Plasma-induced grafting of acrylic acid on bentonite for the removal of U(VI) from aqueous solution

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Abstract
Fabrication of reusable adsorbents with satisfactory adsorption capacity and using environment-friendly preparation processes is required for the environment-related applications. In this study, acrylic acid (AA) was grafted onto bentonite (BT) to generate an AA-graft-BT (AA-g-BT) composite using a plasma-induced grafting technique considered to be an environment-friendly method. The as-prepared composite was characterized by scanning electron microscopy, x-ray powder diffraction, thermal gravity analysis, Fourier transform infrared spectroscopy and Barrett–Emmett–Teller analysis, demonstrating the successful grafting of AA onto BT. In addition, the removal of uranium(VI) (U(VI)) from contaminated aqueous solutions was examined using the as-prepared composite. The influencing factors, including contact time, pH value, ionic strength, temperature, and initial concentration, for the removal of U(VI) were investigated by batch experiments. The experimental process fitted best with the pseudo-second-order kinetic and the Langmuir models. Moreover, thermodynamic investigation revealed a spontaneous and endothermic process. Compared with previous adsorbents, AA-g-BT has potential practical applications in treating U(VI)-contaminated solutions.

Keywords: plasma-induced, grafting, bentonite, U(VI)

(Some figures may appear in colour only in the online journal)

1. Introduction

With the development of nuclear technology, nuclear power has attracted increasing attention over the past few decades. Meanwhile, the generated radioactive pollutants are considered as one of the most important environmental problems due to their long half-life decay time, high toxicity and oncogenicity [1]. Uranium(VI) (U(VI)), as a substance of fission in nuclear reactors, is a typical example [2]. Different techniques have been used to remove U(VI) from aqueous solutions, for example, membrane separation, ion exchange, precipitation, electrodialysis, and adsorption [3]. Among them, adsorption is regarded as an efficient way of concentrating U(VI) from contaminated solutions because of its simple operation, low cost and wide application [4–6].

Various adsorbents have been used in the practice of water purification for U(VI) entrapment, such as hydroxyapatite [7], graphene oxide [4], silica [8], carbonaceous nanofibers [9], resin [10], etc. Among them, bentonite (BT) seems to be one of the most prospective adsorbents taking into account its ability for U(VI) removal from U(VI)-contaminated solutions, due to its considerable ion-exchange
properties, good retardation properties, expansive performance and low cost [11]. Up to now, several types of BT, such as GMZ BT [12], FoCa BT [13], have been used to dispose of high-level radioactive waste repositories. However, the adsorption capacity of natural BT is still far beyond satisfactory for treating U(VI) from U(VI)-contaminated solutions due to insufficient active sites on the surface of natural BT. The surface modification could further strengthen the chemical functionality of BT. Thereby, surface modification of BT is considered to be an effective method of improving its adsorption performance.

Carboxyl groups are known to interact with metal ions with the formation of stable chelation complexes between carboxyl groups and metal ions [14]. Motivated by the powerful chelation property, acrylic acid (AA) with carboxyl groups is selected as the modifying agent for the modification of BT. Therefore, an AA-graft-BT (AA-g-BT) composite may exhibit the remarkable capability of disposing of U(VI) from polluted water. However, the fabrication of AA-g-BT requires a complicated chemical process, which would lead to secondary contamination in the environment [15]. By contrast, plasma grafting technology, a technology with wide application prospects for introducing versatile functional groups to substance surfaces without any secondary pollution, is considered as an environment-friendly method [16–18]. Virtually all solid materials can be modified via this plasma treatment, while minimal or no surface preparation is required. Moreover, since no solvent is involved in this modification process, almost no waste is produced. In view of these advantages, plasma treatment can be used to modify specific functional groups on adsorbent surfaces, which can greatly enhance the chemical functionalities and adsorption properties.

