Adsorption behavior and mechanism on U(VI) from aqueous solutions by polydopamine-modified titanate nanotubes

Yangyang Zuo, Ye Li*, Juntao Hu, Shuang Liu
School of Resources and Environmental Engineering, Wuhan University of Technology, Wuhan, China

*Corresponding author e-mail: whly1218@whut.edu.cn

Abstract. In this work, uniform polydopamine (PDA) layers by self-polymerization of dopamine were successfully coated around titanate nanotubes (TNTs) to enhance its adsorption ability. The polydopamine-functionalized titanate nanotubes (PDA-TNTs) exhibited outstanding U(VI) adsorption capacity (247.53 mg/g) and rapid adsorption efficiency. The nitrogenous groups and phenolic hydroxyl groups of PDA coordinating with UO₂²⁻ was dominant, while ion exchange between Na⁺/H⁺ and U(VI) was of secondary importance. Besides, the introduction of PDA significantly alleviated the competitive adsorption between U(VI) and coexisting metal ions, making it possible for PDA-TNTs to be an effective sorbent to remove U(VI) in radioactive wastewater.

1. Introduction
As new clean energy with no greenhouse-gas emissions, nuclear power is playing an increasingly important role in the worldwide energy system. Whereas, groundwater pollution and radioactive wastewater may generate during the process of nuclear fuels extraction and utilization [1]. Uranium, which was discovered as early as 1896 to have radioactive decay properties and could be utilized in fuels and weapons, is regarded as a national strategic resource for sustainable development [2]. Therefore, great concern is arising on pollution hazard due to the high radioactivity, long half-life and carcinogenicity. It has gone mainstreams including ion exchange [3], chemical precipitation [4], membrane separation [5] and adsorption method [6], to capture radionuclides from aqueous water.

Researchers have spent much effort on the efficiency and mechanism on U(VI) adsorption of TNTs. And the result turns out that the material has good adsorption capacity for U(VI). However, there remains a problem that the single chemical mechanism and limited ion exchange sites of TNTs greatly restrict its adsorption capacity on U(VI). Furthermore, the wide availability (such as Pb, Cd, Cu, and Hg) makes its performance of selective adsorption on U(VI) not very good in actual polluted water [7].

In virtue of the stable TiO₆ octahedron structure of TNTs and plentiful Na⁺/H⁺ that can exchange with U(VI), together with dopamine that contains abundant groups which can coordinate with uranyl ions, we put forward the strategy to functionalize TNTs with dopamine. Both TNTs and PDA-TNTs were applied to capture U(VI) from aqueous solution so as to prove the improvement of PDA functionalization on the adsorption capacity of TNTs. Moreover, the anti-interference ability of the two adsorbents with other metal ions was tested to confirm its selectivity to U(VI). Adsorption kinetics and isotherms models, together with XRD, FT-IR and XPS spectra, were offered for accessing its adsorption behavior and illustrating the potential mechanism.
2. Experiments

2.1. Methods
As described previously [8], TNTs were formulated through a simple hydrothermal way. 2.0 g anatase nano-TiO₂ were dissolved in 50 mL of 10M NaOH solution. Then the mixture was transferred to a hydrothermal reactor lined with PTFE and heated at 130 °C for 12 h. Finally, the obtained precipitate, washed with distilled water for 4~5 times, was dried at 60 ℃ for 6 h.

0.8 g Tris were dissolved in 50ml distilled water, and mixed with 14.7 mL of 0.1M HCl. After dilution, The Tris-HCl buffer with pH of 8.5 was obtained. 0.2 g TNTs and 100 mL ethanol (1:1) were added in this solution and oscillated under ultrasonic conditions for 30 min. Then 0.05 g dopamine hydrochloride was added. The mixture was magnetically stirred at 25°C for 6 h. Finally, PDA-TNTs were obtained after being centrifuged and dried in a vacuum dryer.

2.2. Adsorption experiments
The adsorption capacity and potential mechanism on U (VI) of PDA-TNTs were estimated through batch adsorption experiments, while the dosage level of the adsorbent was 0.2 g/L. The initial U(VI) concentration ranged from 5 to 100 mg/L. The pH of solution, varing from 2.0 to 9.0, was adjusted through adding trace HCl or NaOH (0.1mol/L). Typically, 50 mL of 10 mg/L U (VI) solution was mixed with 10 mg of TNTs or PDA-TNTs in the beaker, oscillating in an oscillator at a certain frequency of 200 rpm. Reaction finished, the adsorbent was separated by a filter and the supernatant was taken for determination of U(VI) concentration by the arsenazo-III spectrophotometric at ~652 nm. Basically, the adsorption capacity and removal efficiency can be calculated as follows [9]:

$$q_e = \frac{(C_0 - C_e) \times V}{m} \quad (1)$$
$$E = \frac{(C_0 - C_e)}{C_0} \times 100\% \quad (2)$$

Where $C_0$ (mg/L) and $C_e$ (mg/L) are the initial and equilibrium concentrations of U(VI) in the solution. $V$ (ml) and $m$ (mg) refer to the volume of the solution and dosage of adsorbents, respectively. All measurements are conducted in duplicate, with the uncertainty no more than 5%.

