The preparation of dodecyl trimethyl ammonium bromide modified titanium dioxide for the removal of uranium

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Research Article

Keywords: Titanium dioxide, Dodecyl trimethyl ammonium bromide, Adsorption, U(VI), XPS

Posted Date: May 12th, 2022

DOI: https://doi.org/10.21203/rs.3.rs-1568684/v1

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Abstract

Radioactive contamination, especially the pollution of uranium, is threatening the ecological environment. How to efficiently and quickly remove the uranium from the environment is a problem to be solved. In this study, the dodecyl trimethyl ammonium bromide embellished titanium dioxide composite (DTAB/TiO$_2$) was synthesized as an adsorbent to adsorb uranium from water. The DTAB/TiO$_2$ composite was composed of nanoparticles and presented a spherical morphology of rough surface. The removal of U(VI) on DTAB/TiO$_2$ was a monolayer adsorption process and the removal process was dependent on solution pH. The capture of U(VI) enhanced with the increase of temperature, indicating an endothermic process. According to the Langmuir model, the removal capacity of DTAB/TiO$_2$ for U(VI) reached 108.4 mg/g. The surface oxygen-containing functional groups, especially hydroxyl groups, played a crucial role in the capture of U(VI). This work can provide useful information for the cleanup of uranium and expand the application of surfactants.

1. Introduction

Uranium(U) is one of the most widespread radioactive wastes in the ecological environment (Boghi et al. 2018, Coyte et al. 2018). Uranium and its decay products can be found in the environment by a series of anthropogenic activities, including nuclear power industry and mining (Wang et al. 2018). Because of high chemical toxicity, long half-life, and high level of mobility in the environment, uranium has been considered to be one of the main environmental pollutants, which poses a severe, long-term ecological and public health threat (Lan et al. 2019, Hettiarachchi et al. 2019). Unfortunately, it is not easy for uranium to degrade into the lower toxic substances by the reason of radioactivity and bioaccumulation in the environment (Sadergaski et al. 2019). In order to protect ecosystem stability and public health, it is required to eliminate uranium before being discharged into the environment, as well as its recovery as an energy resource. In the past decades, a number of methods have been developed for uranium removal from aqueous solutions, such as chemical precipitation, membrane dialysis, bio-concentration, ionic exchange, adsorption, and extraction (Alam et al. 2018, Chi et al. 2019, Li et al. 2017). Among these methods, adsorption is an essential approach to remove uranium from wastewater due to its low cost, high efficiency, and environment friendly and adsorbent is a key factor to determine the final effect of removal process (Ma et al. 2019a, Liu et al. 2019a). Various kinds of adsorbents, such as kaolinite, diatomite, goethite, sepiolite, zeolite, mesoporous silica, montmorillonite, hydrogel, and apatite, have been widely produced and applied for the removal of uranium (Sadergaski and Hixon 2018, Sadergaski et al. 2018, Wang et al. 2019a). However, most of existing adsorbents can not meet current demand.

For the past few years, titanium dioxide (TiO$_2$) obtains wide attention due to its activity, photostability, non-toxicity, and commercial availability (Yusoff et al. 2018). Because of excellent physicochemical property, titanium dioxide has been widely applied in catalyst, cosmetic, pharmaceuticals industry, etc (Philippe et al. 2018, Tan et al. 2018). Besides, titanium dioxide is also the most important white pigment that used in the coating industry. More importantly, titanium dioxide can be used to study the adsorption
of pollutants on positively and negatively charged surfaces over a broad range of pH values by reason of high chemical stability and negligible solubility over a wide pH range, which would not result in secondary pollution (Liu et al. 2019b, Ma et al. 2019b). For instance, Wang et al. (Wang et al. 2019b) found that the adsorption of U(VI) on titanium dioxide was significantly dependent on pH and ionic strength. Lots of recent publications have focused on the application of surfactants in the environmental pollution control. Among these surfactants, dodecyl trimethyl ammonium bromide (DTAB) is the most widely studied in cosmetic, paint, and paper production due to its low cost and biological safety (Lopez-Diaz et al. 2006). Besides, dodecyl trimethyl ammonium bromide can be also used in wastewater treatment and purification of drinking water (Niranjan and Upadhyay 2014). Through the adjustment of pH, temperature, ionic strength, and hydrophilic/hydrophobic balance, various new surfactant based materials can be created (Kotsmar et al. 2009).

