Isotherms, thermodynamic and mechanism studies of removal of low concentration uranium (VI) by *Aspergillus niger*

Xiaoyu Wang, Tieshan Wang, Xinyan Zheng, Yanghao Shen and Xia Lu

**ABSTRACT**

In order to develop an effective and economical method for removing low concentration radioactive wastewater of uranium, the biomass of ‘CMCC(F)-98003’ *Aspergillus niger* was investigated in a batch system. The maximum uranium adsorption capacity of 12.5 mg g⁻¹ was obtained at the initial uranium concentration of 0.75 mg L⁻¹. The biosorption data on a biomass concentration of 0.029 g L⁻¹ fitted well to the Freundlich isotherm with a correlation coefficient ($R^2$) of 0.987. The calculated thermodynamic parameters showed that the biosorption of uranium ions was endothermic (ΔΗ° < 0). The results of scanning electron microscope and Fourier transform infrared spectrometry analysis revealed that nano-particles of uranium precipitation were formed on the cell surfaces after biosorption, and the functional groups of –CH, N-H, –COOH, P = O and the carbohydrates and alcohols were involved in the biosorption process between *A. niger* and uranium ions.

**Key words** | *Aspergillus niger*, biosorption, low concentration, mechanism, physical, uranium

**INTRODUCTION**

Industrial activities, mill tailing, nuclear power testing and nuclear waste disposal are the prime source of uranium contamination in the environment. Especially, uranium mining and hydrometallurgy produce large volumes of diluted waste-water, in which the concentration of uranium is lower than 1 mg L⁻¹. Such low concentrations of uranium may be a potential hazard to human life by migrating and enriching through the food chain, and accumulating in brain, kidney, bone, muscle and spleen (Khani 2011). Canada, USA and China stipulate that the maximum acceptable concentrations of uranium for drinking water are 20, 30 and 50 μgL⁻¹, respectively (Ding et al. 2017a). Conventional methods including chemical precipitation, ion exchange, evaporation, electroplating and membrane processes have been applied to remove radionuclide contaminations from aqueous solutions; however, these methods are either inefficient or expensive for low concentration radionuclide wastewaters (Wang & Chen 2006). Consequently, an effective and economical method should be developed.

Recently, most studies have focused on using different biosorbents such as bacteria, fungi, and algae to remove radionuclides at high concentration (higher than 50 mg L⁻¹) and explored the mechanism between the biosorbents and the metal ions, but ignored the exploration of low concentrations of radionuclides. However, these biosorbents display metal sequestering properties and are able to reduce the concentration of radionuclide solutions from ppt to ppb level with high efficiency and in an environmentally-friendly way (Wang & Chen 2006). Therefore, biosorption is the best candidate for treating low concentrations of radionuclides.

The *Aspergillus niger* (*A. niger*) fungus, as a major strain used in the fermentation process, is easy to obtain from the fermentation and enzymatic industry (Mukhopadhyay et al. 2007). So it is more economical to use waste microbial biomass directly from the industry without chemical modification methods, which may cause secondary pollution. Yakuba and Dudeney demonstrated that *A. niger* was able to remove uranium ions effectively, because the predominant chemical compositions of the cell wall are chitosan and mannan, apart from carbohydrates (Mukhopadhyay et al. 2011). In recent years, chemically modified biosorbents have been used to adsorb low concentrations of uranium (VI) from aqueous media with higher effectiveness (Ding et al. 2014a; Xiao et al. 2016), but the researchers ignored the fact that for low concentration of uranium the manipulations may result in a number of
environmental problems as well as health and safety issues (Fomina & Gadd 2014).

However, there is little focus in the literature on the removal of low concentrations of uranium using A. niger directly from industrial production without any chemical modification. Furthermore, the equilibrium and thermodynamics that may control the efficiency and economy, while suitable for commercial production of the biosorption process, are still uncertain. In this study, the different conditions affecting the biosorption process were investigated, various equilibrium isotherms were utilized to fit the data, and the scanning electron microscope (SEM) and Fourier transform infrared spectrometry (FTIR) analysis were investigated to understand the mechanism of biosorption. In addition, the thermodynamics of the biosorption process are deduced, which is useful to determine the spontaneous state of the biosorption.

