Electronic Supplementary Information (ESI)

Bayberry Tannin immobilized Bovine Serum Albumin Nanospheres: Characterization, Irradiation Stability and Selective Removal Uranyl Ion from Radioactive Wastewater


*State Key Laboratory of Environment-friendly Energy Materials, School of Life Science and Engineering, Southwest University of Science and Technology, Mianyang, Sichuan 621010, PR China.
†Engineering Research Center of Biomass Materials, Ministry of Education; Fundamental Science on Nuclear Wastes and Environmental Safety Laboratory, Mianyang, Sichuan 621010, PR China
‡Institute of Computer Application, China Academy of Engineering Physics, Mianyang, Sichuan, 621900, PR China
§Department of Chemistry and Chemical Engineering, Anhui University, Hefei, 230601, P. R. China

*Corresponding author at: State Key Laboratory of Environment-friendly Energy Materials, School of Life Science and Engineering, Southwest University of Science and Technology, Mianyang, Sichuan 621010, PR China.

E-mail address: zhoujian@swust.edu.cn (J. Zhou).
S1. Batch adsorption

Effect of pH on UO\textsubscript{2}\textsuperscript{2+} adsorption. 0.02g of BSA-BT-NSs was immersed into 50 mL of 100 mg L\textsuperscript{-1} UO\textsubscript{2}\textsuperscript{2+} solution. The pH of the solutions, ranged from 2 to 6, was adjusted using diluted 0.1 M NaOH solution and 0.1 M HNO\textsubscript{3} solution. The adsorption process was conducted at 298 K with constant stirring for 24 h. Then, the suspension was filtered and the concentration of UO\textsubscript{2}\textsuperscript{2+} in filtrate was analyzed by UV-Vis (UV-3900, Hitachi Corp., Tokyo, Japan; the limit of analytical detection of uranium is 0.1 mg L\textsuperscript{-1}) at 650 nm with arsenazo (III) as the complex agent (Fig.S1A). The UO\textsubscript{2}\textsuperscript{2+} concentrations were measured using a calibration curve (Fig.S2B) \(Y = 0.24071X - 0.00255\), where \(X\) is the concentration of UO\textsubscript{2}\textsuperscript{2+} in mg L\textsuperscript{-1} and \(Y\) is the absorbency; \(R^2 = 0.999\). The linear equation was established from the known concentration of standard UO\textsubscript{2}\textsuperscript{2+} solutions (0, 0.4, 0.8, 1.6, 2.4, 3.2, and 4 mg L\textsuperscript{-1}, respectively) [13]. The adsorption capacity of UO\textsubscript{2}\textsuperscript{2+} onto BSA-BT-NSs was calculated from the concentration difference of UO\textsubscript{2}\textsuperscript{2+} before and after the adsorption.

Fig. S1 Absorption spectra of uranium-Arsenazo III complex (A) and standard curve of uranium (B)

Effects of the temperature and the initial UO\textsubscript{2}\textsuperscript{2+} concentration. 0.02g of BSA-BT-NSs was immersed into 50 ml of UO\textsubscript{2}\textsuperscript{2+} solution, where the initial concentration of UO\textsubscript{2}\textsuperscript{2+} ranged from 20 mg L\textsuperscript{-1}, 100 mg L\textsuperscript{-1}, 180 mg L\textsuperscript{-1}, 260 mg L\textsuperscript{-1}, 340 mg L\textsuperscript{-1}, 420 mg L\textsuperscript{-1}. The pH of solutions was 5.0 and the adsorption processes were conducted with constant stirring for 24 h at 288 K, 298 K, 308 K, 318 K and 328 K, respectively. The concentrations of UO\textsubscript{2}\textsuperscript{2+} in residual solutions after adsorption were analyzed by UV-Vis with arsenazo (III) as the complex agent.
**Adsorption kinetics.** 0.02 g of BSA-BT-NSs was suspended in 50 mL of 100 mg L⁻¹ UO₂²⁺ solutions. The pH of the solution was adjusted to 5.0 and the adsorption process was conducted at 298 K with constant stirring. The concentration of UO₂²⁺ was analyzed at a regular interval during adsorption process by UV-Vis. The adsorption capacities at time \( t \) (min) were obtained by mass balance calculation and were denoted as \( q_t \) (mg g⁻¹).

S2. Preparation of BSA-BT-NSs.

![Fig. S2 SEM images of BSA-BT-NSs using different amount tannin to immobilization (A-10%, B-20%, C-30%, D-40%, E-50% and F-60%)](image)

S3. Thermal analysis

![Fig. S3 The thermal analysis of BSA-NSs and BSA-BT-NSs](image)
S4. Uranyl ion removal

**Thermodynamics:** Three basic thermodynamic parameters, free energy change ($\Delta G$), enthalpy change ($\Delta H$) and entropy change ($\Delta S$) were calculated using following equations.

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$  \hspace{1cm} (1)

$$\ln K_L = \Delta S^0 / R - \Delta H^0 / RT$$  \hspace{1cm} (2)

![Fig. S4 The linear relationship between lnK and 1/T for U(VI) adsorption on BSA-BT-NSs](image)

**Isotherm model:** Experimental data was fitted by Langmuir and Freundlich models.

The linear and non-linear form of Langmuir isotherm equation can be written as:

$$\frac{C_e}{q_e} = \frac{1}{K_q q_{max}} + \frac{C_e}{q_{max}}$$ \hspace{1cm} (linear)  

$$q_e = \frac{q_{max} K_q C_e}{1 + K_q C_e}$$ \hspace{1cm} (non-linear)  

The Freundlich Model can be expressed as linear and non-linear forms:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$$ \hspace{1cm} (linear)  

$$q_e = K_F C_e^{1/n}$$ \hspace{1cm} (non-linear)

where $q_e$ (mg g$^{-1}$) represents the equilibrium adsorption of uranium (VI) on the adsorbent, $C_0$ and $C_e$ (mg L$^{-1}$) are initial and equilibrium uranium(VI) concentration,
respectively.