In this study, AA was grafted onto BT to prepare AA-g-BT composite by a plasma-induced grafting technique. The successful fabrication of AA-g-BT was confirmed by scanning electron microscopy (SEM), x-ray powder diffraction (XRD), thermal gravity analysis (TGA), Fourier transform infrared spectroscopy (FT-IR) and Barrett–Emmett–Teller (BET) analysis. The adsorption efficiency and capacity of AA-g-BT was examined by removing U(VI) from U(VI)-contaminated solutions in batch experiments. The kinetics and thermodynamics for the adsorption process were also investigated, as well as the regeneration and recycling of the AA-g-BT composite, which indicated a promising adsorbent of AA-g-BT composite for U(VI) removal.

2. Experimental

2.1. Materials

BT was obtained from Huangshan District (Anhui Province, China), which was purified by immersing and shaking in 5% HCl solution for 20 h at 20°C to dispose of the soluble oxide, followed by rinsing with ultrapure water to remove the impurity. Then the BT was sieved using a 53 μm sieve (the specific surface area of BT is 20.3 m² g⁻¹ based on the

Figure 1. Schematic diagram of the plasma-induced grafting system.

N₂-BET adsorption method). The water residue was removed by drying in an oven at 70°C for 20 h. All the other chemical reagents exploited for this experiment were achieved in analytical pure and used without further purification.

2.2. The experiment setup

A schematic diagram of the plasma-induced grafting system used in this experiment is shown in figure 1. The plasma-induced grafting reactor consisted of a three-necked flask (105 mm × 145 mm), winding coils and plasma power (13.56 MHz). The vacuum pump kept a relative stable vacuum for the three-necked flask, and the Ar cylinders provided the Ar for the three-necked flask to make the reaction carried out under the Ar condition.

2.3. Preparation of the AA-g-BT composite

The fabrication of AA-g-BT was carried out using the plasma-induced grafting technique (radio frequency plasma). Specifically, BT (1.5 g) was placed in a three-necked flask [19]. Then the flask was evacuated and injected with Ar six times to modify the sample surface properties and maintain a vacuum with Ar vacuum degree (2.6 Pa). To our knowledge, the Ar plasma treatment has been used to active the surface of the BT, which is beneficial for grafting functional groups [16–18]. Then plasma was introduced for 20 min with power (100 W) and frequency (13.56 MHz). To avoid cross-linking or degradation reactions of the sample surfaces, the power (100 W) of plasma treatment was broady applied. After plasma treatment, AA (0.1 g) was added to the ultrapure water (50 ml), then the solution was quickly injected into the three-necked flask under Ar atmosphere. Finally, the solution was heated to 80°C with stirring (1000 r min⁻¹) for 12 h. After reaction, the crude composite was washed with ultrapure water and dried at 75°C for 20 h to obtain the purified AA-g-BT composite.

2.4. Characterization

Surface images of the bentonite and AA-g-bentonite composite were obtained using SEM (S-2500, Hitachi, Japan). To reveal the surface functional groups and the structures, the
bentonite and AA-g-bentonite composite were characterized using FT-IR (Nicolet 6700, Thermo Scientific, USA), TGA (Netzsch, Germany) and XRD (Rigaku, Japan). N₂ adsorption measurements were determined using an ASAP 2020 accelerated surface area instrument (Micromeritics) at 77 K using BET calculations for the specific surface area. The zeta potentials were recorded using a Nanosizer ZS instrument (Malvern Instrument Co., UK). The procedure utilized for the Nanosizer ZS instrument can be found in [20, 21].