**METHODS**

**Preparation of biomass**

The thallus used for biosorption was the ‘CMCC(F)-98003’ indigenous strain of A. niger purchased from Shanghai Luwei technology company, and the fungal spores were preserved on PDA (Potato Dextrose Agar) solid medium. First, under completely aseptic conditions, the fungal spores were transferred from the solid medium with sterile forceps to 500 mL Yeast Peptone Dextrose (1% yeast extract, 2% peptone and 2% glucose) liquid medium for cultivating 500 mL Yeast Peptone Dextrose (1% yeast extract, 2% peptone and 2% glucose) liquid medium for cultivating. Then the inoculated medium was placed into a shaker incubator at 200 rpm, 30 °C for 24 h. At this time, the cell surfaces of the biomass were covered in the maximum density of the protein and polysaccharides (Wang et al. 2014). After the formation of mycelium, which had a diameter of approximately 2 cm, these were separated by filtration with filter paper and washed three times with sterile water until the filtrate became neutral, then dried in a dry oven at 30 °C for 24 h. The completely dried mycelium was crushed by mortar to a powder, and sieved through a 150 mesh standard test sieve. Then the dried mycelium powder was mixed with distilled water into a liquid suspension and kept at 4 °C.

**Reagents**

All the materials in the experiments were analytical quality. The standard stock solution of uranium (1 mg mL⁻¹) was prepared through dissolving uranyl nitrate hexahydrate (UO₂(NO₃)₂·6H₂O) in 0.1 M HNO₃. The working uranium solutions were graded diluted in 0.01 M HNO₃ of the standard stock solutions before the experiment. In the experiments, the pH of the test solutions was adjusted using 0.01 M NaOH and 0.01 M HNO₃ solution.

**Adsorption experiments**

For the batch adsorption experiment, the effect of pH, biomass concentration, initial uranium concentration and temperature were explored under proper conditions. The parameters of the corresponding experiment were set at the range of pH (3.0–7.0); adsorbent biomass concentration (0.029–0.58 g L⁻¹); initial uranium concentration (0.1–0.75 mg L⁻¹); temperature (20–40 °C); contact time of 180 min, when the adsorption reached equilibrium; centrifuging at 10,000 rpm for 5 min; and the concentration of supernatant was determined by the trace uranium analyzer (WGJ-III, China) (Ding et al. 2014a). The result of each sorption experiment was conducted in triplicate.

**Analytical procedure**

The removal efficiency (R) and the adsorption capacity (q) of uranium by A. niger were determined from the following balance equations:

\[ R(\%) = \frac{C_O - C_e}{C_O} \times 100\% \]  \( (1) \)

\[ q = \frac{(C_O - C_e)}{C_m} \]  \( (2) \)

where R is the percentage of uranium removal (%), q is the adsorbed capacity of A. niger biomass (mg g⁻¹), C₀ (mg L⁻¹) and Cₑ (mg L⁻¹) are the initial and the equilibrium concentration of the uranium ions, respectively, and Cₘ (g L⁻¹) is the concentration of the biomass used for the adsorption process.

**FTIR and SEM analysis**

In order to further determine the mechanism between the uranium ions and A. niger, the characteristics of the A. niger were determined by SEM and FTIR for the initial concentration of uranium, set as 100 mg L⁻¹, and the biomass concentration, set as 1.6 g L⁻¹. And to prevent precipitation of the high concentration of uranium, the pH was set at
4.5 ± 0.1. The FTIR spectra were obtained using a Nicolet NEXUS 670 (USA) for the samples, which were pressed into KBr pellets. The SEM images used a JSM-6701F (Japan) to study the morphology of A. niger before and after biosorption of uranium.

Modeling

Biosorption modeling is often used for analysing the experimental data, understanding process mechanisms, predicting answers to changes in operational conditions, and optimizing processes (Fomina & Gadd 2014). In the present study, modeling of the experimental data has been applied by equilibrium modeling and thermodynamic modeling.