Fig. S5 The linear (A) and non-linear (C) fitting of Langmuir model of UO$_{2}^{2+}$ adsorption on BSA-BT-NSs; The linear (B) and non-linear (D) fitting of Freundlich model of U(VI) adsorption on BSA-BT-NSs.

Table S1 Characteristic parameters obtained from Langmuir and Freundlich equations

<table>
<thead>
<tr>
<th>Type</th>
<th>$T$ (K)</th>
<th>$q_{m}$ (mg g$^{-1}$)</th>
<th>$K_{L}$ (L mg$^{-1}$)</th>
<th>$R^{2}$</th>
<th>$K_{F}$ (mg g$^{-1}$)(L mg$^{-1}$)$^{1/n}$</th>
<th>$n$</th>
<th>$R^{2}$</th>
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</thead>
<tbody>
<tr>
<td>Linear</td>
<td>288</td>
<td>431.034</td>
<td>0.007</td>
<td>0.983</td>
<td>26.287</td>
<td>2.409</td>
<td>0.911</td>
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<tr>
<td></td>
<td>298</td>
<td>423.729</td>
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<td>0.983</td>
<td>28.449</td>
<td>2.484</td>
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<td>308</td>
<td>409.836</td>
<td>0.008</td>
<td>0.981</td>
<td>36.736</td>
<td>2.767</td>
<td>0.900</td>
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<td>318</td>
<td>431.034</td>
<td>0.008</td>
<td>0.966</td>
<td>40.183</td>
<td>2.819</td>
<td>0.871</td>
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<tr>
<td></td>
<td>328</td>
<td>487.805</td>
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<td>0.966</td>
<td>33.304</td>
<td>2.513</td>
<td>0.870</td>
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<tr>
<td>Non-linear</td>
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<td>404.626</td>
<td>0.008</td>
<td>0.966</td>
<td>33.272</td>
<td>2.682</td>
<td>0.892</td>
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<td></td>
<td>298</td>
<td>402.446</td>
<td>0.008</td>
<td>0.963</td>
<td>35.406</td>
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<td></td>
<td>308</td>
<td>392.336</td>
<td>0.010</td>
<td>0.963</td>
<td>44.304</td>
<td>3.051</td>
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<td>318</td>
<td>408.260</td>
<td>0.010</td>
<td>0.945</td>
<td>49.227</td>
<td>3.142</td>
<td>0.852</td>
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### Adsorption kinetics

Two kinetic models, pseudo-first-order and pseudo-second-order, were employed to evaluate the rate-controlling mechanism of the adsorption process. The linear and non-linear forms of the equations are given as follows:

\[
\ln(q_t - q_e) = \ln q_e - K_1 t 
\]  \hfill (11)

\[
\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{K_2 q_e^2} 
\]  \hfill (12)

The non-linear forms of pseudo-first-order and pseudo-second-order kinetic models can be written as:

\[
q_t = q_e (1 - \exp(-K_1 t)) 
\]  \hfill (13)

\[
q_t = \frac{K_2 q_e^2}{(1 + K_2 q_e)} 
\]  \hfill (14)

where \( t \) (min) is the contact time, \( q_e \) and \( q_t \) (mg g\(^{-1}\)) are the adsorption capacity at any time \( t \) and equilibrium, respectively, and \( K_1 \) (g mg\(^{-1}\) min\(^{-1}\)) and \( K_2 \) (g mg\(^{-1}\) min\(^{-1}\)) are the rate constants of pseudo-first-order and pseudo-second-order adsorption.
Fig. S6 The linear (A) and non-linear (C) fitting of pseudo-first-order kinetic of UO$_2^{2+}$ adsorption on BSA-BT-NSs; the linear (B) and non-linear (D) fitting of pseudo-second-order kinetic model of UO$_2^{2+}$ adsorption on BSA-BT-NSs.

Table S3 Parameters of Pseudo-first-order kinetics and Pseudo-second-order kinetics for U(VI) adsorption on BSA-BT-NSs.

<table>
<thead>
<tr>
<th>Model</th>
<th>Pseudo-first-order</th>
<th>Pseudo-second-order</th>
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</thead>
<tbody>
<tr>
<td>Parameter</td>
<td>$q_e$ (mg g$^{-1}$)</td>
<td>$k_1$ (g/mg*min)</td>
</tr>
<tr>
<td>Linear</td>
<td>7.864</td>
<td>9.080×10$^{-3}$</td>
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<tr>
<td>Non-linear</td>
<td>170.483</td>
<td>2.800×10$^{-2}$</td>
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**S5. Theory calculation**

<table>
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<tr>
<th>Geometric Models</th>
<th>PC-U</th>
<th>PC-U-PC</th>
<th>BT-U</th>
<th>BT-U-BT</th>
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<tbody>
<tr>
<td>$E_b$ (KJ mol$^{-1}$)</td>
<td>693.132</td>
<td>979.315</td>
<td>799.964</td>
<td>1157.846</td>
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