2.5. Adsorption experiments

The adsorption behaviors of BT and the AA-g-BT composite were tested using static adsorption tests in 10 ml polythene centrifugal tubes. The U(VI) solutions (120 mg l⁻¹) were prepared using UO₂(NO₃)₂ - 6 H₂O dissolved in distilled water and the adsorbents (0.9 g l⁻¹) were also prepared. Different volumes of adsorbent and U(VI) were mixed (NaClO₄ was also added if necessary for ionic strength investigation). The pH values were controlled by adjusting with trace amounts of 0.05 M HCl or NaOH solution to reach the desired pH values. For the adsorption kinetics, the concentration of U(VI) and adsorbents was 20 mg l⁻¹ and 0.4 g l⁻¹; the pH of the solution was 5.0 ± 0.1; the temperature was 298 K; and the concentration of NaClO₄ was 0.01 mol l⁻¹. For adsorption isotherms, the concentration of adsorbents was 0.4 g l⁻¹; the temperature was 298 K; and the concentration of NaClO₄ was 0.01 mol l⁻¹. The others are shown in figures 4, 5, 6, 8 and 9. The adsorbents and solutions were isolated via centrifugation (Beckman Coulter 64R) at 8000 rpm for 30 min at room temperature. Finally, the concentration of U(VI) was determined using an Arsenazo III spectrophotometer (UV–vis spectrometry method).

The concentration of U(VI) adsorbed on BT or the AA-g-BT composite was obtained by the difference between initial concentration (C₀, mg l⁻¹) and equilibrium concentration (Cₑ, mg l⁻¹). Adsorption rate (%), distribution coefficient (K_d) and the adsorption capacity (Cₑ, mg g⁻¹) were obtained as follows [22]:

\[
\text{Adsorption(\%)} = \frac{C_0 - C_e}{C_0} \times 100\% \quad (1)
\]

\[
K_d = \frac{C_0 - C_e}{C_e} \times \frac{V}{m} \quad (2)
\]

\[
C_e = \frac{C_0 - C_e}{m} \times V \quad (3)
\]

where \( V \) (l) represents the turbid liquid’s bulk, and \( m \) (g) represents the mass of BT or the AA-g-BT composite. Laboratory data were the mean of duplicate measurements with error less than 5%.

3. Results and discussion

3.1. Characterization of BT or the AA-g-BT composite

SEM images show the external characteristics and sizes of BT and the AA-g-BT composite, as shown in figure 2. The original BT presented a rough layer structure and substantial creases with an average size of several micrometers (figure 2(A)). A similar surface was observed for AA-g-BT, but tighter (figure 2(B)). Moreover, banding objects appeared in figure 2(B).

The FT-IR spectra of BT and the AA-g-BT composite are depicted in figure 3(A). For BT, the peak at 3360–3615 cm⁻¹ belongs to the O–H deformational vibrations [23]. The peak at 1038 cm⁻¹ belongs to Si–O stretching [24]. Al–O–Si and Si–O–Si bending vibrations can be found at 523 cm⁻¹ and 465 cm⁻¹, while the peak at 791 cm⁻¹ is assigned to the quartz admixture in the sample [25]. For the AA-g-BT composite, new peaks at 1730 cm⁻¹ and 2880 cm⁻¹ were also observed, belonging to the –COOH groups and C–H stretching vibrations, respectively, which further confirmed that the activated BT by Ar plasma can initiate AA polymerization and the successfully grafted AA on BT [26, 27].

The XRD patterns of BT and the AA-g-BT composite are shown in figure 3(B). The characteristic peaks at \( 2\theta \) values of 6.02°, 19.92°, 26.71°, 35.21° and 62.02° indicate 2:1 expanding clays of BT [11, 25]. The others are typical quartz and Cal-Fe(Ca)CO₃ peaks [25], as shown in figure 2(B). The appearance of (0 0 1) and (0 6 0) lattice planes imply a dioctahedral morphology of the adsorbent [25].

A TGA of the AA-g-BT composite is shown in figure 2(C). At 80 °C–114 °C, the percentage weight loss was 11.82%, attributed to the loss of moisture [28]. With increasing temperature from 114 °C to 180 °C, the moisture from the evaporation, linked to the exchangeable cations in the structure of bentonite and oxygen-containing substances, started loss [29, 30]. After 180 °C, the main loss is the elimination of the carboxyl functional groups from AA and slight dehydroxylation from the silicate layers [29, 30]. It can be seen that the approximate content of AA of AA-g-BT is about 5.2%.