Herein, the dodecyl trimethyl ammonium bromide embellished titanium dioxide composite (DTAB/TiO$_2$) was synthesized to remove uranium from water. The characteristics of DTAB/TiO$_2$ were tested by X-ray diffraction (XRD), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FT-IR), scanning electron microscope (SEM), X-ray photoelectron spectroscopy (XPS), and Brunauer-Emmett-Teller (BET). The environmental conditions including pH, temperature, and contact time were researched in detail. Besides, the removal mechanism of U(VI) on the DTAB/TiO$_2$ composite was investigated. This work may provide useful information for the cleanup of uranium and expand the application of surfactants.

2. Experimental Section

2.1. Synthetic procedure for DTAB/TiO$_2$

Typically, 5.0 g urea, 1.0 g Ti(SO$_4$)$_2$ and 0.2 g DTAB were moved to distilled water and stirred for 30 min. The mixture was kept at 473 K for 12 h (autoclave). Afterwards, the products were washed and dried at 343 K for 24 h. Finally, the products were calcined at 773 K under a continuous N$_2$ flow for 3 h and then used for the adsorption experiment.

2.2. Instruments

The crystal structure of DTAB/TiO$_2$ was tested on the Bruker D8 Advance with 2θ range from 5 to 80 degree. The XPS spectra before and after adsorption were collected on an X-ray photoelectron spectrometer (Thermo ESCALAB 250) with Al Kα X-ray source. The specific surface area was measured by using Tristar-3020 volumetric adsorption analyzers at 77 K (Quantachrome, United States). The morphology of the composite was detected by the field emission scanning electron microscope (FEI-JSM 6320F). The TEM of DTAB/TiO$_2$ was performed with the JEM-2100F microscope operated at 200 kV. The FT-IR of DTAB/TiO$_2$ was detected by the Tensor 27 equipment (Bruker).

2.3. Batch experiments
In this study, the U(VI) stock solution was prepared by dissolving UO$_2$(NO$_3$)$_2$·6H$_2$O into Milli-Q water. In a typical adsorption process, a certain amount of DTAB/TiO$_2$ suspension, U(VI) stock solution, and NaCl solution were added into a tube. The concentration of U(VI) and solid content were kept at 60 mg/L and 0.5 g/L. The pH in the tube was kept at 5.0±0.1 by adding 0.01-0.1 M HCl or NaOH solutions. After shaking for 10 hours (150 rpm), the tube was separated by centrifugation. The concentration of U(VI) in supernatant was measured by inductively coupled plasma-optical emission spectrometry (ICP-OES). The removal capacity of DTAB/TiO$_2$ for U(VI) can be expressed as:

$$q_e = \frac{(C_0 - C_e)V}{m}$$  \hspace{1cm} (1)

where $C_0$ and $C_e$ (mg/L) are the original and equilibrium concentrations of U(VI), $q_e$ (mg/g) is the removal capacity, $V$ (L) represents the solution volume, $m$ (g) denotes the mass of DTAB/TiO$_2$.

3. Results And Discussion

3.1. Characterization of DTAB/TiO$_2$

The surface structure of DTAB/TiO$_2$ was given in Figure 1. As illustrated in Figure 1a, the composite revealed an spherical morphology with rough surface. The high-magnification SEM image proved that the composite was composed of tens of thousands of nanoparticles (Figure 1b). The spherical structure and nanoparticles of DTAB/TiO$_2$ can provide larger specific surface area and more functional groups to remove U(VI). As can be seen from Figure 1c, the TEM image also indicated the circular structure of DTAB/TiO$_2$, which was consistent with the result of the SEM image. It is clear that the radius of DTAB/TiO$_2$ was about 0.45 μm. Figure 1d showed the high-magnification TEM image of DTAB/TiO$_2$, which contributed to observe the micro nanostructure of the composite. As illustrated in Figure 1e and 1f, the elemental mapping images of DTAB/TiO$_2$ confirmed the successful preparation of the composite. The crystal structure of DTAB/TiO$_2$ was investigated by the XRD pattern. As can be observed from Figure 2a, the diffraction peaks at (101), (004), (200), (105), (211), (204), (116), (220), and (215) can be attributed to TiO$_2$ (JCPDS 73-1764). From Figure 2b, one can see that the specific surface area of DTAB/TiO$_2$ reached 144.0 m$^2$/g. Because of the surface modification of dodecyl trimethyl ammonium bromide, the composite can possess better morphology and larger specific surface area, which was beneficial to the capture of U(VI). The FT-IR of DTAB/TiO$_2$ was given in Figure 2c. The peaks at 3197 cm$^{-1}$ and 1629 cm$^{-1}$ can be attributed to the hydroxyl groups (Kang et al. 2015). The absorption peak at 1384 cm$^{-1}$ was ascribed to the amide groups. The peak at 1143 cm$^{-1}$ was assigned to the vibration of Ti-O (Khan and Fulekar 2016). As shown in Figure 2d, the XPS spectrum revealed the peaks of Ti 2p and O 1s on the surface of DTAB/TiO$_2$. 