Equilibrium modeling

The equilibrium data from the removal of uranium by A. niger was fitted into various isotherm models that can be used for designing a biosorption process, which are expressed as an equilibrium isotherm curve. The Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (D-R) isotherms are given as the following equations, respectively. The best fit of each isotherm model was assessed by the coefficient of correlation ($R^2$).

\[
\frac{1}{q_e} = \frac{1}{q_{\text{max}}} + \frac{1}{bq_{\text{max}}C_e}
\]

\[
\ln q_e = \ln K_f + \frac{1}{n}\ln C_e
\]

\[
q_e = B\ln k_T + B\ln C_e
\]

\[
\ln q_e = \ln q_{\text{max}} + \delta e^2 \quad \epsilon = RT\ln\left(1 + \frac{1}{C_e}\right)
\]

where $C_e$ (mg L$^{-1}$) is the equilibrium uranium concentration in solution, $q_e$ (mg g$^{-1}$) is the adsorption capacity of uranium at equilibrium, and $q_{\text{max}}$ (mg g$^{-1}$) is the maximum adsorption capacity of uranium.

Thermodynamic studies

The thermodynamic parameters, including enthalpy ($\Delta H^\circ$), entropy ($\Delta S^\circ$) and Gibbs free energy ($\Delta G^\circ$), are the actual indicators for practical application of an adsorption process and determining whether the adsorption reaction is endothermic or exothermic (Pang et al. 2011).

The three thermodynamic parameters were calculated as the following equation:

\[
\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ
\]

The linear form of the thermodynamic equation is expressed by the following equation:

\[
\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}
\]

\[
K_d = \frac{C_0 - C_e}{C_0C_m}
\]

where $K_d$ is the thermodynamic distribution coefficient for the biosorption process, $R$ is the universal gas constant ($R = 8.314$ J mol$^{-1}$ K$^{-1}$), $T$ (K) is the absolute temperature, $C_0$ (mg L$^{-1}$) and $C_e$ (mg L$^{-1}$) are the initial and the equilibrium concentration of the uranium ions, respectively, and $C_m$ (g L$^{-1}$) is the concentration of the biomass used for the adsorption process.

RESULTS AND DISCUSSION

Effect of the pH

The pH of the biosorption medium is an important parameter affecting the biosorption process, which influences the precipitation of metal ions and ionization of surface functional groups (Gok & Aytas 2009). For the A. niger, the cell walls were mainly composed of polysaccharides and carbohydrate, e.g., cellulose, chitosan and mannans, providing many side groups and ligands such as amino, carboxyl, carbonyl, alcohol, phosphate and sulphide groups, which cover the cell wall with negative charge (Bayramoglu et al. 2006). The effect of pH on the biosorption of low concentrations of uranium ($1$ mg L$^{-1}$) onto the A. niger was determined from pH 3.0–7.0, and the results are displayed in Figure 1.

As seen from the figure, the uranium removal was only 50% at pH 3.0. The low biosorption capacity at low pH could be attributed to the protonation of the cell walls’ active sites, resulting in H$_3$O$^+$ competing with uranium ions for occupancy of the binding sites (Parab et al. 2005). The uranium uptake by the A. niger increased with increasing the pH from 3.0 to 5.5, because the binding sites were deprotonated and formed negatively charged sites, reaching a maximum at pH 5.5, which was used in further
studies. Thus, increasing the pH from 5.5 to 7.0 caused a decrease in the biosorption rate, which could be explained by the type of uranium ion species present in the solution and the increase in the dissolved carbonate concentration (Pang et al. 2011). Lu (Lu et al. 2013) simulated the relative species distribution of 1 mg L\(^{-1}\) U(VI) in the presence of CO\(_2\), showing that below pH 4.0, the prominent species was UO\(_2^+\); at pH 5.5–6.0, the prominent species was UO\(_2\)OH\(^+\); and at pH 6.0–7.0, the dominant species of precipitate UO\(_2\)CO\(_3\) appeared. The increasing number of dissolved carbonate and bicarbonate anions competed with the uranium ions for the biosorption sites, resulting in a continuous reduction in the biosorption capacity (Barnett et al. 2006).

**Effect of the biomass concentration on biosorption**

The dosage of biosorbent is an important parameter to determine the capacity of the biosorbent at a known initial low concentration of uranium (1 mg L\(^{-1}\)). The effect of biomass concentration on the adsorption of uranium is shown in Figure 2.