The zeta potential of AA-g-BT and BT were measured at a pH range from 2.0 to 9.0, as shown in figure 3(D). The zeta potential of AA-g-BT is less than that of BT due to the negatively charged carboxyl groups being grafted on the surface of the AA-g-BT composite [31]. A further increase in pH value would increase the ionized carboxyl groups [32].
Moreover, the zero potential value of AA-g-BT is 6.73. This indicates a positive surface of the AA-g-BT composite at $\text{pH} < 6.73$. Similarly, at $\text{pH} > 6.73$, the surface becomes negative.

In a word, the grafting of AA leads to the surface of BT having suitable chemical functionality for molecule interaction at the interface by the radio frequency plasma grafting technique. In addition, the polymerization mechanism of AA and BT can be described as follows. First, the active groups (such as $-\text{OH}$) on the surface of BT can be activated; then, the AA-g-BT composite is formed by reactive groups of BT and $\text{C}=\text{C}$ of AA. The phenomenon is similar to a previous study [5]. Moreover, the specific surface area of the AA-g-BT composite was 15.7 m$^2$ g$^{-1}$, which is shorter than the BT due to AA being grafted on the surface of BT. Although the the specific surface area slightly decreases, the active sites (such as $-\text{COOH}$) increase, which is beneficial for adsorbing U(VI).

### 3.2. Adsorption kinetics

The influence of the contact time for U(VI) adsorbed onto BT and the AA-g-BT composite was investigated (figure 4(A)). For both adsorbents, the adsorption efficiencies were observed, and reached the maximum adsorption capacities within 20 min. In order to further understand the adsorption process, pseudo-second-order [22] and intra-particle diffusion kinetics [33] were used to describe the U(VI) adsorption, as shown in figure 4. The simulation data of kinetic models are collected in table 1. The hierarchical order of the correlation co-efficiency is: 0.9998 (pseudo-second order) $>$ 0.9231 (intra-particle model) for the AA-g-BT composite, indicating...
affinity of AA-g-BT is higher than that of AA-g-BT. A higher percentage of U(VI) can be removed with increasing amount of adsorbent due to the increased active sites. By comparing the adsorption percentage, the higher adsorption capacity of the AA-g-BT composite was observed, especially within the adsorbent amount from 0 to 1.5 g l⁻¹, which can be ascribed to the active carboxyl functional groups from AA by plasma treatment [34]. Different from the increasing adsorption percentage, a decreased distribution coefficient was obtained with increasing adsorbent amount, which is similar to that previously reported [35].

### 3.4. Effect of pH and ionic strength

The pH value can also influence the adsorption efficiency and capacity by changing the surface properties of the AA-g-BT composite and the speciation of U(VI). Figure 6(A) illustrates the adsorption efficiency of the AA-g-BT composite at various pH values. The maximum adsorption efficiency can be observed at about pH = 6.55. Meanwhile, the existing species distribution for U(VI) at various pH values were calculated according to the parameters for different reactions (table 2) [36]. The result is shown in figure 6(B). The main existing forms of U(VI) are UO₂²⁺, (UO₂)₂(OH)²⁻, UO₂(OH)⁺, (UO₂)₃(OH)⁵⁺, (UO₂)₄(OH)⁷⁺ at pH < 6.5, which exhibited low adsorption efficiency with positive AA-g-BT composite, as expected, due to the surface charge of the AA-g-BT blocking U(VI) from reaching the surface of the adsorbent. Within pH = 6.5–7, while the main existing species of U(VI) remained positively charged ([(UO₂)₃(OH)₅⁺, and (UO₂)₄(OH)⁷⁺]), the surface of AA-g-BT was gradually became negatively charged, which can enhance the adsorption capacity. This change resulted in the maximum adsorption efficiency. After pH > 7, the positively charged [(UO₂)₃(OH)₅⁺, and (UO₂)₄(OH)⁷⁺] also exist but the adsorption capacity decrease due to the concentration of [(UO₂)₃(OH)₅⁺ and (UO₂)₄(OH)⁷⁺] decreasing and the concentration of UO₂(CO₃)²⁻ and UO₂(CO₃)⁵⁻ increasing. Furthermore, protonation–deprotonation reactions of carboxyl functional groups are an essential factor to promoting U(VI) adsorption by improving or decreasing the charge of the surface of the AA-g-BT composite [15]. The protonation for AA-g-BT is presented (BT – COOH + H⁺ → BT – COO⁻ + H⁺) and the deprotonation is presented (BT – COOH ↔ BT – COO⁻ + H⁺).