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3.2. Influence of pH and Coexisting Ions

The solution pH can significantly affect the speciation of U(VI) and the surface binding-sites of DTAB/TiO₂, the adsorption of U(VI) on the composite as a function of pH was investigated. As shown in Figure 3a, the adsorption of U(VI) on DTAB/TiO₂ enhanced obviously from pH 2.0 to 6.0 and then reached the maximum at pH 6.0, whereas the decreased removal of U(VI) was observed at pH > 6.0. This phenomenon can be explained by the existent form of U(VI) at different solution pH values. The distribution of uranium in water was primarily as positively charged species (i.e., UO₂⁡²⁺, (UO₂)₃(OH)₅⁺) at pH < 6.0 and the increased removal of U(VI) on DTAB/TiO₂ from pH 2.0 to 6.0 can be assigned to strong surface complexation (Zhang et al. 2015a). Because of the occurrence of dissolved inorganic carbon at high pH values, the predominance of carbonato-uranyl complexes (UO₂(CO₃)₂⁻ and UO₂(CO₃)₃⁴⁻) appeared in alkaline conditions, which caused the decreased removal of U(VI) at pH > 6.0 (Zhang et al. 2015b). Therefore, the dissolved carbonate played an important role in uranium subsurface transport by reason of its great affinity to form aqueous complexes with uranium and its ubiquity in groundwater. As can be seen from Figure 3b, the influence of coexisting ions on U(VI) adsorption was performed in 0.01 M of C₂H₅NaO₂, MnCl₂, Na₂CO₃, MgCl₂, NaClO₄, NaCl, NaNO₃, KCl, ZnCl₂, and Na₂SO₄ solutions, respectively. The results showed that these coexisting ions hardly affect the adsorption of U(VI), indicating a huge advantage of the composite.

3.3. Influence of Contact Time

The impact of adsorption time on U(VI) removal was shown in Figure 3c. It is clear that the adsorption of U(VI) was composed of three stages. The removal of U(VI) on DTAB/TiO₂ increased sharply at the first contact time of 0-120 min, and then increased slowly at 120-240 min. Finally, the removal process reached equilibrium after 240 min. The fast adsorption rate at the first contact time can be attributed to the larger active sites on the surface of DTAB/TiO₂ and the higher concentration gradient of U(VI) in the solution. With the decrease of active sites, the amount of U(VI) adsorbed increased slowly and gradually reached adsorption equilibrium. The results indicated that the contact time of 240 min was sufficient to achieve adsorption equilibrium.

3.4. Adsorption Isotherms

The adsorption temperature is an important factor that can affect the removal efficiency. The adsorption of U(VI) was performed at 298 K, 313 K, and 328 K, respectively. From Figure 3d, one can see that the U(VI) removal increased with the increase of temperature, indicating an endothermic process. In order to study the removal mechanism, the adsorption process was fitted by the Freundlich model and Langmuir model. As shown in Table 1, the uptake of U(VI) on DTAB/TiO₂ can be better simulated by the Langmuir model rather than the Freundlich model, implying a monolayer removal process. According to the Langmuir model, the adsorption capacity of DTAB/TiO₂ for U(VI) reached 108.4 mg/g.

The Freundlich model can be expressed as (Yu et al. 2013):
The Langmuir model is described as (Yu et al. 2013):

\[ q_e = K_f C_e^b \]

where \( q_e \) (mg/g) is the removal capacity; \( C_e \) (mg/L) is the equilibrium concentration of U(VI) in solution; \( b \) (L/mg) is the Langmuir constant; \( Q_0 \) (mg/g) denotes the theoretical saturated adsorption capacity; \( K_f \) (mg/g) and \( n \) are Freundlich adsorption coefficients.

Table 1. Langmuir and Freundlich parameters for U(VI) adsorption.