As shown in Figure 2, the increase in the A. niger biomass concentration from 0.029 g L\(^{-1}\) to 0.175 g L\(^{-1}\) resulted in a significant increase in uranium ion removal. During the biomass concentration, as the A. niger biomass dose increased, the surface area of the cells and the availability of functional groups increased in the adsorption process, thus more binding sites were provided for removal of uranium ions (Bayramoglu et al. 2015). When the biomass concentration exceed 0.175 g L\(^{-1}\), the maximum adsorption rate reached 85%, but the increment of uranium adsorption capacity was insignificant, for the amount of uranium ions left in the solution had become very low (≈0.15 mg L\(^{-1}\)). At a low uranium concentration, due to the lower concentration gradient pressure (a driving force), uranium removal was difficult (Solat et al. 2014). Meanwhile, it cannot be ignored that with the increased concentration of the biomass, the relative uranium adsorption quantity reduced; what is more, the uranium adsorption quantity at a biomass concentration of 0.029 g L\(^{-1}\) (16 mg g\(^{-1}\)) is an order of magnitude lower than the 0.580 g L\(^{-1}\) (1.5 mg g\(^{-1}\)).

**Effect of the initial uranium ion concentration**

Few researches have studied a low concentration of uranium (less than 1 mg L\(^{-1}\)), because it is more difficult and the driving force provided by the low initial uranium concentration may prevent the adsorption process. As can be seen from Figure 2, the removal efficiency of uranium increased with the adsorbent concentration, but when the amount of uranium ions left in the solution becomes very low (≈0.15 mg L\(^{-1}\)), no matter how much the biomass increases, the increment of uranium adsorption capacity becomes less significant. The uranium uptake by A. niger at different concentrations was investigated at initial uranium concentrations from 0.10 mg L\(^{-1}\) to 0.75 mg L\(^{-1}\) and the results are shown in Figure 3. And the comparison of other adsorbents for removal of low concentrations of uranium are presented in Table 1.
As observed from Figure 3(a), there was a step reduction in the sorption uptake when the initial uranium concentration was increased at a fungal biomass concentration of 0.029 g L\(^{-1}\), since there was insufficient fungal biomass in the adsorption system, and the cells could only offer a finite number of surface attachment sites. With an increase in uranium concentration, the adsorption capacity increased imperceptibly; therefore, the fungal biomass in the adsorption system had reached its saturation point. As shown in Figure 3(b), the uranium adsorption capacity increased linearly with the initial uranium concentration at different concentrations of biomass. The uranium adsorption capacity was 12.5 mg g\(^{-1}\) and 3.5 mg g\(^{-1}\) for a fungal biomass of 0.029 g L\(^{-1}\) and 0.175 g L\(^{-1}\), respectively, at an initial uranium concentration of 0.75 mg L\(^{-1}\). Hence, it can be said that when the biomass has not reached the saturation point, the initial uranium concentration has a distinct influence on the uranium adsorption capacity. In order for the driving force to overcome the mass-transfer resistance the uranium concentration and the biomass concentration gradient between the biomass surface and the metal solution was increased, so that the electrostatic forces between the uranium ions and functional groups of the biomass increased (Solat et al. 2014). In short, the sorption has a maximum percentage at a lower uranium concentration, i.e., the biosorption is more efficient in dilute solutions, but the uranium uptake quantity is greater at a higher uranium concentration (Amini et al. 2013).

### Adsorption isotherm

Based on Figure 3, the data were fitted with the different equilibrium isotherms as presented in Figure 4. The results of the correlation coefficient exhibited in Table 2 demonstrated that the data of both biomass concentrations fitted the D-R isotherm well, with satisfactory correlation coefficient values (\(R^2\))

