Protonated Titanate Nanotubes and their adsorption behaviors for U(VI) in Aqueous Solutions

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Abstract. Titanate nanotubes was rapidly synthetized by nano anatase with mild hydrothermal method, and its protonation was carried by Nitric acid to prepare TNTs and TNTs-H with different H⁺/Na⁺ for further application of uranium removal in the wastewater. It was characterized by XRD, TEM and FT-IR. The results showed that at 298 K and pH 7, the adsorption rates of TNTs and TNTs-H to 10 mg/L U(VI) were 77.90% and 97.78% respectively, and the maximum adsorption capacity of U(VI) were 41.494 mg/g and 49.505 mg/g respectively. The adsorption processes all followed a pseudo second-order kinetic model and were in accordance with isotherm adsorption models like Langmuir model.

1. Introduction

Uranium is the main fuel of nuclear energy, so the geological disposal or storage of nuclear waste will release a considerable amount of uranium in the natural water and soil environment, which has received increasing attention worldwide[1-3]. U(VI) is an important class of harmful ions, which is extremely toxic and radioactive. Even at trace levels, the toxicity profile of U(VI) has been a public health issue[3]. Therefore, it is very important to study the effective treatment of U(VI) in wastewater.

In order to prevent the migration of radionuclides, various methods have been proposed to capture or concentrate these radionuclides, including ion exchange methods, chemical precipitation methods, membrane separation methods, adsorption methods and so on[4]. Among these technologies, adsorption is considered one of the most promising methods due to its versatility, simplicity, low cost and high efficiency.

In recent years, represented by titanate nanotube, it not only has many excellent properties brought by nano-micro size, but also has many advantages such as wide source of raw materials, large reserves, simple preparation method, many ion exchange sites and excellent adsorption performance[5]. Therefore, it has a broad prospect in the adsorption application field of pollutants in water.
2. Experiments

2.1. Methods

In this work, the nano anatase powder replaces the conventional P25 as a titanium source to prepare trititanic acid nanotubes under milder conditions. The aim is to shorten the material preparation cycle to facilitate the protonation modification of acid foam, and to investigate the adsorption effect of the material on U(VI). The specific preparation method is as follows [6]:

80 mL of 8 mol/L NaOH solution was measured into a 250 mL Erlenmeyer flask, and then 0.8 g of anatase TiO$_2$ nanopowder was added and stirred for 12 h to complete mixing. After the stirring was completed, the mixture was transferred to a Teflon-lined stainless steel reactor (effective volume 100 mL), which was then sealed and heated at 130°C for 6 h. After the hydrothermal reaction was completed, the reaction kettle was taken out, and the mixed solution was centrifuged at a speed of 4000 r/min for 5 minutes to obtain a white solid. The obtained white solid was washed with deionized water several times, and then dispersed with anhydrous ethanol, and finally dried in an oven at 60°C. for 6 h to obtain titanate nanotubes, which were recorded as TNTs.

The TNTs prepared above were fully immersed in a 0.1 mol/L HNO$_3$ solution, and after soaking for 1 hour, they were washed with deionized water several times. The solid product was dispersed with absolute ethanol and was dried in an oven, which was controlled at 60°C. After drying for 6 h, protonated titanate nanotubes were obtained, which were labeled as TNTs-H.

2.2. Batch adsorption experiments

0.004g TNTs and TNTs-H were added to the 50 mL centrifuge tube respectively, followed by 20 mL 10 mg/L U(VI) standard solution (both 0.2 g/L), and then put into the air bath constant temperature oscillator shaker at a speed of 150r/min at a certain temperature for a period of time. The adsorbed solution was then centrifuged, and the supernatant was taken and the U(VI) content was determined using azosulfonium III spectrophotometry. The adsorbed solution was then centrifuged, and the U(VI) content of the supernatant was determined by arsenazo III spectrophotometry.

The calculation method of adsorption capacity and adsorption rate are as follows [7]:

\[
Q_e = (C_0 - C_e)V/m
\]

\[
E = (C_0 - C_e)/C_0 	imes 100%
\]

The pseudo-first-order kinetic equation[8]:

\[
Q_t = Q_e(1 - \exp(-k_1t))
\]

The pseudo-second-order kinetic equation[9]:

\[
t/Q_t = 1/k_2Q_e^2 + t/Q_e
\]

The linear expression of Langmuir adsorption isotherm[10]:

\[
C_e/Q_e = C_e/Q_m + 1/k_LQ_m
\]

The linear expression of Freundlich adsorption isotherm[11]:

\[
\ln Q_e = \ln k_F + 1/n\ln C_e
\]