### 3.3. Effect of the solid/liquid ratio

Figure 5 depicts the dependence of U(VI) adsorption onto the AA-g-BT composite or BT as a function of adsorbent amount from 0.2 to 3.0 g l⁻¹ without changing other variables. To investigate the interaction of U(VI) with the adsorbent and liquid, the distribution coefficient, Kₐ, is also presented [22]. Kₐ is a vital parameter of the solid/liquid ratio, which can reflect the affinity of the adsorbents. It can be observed from figure 5 that Kₐ is almost dependent on the adsorbents content at 0 to 3 g l⁻¹ and decreases with increasing solid/liquid ratio because of the higher energy sites of the AA-g-BT composite covered with a plenty of lower energy sites at a high adsorbent content. Moreover, there is found affinity of the adsorbents before the content is less 0.5 g l⁻¹ (lg(Kₐ) > 3.5 ml g⁻¹). The Kₐ of AA-g-BT is higher than that of BT, implying the

<table>
<thead>
<tr>
<th>Model</th>
<th>Equation</th>
<th>Parameters</th>
<th>AA-g-BT</th>
<th>BT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pseudo-second-order</td>
<td>( \frac{t}{C_t} = \frac{1}{k_e C_e} + \frac{t}{C_e} )</td>
<td>( k_e ) (g mg⁻¹ min⁻¹), ( C_e ) (mg g⁻¹)</td>
<td>0.035</td>
<td>0.042</td>
</tr>
<tr>
<td>Intra-particle diffusion</td>
<td>( C_t = k_d t^{1/2} + A )</td>
<td>( R^2 ), ( k_d ) (g mg⁻¹ min⁻¹), ( A ) (mg g⁻¹)</td>
<td>0.9998</td>
<td>0.9987</td>
</tr>
</tbody>
</table>

\( k_e, k_d \) and \( A \) are the constants of the kinetic equations. \( C_e \) and \( C_t \) are the amount of U(VI) adsorption onto adsorbents at equilibrium and at time \( t \).
The effect of ionic strength on the U(VI) adsorbed on AA-g-BT was also tested under various NaClO₄ concentrations (i.e. 0.001 mol l⁻¹ NaClO₄, 0.01 mol l⁻¹ NaClO₄, 0.1 mol l⁻¹ NaClO₄), as shown in figure 6(A). The adsorption efficiency of AA-g-BT composite decreased with increasing NaClO₄ concentrations due to the restricted movement of U(VI) from liquid to the AA-g-BT composite. The different ionic strength led to a change in the double electrode layer [37]. Moreover, the ionic strength can change the potential of the AA-g-BT composite. In addition, outer-sphere surface complexation and cation exchange are susceptible to the ionic strength [38]. Therefore, the mechanism of U(VI) on the AA-g-BT composite can be attributed to cation exchange and outer-sphere surface complexation expressed by the following equations:

(1) Outer-sphere surface complexation (such as: UO₂²⁺)

\[
\text{BT} + \text{COOH}^+ + \text{UO}_2^{2+} \rightarrow \text{BT} - \text{COO}^- + \text{UO}_2\text{CO}_2^{2-} + 2\text{H}^+ \tag{4}
\]