3. Results and Discussion

3.1. Characterization of TNTs and PDA-TNTs

3.1.1. TEM analysis. As showed in Fig. 1a, both TNTs and PDA-TNTs exhibit distinct tubular structure, hollow and multilayered, suggesting that the process of self-polymerization for dopamine to form PDA layers on the surface of TNTs did not destroy the original microstructure. In Fig. 1b with higher magnification, it can be clearly seen that a uniform layer was coated around the surface of the nanotube, indicating that the PDA layers had successfully functionalized TNTs.

![Figure 1. TEM and XRD patterns of TNTs and PDA-TNTs.](image)
3.1.2. XRD analysis. As can be seen in Fig. 2, a series of characteristic diffraction peaks at \( 2\theta = 9.6^\circ, 24.2^\circ, 28.3^\circ, 48.3^\circ \) and \( 61.8^\circ \), which are attributed to sodium titanate, can be distinctly observed for both TNTs and PDA-TNTs. The strong diffraction peak at \( 2\theta = 9.6^\circ \), corresponding to the diffraction surface (200), representing the interlayer spacing of nanotubes, indicates that both TNTs and PDA-TNTs have a multilayer structure. The peak at \( 2\theta = 28.3^\circ \) is assigned to the characteristic crystal plane (600) of \( \text{Na}_2\text{Ti}_3\text{O}_7 \). Besides, peaks at \( 2\theta = 24.2^\circ \) and \( 48.3^\circ \) correspond to the characteristic crystal planes (110) and (020) respectively, which belong to the diffraction peaks of \( \text{H}_2\text{Ti}_3\text{O}_7 \), indicating that the synthesized TNTs and PDA-TNTs both have a TiO\(_6\) octahedral structure. Most importantly, there appears no new characteristic peak in the pattern of PDA-TNTs, indicating that the cross-linked composite layer formed by the oxidative polymerization of dopamine on the TNTs will not affect its tubular structure.

3.2. Effect of pH

The pH of solution can make a great difference to the adsorption efficiency of materials. On the one hand, U(VI) exists in different forms under different pH conditions, and it’s showed detailedly in Fig. 3a. Other, pH changes the surface charge as well as adsorption sites of the adsorbents [10]. As showed in Fig. 3b, the adsorption efficiencies on U (VI) of both TNTs and PDA-TNTs increased markedly with the pH increasing from 2.0 to 5.0, then they dropped. And it could be well explained by competitive adsorption and existing forms of U (VI). While the pH was relatively low (2~4), U(VI) primarily existed as uranyl ion (UO\(_2^{2+}\)), with which a large amount of H\(^+\) competed for adsorption sites located on the surface of the adsorbent, suppressing its adsorption on uranyl ions. With the pH rising, UO\(_2^{2+}\) was gradually hydrolyzed and the positive charge carried by itself turned into negative one, which would lead to electrostatic repulsion with the adsorbent, resulting in the decrease of the adsorption efficiency on U(VI).
3.3. Adsorption kinetics
With the aim to tell the adsorption behavior and mechanism on U(VI) for PDA-TNTs, it was proposed to use the pseudo-first-order (Fig. 4a), pseudo-second-order (Fig. 4b) and intraparticle diffusion models (Fig. 4c) to fit the experimental data. The results show the best relevance to experimental data with pseudo-second-order model ($R^2 = 0.999$). While the initial concentration of U(VI) is 10 mg/L, the theoretical adsorption capacity of PDA-TNTs fitted according to pseudo-second-order model is 45.662 mg/g, which is very close to the actual value (44.698 mg/g). And this indicates that the adsorption reaction is mainly driven by chemical adsorption mechanism. The initial stage of adsorption is the diffusion of U(VI) to the surface of adsorbents, with a faster adsorption efficiency and better adsorption capacity. Subsequently, as the amounts of U(VI) on the surface increase, the adsorption sites are gradually occupied, finally the reaction approaching equilibrium.

3.4. Adsorption isotherms
The Langmuir (Fig. 5a) and Freundlich isotherms (Fig. 5b) are used to analyze the relationship between adsorption capacity and corresponding equilibrium concentration. The fitting result suggests that the Langmuir model ($R^2 = 0.994$) accords closer with experimental data than the Freundlich model ($R^2 = 0.963$) does, indicating that the adsorption behavior is most likely to be monolayer. Besides, the maximum adsorption capacity of PDA-TNTs on U(VI) calculated by the Langmuir equation is 247.53 mg/g, much higher than that of TNTs (143.47 mg/g). Table 3 shows the adsorption capability under optimal pH of various nanomaterials on U(VI) and we can see that PDA-TNTs are suitable for U(VI) removal with competitive adsorption capability.

