideal gas constant, $8.314 \text{ J}\cdot(\text{mol}\cdot\text{K})^{-1}$, and E represents the adsorption free energy.

Figure 12 is the fitting curve of each isotherm equation, and the specific parameter results are shown in table 5. It can be seen from table 5 that the degree of fitting of the Freundlich isotherm adsorption equation ($R^2=0.998$) is higher than the degree of fitting of the Langmuir isotherm adsorption equation ($R^2=0.583$) and the fitting degree of the D-R isotherm adsorption equation ($R^2=0.971$). Therefore, the adsorption isotherms of zeolite X to uranyl ions conform to the Freundlich isothermal model.

[Fig. 12]

[Table 5]

3.7. Potential mechanism of adsorption of uranyl ions by zeolite X

In order to further study the adsorption mechanism of zeolite X to uranyl ions, the changes of surface functional groups before and after adsorption of zeolite X were analyzed by XPS characterization. As shown in Figure 13a, the zeolite X showed a clear U 4f binding energy peak after adsorption, which indicated that the zeolite X successfully adsorbed uranyl ions. In addition, Figure 13a also shows that the Na1s binding energy peak intensity decreases after adsorption, so there is ion exchange during the adsorption process. From the O1s XPS spectrum in figure 13b, we can get the binding energy peaks at 530.99 eV and 530.16 eV, respectively, corresponding to -OH and C=O. After the adsorption of uranyl ions, the O1s peak shifts to a lower level. The binding energy peaks changed to 530.78 eV and 529.88 eV, respectively. The shift of peak position and the change of peak area show that -OH and C=O play an

indispensable role in the adsorption process. As shown in Figure 13c, by comparing the characteristic peaks of C 1s in the XPS spectra before and after adsorption, it can be observed that the characteristic peaks of the binding energy of C=O and C-OH have changed after zeolite X adsorbs uranyl ions. This is due to the chemical adsorption of uranyl ions with -OH and -COOH. According to the above analysis, the adsorption of uranyl ions by zeolite X is mainly through the complexation of -COOH and -OH with uranyl ions, and then the ion exchange between zeolite X and uranyl ions.

[Fig. 13]

3.8. Desorption and reusability of basalt-based zeolite X

Using 30 mL 2.0 mol·L⁻¹ NaOH as eluate to desorb uranyl ions from zeolite X after adsorption reaction, the recycling performance of the prepared zeolite X adsorbent to adsorb uranyl ions was investigated, and the results are shown in Figure 14. The prepared zeolite X adsorbent has a removal rate of 93.06% for uranyl ions when it is used for the first time, and the removal rate of uranyl ions for the fifth cycle is still 80.13%. After five cycles of adsorption and regeneration, the adsorption performance of zeolite X to uranyl ions did not decrease significantly. The above data indicates zeolite X is a reusable adsorption material after regeneration.

[Fig. 14]

4. Conclusions

Using waste basalt powder as raw material, high-purity zeolite X is prepared by the alkaline fusion hydrothermal method, and its specific surface area is as high as 623.395 m²·g⁻¹. The adsorption performance of zeolite X for uranyl ions in aqueous solution was investigated. When the adsorption time is 720 min, the adsorption temperature is 30 °C, the initial uranyl ions concentration is 35 mg·L⁻¹, pH is 6.0, and the adsorbent dosage is 5/35 mg·mL⁻¹, the maximum adsorption capacity of zeolite X for uranyl ions is 228.4 mg·g⁻¹. The adsorption process of uranyl ions by zeolite X accords with the quasi-second-order kinetic equation and the Freundlich adsorption isotherm

model. $\Delta G < 0$, $\Delta S < 0$, and $\Delta H < 0$ indicate that the adsorption reaction is a process of exotherm and entropy reduction.

zeolite X has good adsorption performance for uranyl ions and is an environmentally friendly adsorption material with good performance.

Conflicts of interest

There are no conflicts to declare.