(2) Cation exchange (Na⁺, H⁺)

\[
2\text{BT} - \text{Na}^+ + \text{UO}_2^{2+} \rightarrow (\text{BT})_2 - \text{UO}_2 + 2\text{Na}^+ \tag{8}
\]

\[
2\text{BT} - \text{H} + \text{UO}_2^{2+} \rightarrow (\text{BT})_2 - \text{UO}_2 + 2\text{H}^+. \tag{9}
\]

In conclusion, the results suggest that the adsorption capacity of the AA-g-BT mainly depends on cation exchange (such as: Mg²⁺, Al³⁺, Na⁺) in the exchangeable cation layer and the carboxyl functional groups from AA by a plasma-induced grafting technique. At low solution pH, the electrostatic repulsion of the AA-g-BT could lead to a decrease in the adsorption capacity for U(VI). However, the zeta potential of AA-g-BT decreases and the deprotonation reaction of carboxyl functional groups gradually increases with pH increase, which can enhance the adsorption performance. At high pH, the electrostatic repulsion also blocks U(VI) from reaching the surface of the adsorbent. In order to better explain the reaction mechanism for removal U(VI), the structure of BT, AA-g-BT and a schematic diagram of the adsorption mechanism are depicted in figure 7 according to the characterization and previous studies [11, 39].

Table 2. Parameters for different reactions.

<table>
<thead>
<tr>
<th>Reactions</th>
<th>lg(K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UO₂²⁺ + H₂O = UO₂OH⁺ + H⁺</td>
<td>−5.25</td>
</tr>
<tr>
<td>UO₂²⁺ + 2H₂O = UO₂(OH)₂⁺ + 2H⁺</td>
<td>−12.15</td>
</tr>
<tr>
<td>UO₂²⁺ + 3H₂O = UO₃(OH)⁻ + 3H⁺</td>
<td>−20.25</td>
</tr>
<tr>
<td>2UO₂²⁺ + H₂O = (UO₂(OH)_2)⁺ + H⁺</td>
<td>−2.70</td>
</tr>
<tr>
<td>2UO₂²⁺ + 2H₂O = (UO₂(OH)₂)₂⁺ + 2H⁺</td>
<td>−5.62</td>
</tr>
<tr>
<td>3UO₂²⁺ + 4H₂O = (UO₂(OH)₃)₂⁺ + 4H⁺</td>
<td>−12.08</td>
</tr>
<tr>
<td>3UO₂²⁺ + 5H₂O = (UO₂(OH)_4)⁺ + 5H⁺</td>
<td>−15.55</td>
</tr>
<tr>
<td>3UO₂²⁺ + 7H₂O = (UO₂(OH))₇⁺ + 7H⁺</td>
<td>−32.20</td>
</tr>
<tr>
<td>4UO₂²⁺ + 7H₂O = (UO₂(OH))⁺ + 7H⁺</td>
<td>−21.90</td>
</tr>
<tr>
<td>UO₂²⁺ + CO₂⁻ = UO₂CO₂(aq)</td>
<td>9.94</td>
</tr>
<tr>
<td>UO₂²⁺ + 2CO₂⁻ = UO₂(CO₂)₂⁻</td>
<td>16.61</td>
</tr>
<tr>
<td>UO₂²⁺ + 3CO₂⁻ = UO₂(CO₂)₃⁻</td>
<td>21.84</td>
</tr>
<tr>
<td>2UO₂²⁺ + CO₂⁻ + 3H₂O = (UO₂)₂CO₂(OH)⁻ + 3H⁺</td>
<td>−0.86</td>
</tr>
</tbody>
</table>

Figure 6. Effect of pH and various ionic strengths on U(VI) adsorption with BT and the AA-g-BT composite (A), and distribution of U(VI) species in aqueous solutions (B). m/V = 0.4 g l⁻¹, T = 298 K, C₀ = 20 mg l⁻¹, p(CO₂) = 0.0003 8 atm, t= 24 h.
3.5. Adsorption isotherms and thermodynamics

The adsorption isotherm is regarded as a fundamental source of information on the adsorption process. To evaluate the influence of temperature on U(VI) adsorption, the isotherms of U(VI) adsorbed onto the AA-g-BT composite at 298, 308 and 318 K, respectively, were obtained and are displayed in figure 8(A), which reveals the relationships of U(VI) between liquid and adsorbent, including physical or chemical adsorption and various thermodynamic parameters.