3.5. Potential adsorption mechanism
The possible adsorption mechanisms on U(VI) of PDA-TNTs are in compliance with the following two rules. On the one hand, U(VI) ions diffuse into the interlayers of the TiO$_6$ octahedral structure and exchange with Na$^+$/$\text{H}^+$ at the ion exchange sites of PDA-TNTs. On the other hand, there exists coordination interaction between uranyl ions and the nitrogenous groups (-NH, -NH$_2$ and -NH$_3^+$) or
catechol groups (-OH) located on the PDA layers. Generally, the uranyl ion coordinates with two nitrogen or oxygen atoms from two ligands on PDA-TNTs to form a stable coordination structure. The potential adsorption mechanisms on U(VI) of PDA-TNTs are showed in Fig. 6.

Figure 6. Potential adsorption mechanisms on U(VI) of PDA-TNTs

4. Conclusion
In summary, the nanomaterial (PDA-TNTs) is pH-dependent, but exhibits outstanding adsorption capacity (247.53 mg/g) and rapid adsorption kinetics up to equilibrium within 60 min. It mainly owes to the double adsorption mechanisms, where the TiO$_6$ octahedron structure of TNTs contains plentiful Na$^+$/H$^+$ that can exchange with U(VI), and dopamine can provide abundant nitrogenous groups (–NH, -NH$_2$ and -NH$_3^+$) and catechol functional groups (-OH) that can coordinate with uranyl ions. Obviously, PDA-TNTs can be taken as an effective adsorbent to remove U(VI) from aqueous solution, but the point is that the double adsorption mechanisms with both ion exchange and coordination interaction can be a strategy to provide new insights into the material synthesis field.

Acknowledgments
This work was financially supported by National Key Project of Research and Development Plan (Grant No.2016YFC1402504). The authors were particularly grateful to financial support for this study.

References
[1] Le Guernic A, Sanchez W, Bado-Nilles A, Palluel O, Turies C, Chadili E, Cavalie I, Delahaut L, Adam-Guillermin C, Porcher J-M, Geffard A, Betoulle S, Gaignaire B (2016) In situ effects of metal contamination from former uranium mining sites on the health of the three-spined stickleback (Gasterosteus aculeatus, L.). Ecotoxicology 25 (6):1234-1259.
[2] Sekiya M, Yamasaki M (2015) Antoine Henri Becquerel (1852-1908): a scientist who endeavored to discover natural radioactivity. Radiological physics and technology 8 (1):1-3.
[3] Wen Z, Huang K, Niu Y, Yao Y, Wang S, Cao Z, Zhong H (2020) Kinetic study of ultrasonic-assisted uranium adsorption by anion exchange resin. Colloids and Surfaces a-Physicochemical and Engineering Aspects 585.
[4] Matlock MM, Howerton BS, Atwood DA (2002) Chemical precipitation of heavy metals from acid mine drainage. Water Research 36 (19):4757-4764.
[5] Bessbousse H, Rhlalou T, Verchere JF, Lebrun L (2008) Removal of heavy metal ions from aqueous solutions by filtration with a novel complexing membrane containing poly(ethyleneimine) in a poly(vinyl alcohol) matrix. Journal of Membrane Science 307 (2):249-259.
[6] Li YH, Di ZC, Ding J, Wu DH, Luan ZK, Zhu YQ (2005) Adsorption thermodynamic, kinetic
and desorption studies of Pb\textsuperscript{2+} on carbon nanotubes. Water Research 39 (4):605-609.

[7] Li N, Zhang L, Chen Y, Tian Y, Wang H (2011) Adsorption behavior of Cu(II) onto titanate nanofibers prepared by alkali treatment. Journal of Hazardous Materials 189 (1-2):265-272.

[8] Li X-F, Zhao Y, Jiao Q-Z, Li H-S, Wu H-Y, Liu H-B, Cui W-J (2011) Preparation of One-Dimensional Titanate Nanomaterials Using Different Titania Sources. Acta Physico-Chimica Sinica 27 (8):1996-2000.

[9] Yang W, Bai Z, Shi W, et al. MOF-76: from a luminescent probe to highly efficient U(VI) sorption material[J]. Chen Commun, 2013,49(88):10415-10417.

[10] Zeng J, Zhang H, Sui Y, Hu N, Ding D, Wang F, Xue J, Wang Y (2017) New Amidoxime-Based Material TMP-g-AO for Uranium Adsorption under Seawater Conditions. Industrial & Engineering Chemistry Research 56 (17):5021-5032.