<table>
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<th>T (K)</th>
<th>Langmuir model</th>
<th>Freundlich model</th>
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<td>( q_{max} ) (mg/g)</td>
<td>( R^2 )</td>
</tr>
<tr>
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<td>108.4</td>
<td>0.995</td>
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<tr>
<td>313</td>
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<td>0.984</td>
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<tr>
<td>328</td>
<td>119.6</td>
<td>0.980</td>
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3.5. Adsorption Mechanism

To study the elimination mechanism of U(VI), the DTAB/TiO\(_2\) composites before and after adsorption were investigated by XPS spectra. Figure 4a showed the wide scan XPS spectra of DTAB/TiO\(_2\). The peaks of Ti 2p and O 1s can be seen on the surface of DTAB/TiO\(_2\). Furthermore, the obvious peak of U 4f also can be observed after adsorption. As can be seen from Figure 4b, the high U 4f deconvolution of DTAB/TiO\(_2\) after adsorption can be divided into two peaks at 380.33 eV (U 4f\(_{7/2}\)) and 391.54 eV (U 4f\(_{5/2}\)), respectively, confirming the capture of uranium on the surface of the composite (Haldorai et al. 2014). From Figure 4c, one can see that the high-resolution of O 1s was decomposed into two peaks at 530.79 eV (O-H) and 530.09 eV (Ti-O), respectively. Figure 4d showed that the intensity of the peak for O 1s changed significantly after U(VI) adsorption. Compared to the composite before adsorption, the relative area ratio of O-H after adsorption decreased from 34.35% to 32.12%, implying that the hydroxyl groups participated in the removal process (Table 2). In the meantime, the relative area ratio of Ti-O increased from 65.65% to 67.88% after adsorption. The XPS results showed that the surface oxygen-containing functional groups, particularly hydroxyl groups, played a significant role in the capture of U(VI).

Table 2. The high deconvolution of O 1s spectra of DTAB/TiO\(_2\) before and after adsorption.
### 4. Conclusion

The dodecyl trimethyl ammonium bromide modified titanium dioxide composite was prepared for the adsorption of uranium. The DTAB/TiO$_2$ composite was composed of tens of thousands of nanoparticles and revealed a spherical morphology of rough surface. The capture of U(VI) on DTAB/TiO$_2$ enhanced with the increase of temperature. The removal of U(VI) was a monolayer adsorption process and the removal process was affected by solution pH. Furthermore, the adsorption of U(VI) was better simulated by the Langmuir model and the adsorption capacity of DTAB/TiO$_2$ for U(VI) reached 108.4 mg/g. The XPS results proved that the surface oxygen-containing functional groups, particularly hydroxyl groups, played a significant role in the elimination of U(VI). This work can offer new ideas for the purification of radioactive waste.

### Declarations

**Ethical Approval, Consent to Participate, Consent to Publish**

This section is “not applicable” for this study as the study does not involve any human participants nor their data or biological material.

**Authors Contributions**

Jian Wang: Writing - original draft, Project administration, Funding acquisition.

Ran Ma: Supervision.

Zheng Jiang: Validation, Investigation.

**Funding**

This work was supported by the National Natural Science Foundation of China (22106046), the Fundamental Research Funds for the Central Universities (JB2022166), and the National Key Research and Development Program of China (2017YFA0207002).

**Competing Interests**
The authors declare no competing financial interest.

Availability of data and materials

The datasets used and/or analyzed under the current study are available from the corresponding author upon the reasonable request.

References


Figures
Figure 1

The SEM image (a) and high-magnification SEM image (b) of DTAB/TiO$_2$; TEM image (c) and high-magnification TEM image (d) of DTAB/TiO$_2$; elemental mapping images (e and f) of DTAB/TiO$_2$. 
Figure 2

The XRD pattern (a), N$_2$ adsorption-desorption isotherms (b), FT-IR spectrum (c), and XPS spectrum (d) of DTAB/TiO$_2$.

Figure 3

Influence of pH on U(VI) removal (a) (U(VI) initial concentration = 60 mg/L, m/V = 0.5 g/L, T = 298 K, adsorption time = 10 h, I = 0.01 M); influence of coexisting ions on U(VI) removal (b) (U(VI) initial concentration = 60 mg/L, m/V = 0.5 g/L, T = 298 K, pH = 5.0 ± 0.1, I = 0.01 M); influence of time on U(VI) removal (c) (U(VI) initial concentration = 60 mg/L, m/V = 0.5 g/L, T = 298 K, pH = 5.0 ± 0.1, I = 0.01 M); adsorption isotherms for U(VI) (d) (the solid lines represent the Langmuir model, the dash lines represent the Freundlich model).

Figure 4

XPS spectra: the wide scan of DTAB/TiO$_2$ before and after adsorption (a); the peaks for U 4f (b); the high O 1s deconvolution of DTAB/TiO$_2$ before (c) and after (d) adsorption.