The Langmuir adsorption isotherm model \[3\] is the simplest and the most widely used model for physical or chemical adsorption, assumes that the activity sites of the adsorbent have the same adsorption capacity and are proportionally distributed, and that there is no transmigration of adsorbate in the plane of the surface. The model also assumes the process as being monolayer adsorption: when an ion occupies an activity site, no further adsorption occurs in that site. On account of these assumptions, the Langmuir equation is shown \[3, 40\]:

\[
\frac{C_a}{C_s} = \frac{1}{C_{\text{max}} b} + \frac{C_a}{C_{\text{max}}} \quad (10)
\]

where \( b \) (l mg\(^{-1}\)) represents the constants of the isotherm equations, \( C_{\text{max}} \) (mg g\(^{-1}\)) represents the adsorption performance of U(VI) on the AA-g-BT composite relating to monolayer adsorption.

The Freundlich isotherm model \[3, 40\] is suitable for the heterogeneous adsorbent with active sites and energies distributed exponentially. The more powerful active sites of the adsorbent are covered first, until adsorption energy rapidly decreases to approach the accomplishment of the adsorption process. In addition, the formula can be applied to multilayer adsorption, which can be denoted by the form:

\[
\log(C_a) = \log(K_F) + \frac{1}{n} \log(C_s) \quad (11)
\]

where \( K_F \) (mg\(^{1-n}\) L\(^n\) g\(^{-1}\)) and \( n \) reflect the adsorption performance and the adsorption intensity, respectively.

The Dubinin–Radushkevich (D–R) isotherm \[41\] is not only suitable for the homogeneous surfaces of the adsorbent but also fits for the heterogeneous surfaces. Therefore, it is widely used to explain the adsorption behavior. However, the concentration of the adsorbate must be low. The original equation can be shown as:

\[
C_s = C_{\text{max}} \exp(-\beta e^2) \quad (12)
\]

![Figure 7. The mechanism of U(VI) on the AA-g-BT composite.](image)
and the linear form of the original equation:
\[ \ln(C_e) = \ln(C_{max}) - \beta g^2 \]  \hspace{1cm} (13)
where \( \beta \) (mol² kJ⁻²) represents the constant connected to the mean adsorption energy and \( \varepsilon \) represents the Polanyi potential expressed as:
\[ \varepsilon = RT \ln \left( 1 + \frac{1}{C_e} \right). \]  \hspace{1cm} (14)

\( E \) (kJ mol⁻¹) represents the free energy change. The formula is shown as follows:
\[ E = \frac{1}{\sqrt{2\beta}}. \]  \hspace{1cm} (15)

The adsorption isotherms of U(VI) were fitted by the Langmuir (figure 8(B)), Freundlich (figure 8(C)) and D–R models (figure 8(D)). All experiment data are presented in table 3. The Langmuir model presented a better fitting relationship than the Freundlich and D–R models comparing the correlation efficiency, \( R^2 \), i.e. a monolayer adsorption process rather than the multilayer adsorption process, and the maximum adsorption was calculated to be 89 mg g⁻¹ at pH = 5. To further certify the adsorption performance of the AA-g-BT composite, some previous adsorbents are presented in the table 4. One can find that the AA-g-BT composite has a relatively higher adsorption capacity and a faster equilibrium time than others.