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>(C_{\text{U(VI)}} (\text{mg L}^{-1}))</th>
<th>(Q_{\text{max, U(VI)}} (\text{mg g}^{-1}))</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermally activated sodium feldspar</td>
<td>0.5</td>
<td>0.239</td>
<td>Li et al. (2014)</td>
</tr>
<tr>
<td>Acid-activated sodium feldspar</td>
<td>0.5</td>
<td>0.346</td>
<td>Ding et al. (2014b)</td>
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<tr>
<td>Ethylenediamine-modified biomass of Aspergillus niger</td>
<td>0.5</td>
<td>6.789</td>
<td>Ding et al. (2014a)</td>
</tr>
<tr>
<td>Diethylenetriamine functionalized Cycas revolute leaves</td>
<td>0.01</td>
<td>0.024</td>
<td>Xiao et al. (2016)</td>
</tr>
<tr>
<td>Aspergillus niger</td>
<td>0.5</td>
<td>8.85</td>
<td>Present work</td>
</tr>
<tr>
<td>Aspergillus niger</td>
<td>0.1</td>
<td>2.25</td>
<td>Present work</td>
</tr>
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</table>
higher than 0.97. Thus it can be concluded that the biosorption process was a characteristic Gaussian energy distribution onto the heterogeneous surface of the *A. niger* cells. And the calculated values of energy $E$ (J mol$^{-1}$) ($E = 1/\sqrt{2\delta}$) of the biosorption in the D-R isotherm were about 0.14 J mol$^{-1}$ for both biomass concentrations, which indicated the biosorption was a physical process (Bayramoglu et al. 2015).

However, the biomass concentration of 0.029 g L$^{-1}$ was better fitted with the Freundlich isotherm, with a coefficient of determination ($R^2$) higher than 0.987, showing that under this condition, the biosorption process was a non-ideal, reversible and heterogeneous adsorptive process. The Freundlich isotherm is an empirical equation, and the higher measured $K_f$ value of the fungal biomass shows easier adsorption, and the $n > 1$ represents favorable adsorption conditions (Bayramoglu et al. 2015). The values of $K_f$ were 25.577 and 29.412 for biomass concentrations of 0.029 g L$^{-1}$ and 0.175 g L$^{-1}$, respectively. This means that the higher the biomass concentration, the easier the adsorption, but it cannot be ignored that the $n$ is less than 1 at the higher biomass concentration, for the biomass had reached saturation point and the adsorption conditions was not very favorable.

At the biomass concentration of 0.029 g L$^{-1}$, the maximum adsorption capacities ($q_{\text{max}}$) for the Langmuir and D-R isotherms were 19.398 mg g$^{-1}$ and 14.977 mg g$^{-1}$, respectively, which were well described by the experimental data (12.543 mg g$^{-1}$). When the biomass concentration was 0.175 g L$^{-1}$, the maximum adsorption capacities ($q_{\text{max}}$) for the Langmuir and D-R isotherms were 8.89 mg g$^{-1}$ and 7.8 mg g$^{-1}$, respectively, much larger than the experimental data (3.5 mg g$^{-1}$). This means that the equilibrium sorption
models provide some basic information on a given system, but the equilibrium value of the adsorption capacities is plotted against the concentration of biomass (Gadd 2009). When the biomass reached the saturation point, the equilibrium isotherms could only reflect the experimental curves but failed to reflect the mechanism (Fomina & Gadd 2013).

**Effect of the contact time and temperature**

The experimental results for the biosorption of uranium ions by A. niger at different temperatures (20–40°C) are shown in Figure 5. The results reveal that, at different temperatures, the biosorption increased rapidly within the first 5 min, then the rate of adsorption became slower and achieved a kinetic equilibrium; after that, it did not change significantly.

For the low concentration of uranium (1 mg L⁻¹), the adsorption rate was higher and faster in the initial stage, and had reached equilibrium after only 60 min, which may be due to the availability of the larger surface area of the fungal biomass for adsorption of the low number of uranium ions. The rapid uptake of uranium ions had been suggested, as A. niger is a good biosorbent because it allows a short contact time (Faghihian & Peyvandi 2012). Therefore, A. niger has significant practical applications in bioreactor operation where the operational time for the solution-sorbent is very limited (Saini & Melo 2013).

It can also be seen from Figure 5, for the increase in temperature from 20°C to 40°C, the uranium uptake by the fungal biomass increased at the same contact times, suggesting the adsorption was an endothermic process. The rise in adsorption rate at a higher temperature may due to the increasing frequency of molecular collisions between the biosorbent and the solute, which resulted in increasing adsorption on the surface of the A. niger (Saini & Melo 2013).