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Table caption:

Table 1: Chemical composition of basalt powder

Table 2: The BET characterization result of the sample

Table 3: Thermodynamic parameters of adsorption

Table 4: Kinetic model parameters for remove of U(VI) by zeolite X

Table 5: Adsorption isotherm parameters

Table 1. Chemical composition of basalt powder

Components	Al ₂ O ₃	SiO ₂	Fe ₂ O ₃	CaO	Na ₂ O	SO ₃	MgO	K ₂ O	Ignition Loss	Total
wt. %	19.17	47.90	14.67	5.61	2.10	0.07	4.3	1.50	3.19	99.51

Table 2. The BET characterization results of the sample

Sample	Specific surface area (A) m^2/g	Pore volume (V_m) mL/g	Pore size($\bar{d}$) nm
X zeolite	623.395	0.320844	2.22706

Table 3. Thermodynamic parameters of adsorption

T/K	$\Delta G/(kJ/mol)$	$\Delta H/(kJ/mol)$	$\Delta S/[J/(mol \cdot K)]$
303	-10.64		
308	-10.21	-33.01	-73.88
313	-9.86		

Table 4. Kinetic model parameters for remove of U(VI) by zeolite X

quasi-first-order	Value	quasi-second-order	Value	$Q_e(\text{exp})/(\text{mg/g})$
$K_1/(\text{min}^{-1})$	0.00634179	$K_2/(\text{mg g}^{-1} \cdot \text{min}^{-1})$	0.000112528	220.93
$Q_e/(\text{mg/g})$	75.57	$Q_e/(\text{mg g}^{-1})$	234.19	
R_1^2	0.894	R_2^2	0.996	

Table 5. Adsorption isotherm parameters

T $^{\circ}\text{C}$	Langmuir isotherm			Freundlich isotherm			D-R isotherm		
	Q_m $/(\text{mg} \cdot \text{g}^{-1})$	K_L $/(\text{L} \cdot \text{mol}^{-1})$	R^2	K_F $/(\text{mg} \cdot \text{g}^{-1})/(\text{mg} \cdot \text{L}^{-1})^{1/n}$	n	R^2	Q_m $/(\text{mg} \cdot \text{g}^{-1})$	E $/(\text{kJ} \cdot \text{mol}^{-1})$	R^2
30	211.42	0.116	0.998	141.77	5.608	0.583	216.08	1125.49	0.971

Figure caption:

Fig. 1. SEM images of samples. (a) zeolite X, (b) zeolite X after adsorption of uranyl ions

Fig. 2. XRD pattern of samples. (a) zeolite X, (b) zeolite X after adsorption of uranyl ions

Fig. 3. FT-IR spectra of samples. (a) zeolite X, (b) zeolite X after adsorption of uranyl ions

Fig. 4. EDS analysis of samples. (a) zeolite X, (b) zeolite X after adsorption of uranyl ions

Fig. 5. Effect of adsorbent dosage

Fig. 6. Effect of the initial concentration of uranyl ions on adsorption performance

Fig. 7. Influence of pH on adsorption performance

Fig. 8. Influence of adsorption time on adsorption performance

Fig. 9. Influence of temperature on adsorption performance

Fig. 10. Linear plots of $\ln K_d$ against $1/T$

Fig. 11. Adsorption kinetic simulation curve. (a) quasi-first-order kinetic model, (b) quasi-second-order kinetic model

Fig. 12. Linear fitting of adsorption isotherm. (a) Langmuir adsorption isotherm, (b) Freundlich adsorption isotherm, (c) Dubinin-Radushkevich adsorption isotherm

Fig. 13. XPS spectrum of zeolite X (a) , and the XPS fine spectrum of O 1s (b), and C 1s (c).

Fig. 14. Influence of cycle times on adsorption performance

Fig. 1. SEM images of samples. (a) zeolite X, (b) zeolite X after adsorption of uranyl ions

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Author contributions:

Pengfei Yang, Yong Ai contributed to the conception of the study; Yong Ai, Na Yin performed the experiment; Pengfei Yang, Yong Ai, Yanquan Ouyang contributed significantly to analysis and manuscript preparation; Pengfei Yang, Yong Ai, Yuanxin Xu performed the data analyses and wrote the manuscript; Pengfei Yang, Yong Ai helped perform the analysis with constructive discussions.