Where $Q_e$ (mg/g) is the adsorption capacity, $C_0$ (mg/L) is the initial concentration of the target ion, $C_e$ (mg/L) is the equilibrium concentration under certain conditions and time, $V$ (L) is the solution volume, and $m$ (g) is the adsorbent dosage, $E$(%) is the adsorption rate, $Q(t)$ (mg/g) represents the adsorption capacity at time $t$, $k_1$(min$^{-1}$) is the equation rate constant, $k_2$(g·mg$^{-1}$·min$^{-1}$) is the equation rate constant, $Q_m$(mg/g) represents the maximum adsorption capacity of single-layer saturated adsorption under certain conditions, and $k_L$(L/mg) represents the Langmuir reaction constant, $k_F$(mg/g) represents the Freundlich adsorption constant, and $1/n$ is usually a constant between 0 and 1, indicating the adsorption in order of difficulty.
3. Results and Discussion

3.1. Characterization of TNTs and TNTs-H

3.1.1. XRD analysis. It can be seen from the Fig. 1 that the strong diffraction peak of 2θ≈10° represents the interfacial structure diffraction of the TNTs, which indicates that the synthesized TNTs have a multilayer structure. 2θ≈28° corresponds to the characteristic crystal plane of Na$_2$Ti$_3$O$_7$; 2θ≈24°, 48° corresponds to the diffraction peak of H$_2$Ti$_3$O$_7$, indicating that the hydrothermal synthesis material is sodium trititanate, and the basic skeleton of the material is triple TiO$_6$ octahedron, with a layered structure [12]. Compared with TNTs, it can be clearly seen from the XRD pattern of TNTs-H that the characteristic peak of Na$_2$Ti$_3$O$_7$ corresponding to 2θ≈28° is weakened: 2θ≈24°, and the diffraction peak of H$_2$Ti$_3$O$_7$ corresponding to 48° was enhanced, indicating that in the protonation process, the high concentration of H$^+$ in the resolution and Na$^+$ in the material have made ion exchanges. The inter-layer structure peaks appearing at 2θ≈10° gradually become inconspicuous, showing that the high protonation process has some damage to the layered structure of the material. Moreover, the peaks increase significantly, indicating that the protonation process has a certain destructive effect on the crystal form of the material [13].

![Fig. 1 X-ray diffraction patterns of TNTs and TNTs-H](image)

3.1.2. TEM analysis. As shown in Fig. 2 (a) and (b), the titanate nanotubes prepared by experiments have a clear and complete microstructure, presenting a partially agglomerated elongated tube with the tube length of about 50 to 150 nm, the tube outer diameter of about 10 nm and the inner diameter is about 5 nm. The center of the material is a blank area, indicating that the material is a hollow tubular structure.

![Fig. 2 TEM images of TNTs and TNTs-H](image)
3.2. Adsorption kinetics
Fig. 3 showed that the linear fitting coefficient $R^2 (\geq 0.998)$ of the pseudo-second-order model was the highest. The theoretical adsorption $Qe$ of TNTs and TNTs-H for U(VI) were 41.494 mg/g and 49.505 mg/g, and the relative error between the experimental values of 40.200 mg/g and 48.415 mg/g were small. Hence, it can be considered that the adsorption of U(VI) by TNTs and TNTs-H conformed to the pseudo-second-order kinetic model, indicating that the adsorption process was mainly chemical adsorption.

![Image of Adsorption Kinetic Model](image)

Fig. 3 Adsorption kinetic model fitting for adsorption of U(VI) on TNTs and TNTs-H

3.3. Adsorption isotherm
As can be seen from Fig 4, in the two models, the Langmuir model of TNTs and TNTs-H adsorption U(VI) had a large linear fitting correlation coefficient $R^2$, indicating that the adsorption behavior of the adsorption material for U(VI) was most consistent with the Langmuir isothermal adsorption model, the adsorption process was more inclined to monolayer adsorption. By calculation, when the temperature was 298 K, the maximum adsorption capacities of TNTs and TNTs-H for U(VI) can theoretically reach 149.253 mg/g and 166.667 mg/g, respectively.
4. Conclusion

In this study, TNTs and TNTs-H with different H⁺/Na⁺ were successfully prepared, both of which were sodium trititanate. The basic skeleton of the materials were triple TiO₆ octahedron structures with layered structures, which were used for U(VI) of adsorption. Adsorbents exhibited fast removal performance reaching equilibrium within 60 min. The results showed that at pH 7, the equilibrium adsorption rates of TNTs-H for U(VI) was increased by about 20% compared with TNTs. The kinetics of the adsorption processes can be well interpreted by the pseudo-second-order model. Langmuir isotherm described suitably the experimental data of the adsorption of the ions by the examined adsorbents.

Acknowledgments

This work was supported in part of the project titled “The National Key Project of Research and Development Plan” funded by the Ministry of Science and Technology of the People's Republic of China (Grant No.2016YFC1402504). The authors are grateful to financial support for this study.

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