As observed from figure 8(A), the efficiency of U(VI) adsorbed on the AA-g-BT composite decreases as the temperature decreases. The thermodynamic parameters \( (\Delta H^0, \Delta S^0) \) and \( \Delta G^0 \) for U(VI) adsorption on the AA-g-BT composite can be obtained from figures 8(E) and (F). \( \Delta G^0 \) can be calculated using the formula:
\[ \Delta G^0 = -RT \ln(K^0) \]  \hspace{1cm} (16)
where \( R \) is 8.314 J mol⁻¹ K⁻¹, \( T \) represents the temperature (K), \( K^0 \) represents a constant on behalf of the adsorption capacities of the AA-g-BT composite towards U(VI). \( \ln(K^0) \) can be calculated by plotting \( \ln(K_d) \) versus \( C_e \) as presented in figure 8(E). \( \Delta H^0 \) and \( \Delta S^0 \) were obtained according to the properties of the two formulas [20]:
\[ \Delta S^0 = \left( \frac{\partial \Delta G^0}{\partial T} \right)_p \]  \hspace{1cm} (17)
\[ \ln(K^0) = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}. \]  \hspace{1cm} (18)

The relationship between \( \ln(K^0) \) and \( 1/T \) for U(VI) adsorption on the AA-g-BT composite can be found from figure 8(F) and collected in table 5. \( \Delta G^0 \) was calculated to be negative, demonstrating a spontaneous adsorption process. Meanwhile, positive \( \Delta H^0 \) was obtained, indicating an endothermic adsorption process. U(VI) appearing on the AA-g-BT composite can damage the hydration sheaths of U(VI) due to the entire dispersal of U(VI) in water [15]. In addition, \( \Delta S^0 \) is a positive value, indicating that the appearance of the AA-g-BT composite can undergo changes and the disorder degree can increase between the U(VI) and the surface of the AA-g-BT composite [15].
as the desorbing agent. Moreover, AA- combined with the positive compound, so EDTA was chosen as the desorbing agent. EDTA as a chelating agent is ben

Adsorbate pH $C_{\text{max}}$ (mg g$^{-1}$) Time (min) References
Na-BT 5.0 65.02 60 [30]
Modified silica gel 6.0 8.46 none [13]
Poly(methacrylic acid) grafted chitosan/BT composite 5.5 111.9 >100 [42]
CTAB-BT 8 280 60 [43]
AA-g-BT 5.0 89.0 20 This study

The regeneration and recycling of the AA-g-BT composite was also tested for potential practical applications (figure 9). As we know, EDTA as a chelating agent is beneficial when combined with the positive compound, so EDTA was chosen as the desorbing agent. Moreover, AA-g-BT presents weak adsorption performance in an acid medium, indicating that the absorbed U(VI) ions can be removed from AA-g-BT by adding HNO$_3$. The adsorption performance is still high after five cycles using EDTA and HNO$_3$ [22], indicating the good regeneration ability of AA-g-BT as a promising potential candidate in radioactive pollution management.

4. Conclusions

In conclusion, a AA-g-BT composite was synthesized by a plasma-induced grafting technique. The U(VI) adsorption capacity of the AA-g-BT composite was significantly enhanced, which suggests that the introduction of the carboxyl functional groups make a powerful separation material for the selective separation of U(VI). The mechanism for U(VI) on the AA-g-BT composite can be attributed to the cation exchange and outer-sphere surface complexation. The pseudo-second order kinetics and the Langmuir model can describe the experimental process. The adsorption thermodynamic investigation indicates a spontaneous and endothermic process. Moreover, the adsorption performance of AA-g-BT composite is still high after five cycles. Therefore, the AA-g-BT composites presents promising potential in radioactive pollution management.

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References

[8] Zhao Y G et al 2014 RSC Adv. 4 32710
[19] Duan S X et al 2017 RSC Adv. 7 21124
[34] Xiong J et al 2017 ACS Sustainable Chem. Eng. 5 1924
[37] Baeyens B and Bradbury M H 1997 J. Contam. Hydrol. 27 199