**Thermodynamic studies**

The enthalpy change and entropy change for the biosorption process were obtained from the plot of lnKₐ drawn against 1/T, which is shown in Figure 6 (R² = 0.9852). The calculated thermodynamic parameters are presented in Table 3. The ΔH and the ΔS were given values of 7.64 kJ mol⁻¹ and 37.66 J mol⁻¹ K⁻¹, respectively. Generally, the positive value of ΔH shows that uranium adsorption by the A. niger was endothermic, indicating that higher

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<table>
<thead>
<tr>
<th>Table 2</th>
<th>Isotherm model constants for the adsorption of uranium at the different concentrations of biomass</th>
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</thead>
<tbody>
<tr>
<td><strong>Models</strong></td>
<td><strong>Parameters</strong></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Langmuir</td>
<td>q_max (mg g⁻¹)</td>
</tr>
<tr>
<td></td>
<td>b (L mg⁻¹)</td>
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<tr>
<td></td>
<td>R²</td>
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<tr>
<td>Freundlich</td>
<td>K_f (mg¹⁻¹(1/n) L¹/n g⁻¹)</td>
</tr>
<tr>
<td></td>
<td>N</td>
</tr>
<tr>
<td></td>
<td>R²</td>
</tr>
<tr>
<td>Temkin</td>
<td>K_T (L g⁻¹)</td>
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<tr>
<td></td>
<td>B</td>
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<tr>
<td></td>
<td>R²</td>
</tr>
<tr>
<td>D-R</td>
<td>q_max (mg g⁻¹)</td>
</tr>
<tr>
<td></td>
<td>δ</td>
</tr>
<tr>
<td></td>
<td>E (J mol⁻¹)</td>
</tr>
<tr>
<td></td>
<td>R²</td>
</tr>
</tbody>
</table>

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(Figure 5) Effect of contact time on biosorption of uranium by A. niger at different temperatures (pH = 5.5 ± 0.1, biomass dosage = 0.175 g L⁻¹, and initial uranium ion concentration = 1 mg L⁻¹).

(Figure 6) Thermodynamic relationship between the Gibbs free energy and temperature.
temperature favors the adsorption process. The positive value of entropy $\Delta S$ suggested that the increased randomness at the solid-solution interface is attributed to the liberation of free water molecules during the adsorption of uranyl ions on the active sites of the fungal biomass, and also represented a degree of freedom of the adsorbed species (Bai et al. 2013; Bayramoglu et al. 2013).

As seen in Table 3, all the values of $\Delta G$ were negative under different temperatures (20–40 °C), indicating the feasibility of the process and the adsorption of uranium by A. niger were spontaneous. Meanwhile, the gradual decrease of $\Delta G$ with the increased in the temperature indicated that a higher temperature was conducive to uranium adsorption. Previous studies have found that a $\Delta G$ value in the range of 0 to $-20$ kJ mol$^{-1}$ is for physical adsorption (Khani 2011).

### Biosorbent characterization

The SEM micrographs of the surface of A. niger and the FTIR spectrum before and after biosorption of uranium are shown in Figures 7 and 8, respectively.

As shown in Figure 7(a), after the process of crushing, the cells of A. niger were damaged and appeared to have different sizes of hollows, which increased the cells’ surface area and may contribute to the higher adsorption capacity. After biosorption of uranium for 3 h, the A. niger cells’ surfaces were uniformity covered with uranium precipitation.

![Figure 7](https://iwaponline.com/wst/article-pdf/75/12/2727/452475/wst075122727.pdf)

**Figure 7** The SEM micrographs before biosorption (a) and after (b), (c), (d) is the detail of (c) (pH $= 4.5 \pm 0.1$, biomass dosage $= 1.6$ g L$^{-1}$, uranium ion concentration $= 100$ mg L$^{-1}$, temperature $= 30$ °C, contact time $= 180$ min).

### Table 3 | Thermodynamic parameters and correlation coefficient value for uranium biosorption onto A. niger

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$\Delta G$ (kJ mol$^{-1}$)</th>
<th>$\Delta H$ (kJ mol$^{-1}$)</th>
<th>$\Delta S$ (J mol$^{-1}$ K$^{-1}$)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>$-3.39$</td>
<td>$7.64$</td>
<td>$37.66$</td>
<td>0.9852</td>
</tr>
<tr>
<td>30</td>
<td>$-3.77$</td>
<td>$7.64$</td>
<td>$37.66$</td>
<td>0.9852</td>
</tr>
<tr>
<td>40</td>
<td>$-4.15$</td>
<td>$7.64$</td>
<td>$37.66$</td>
<td>0.9852</td>
</tr>
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</table>
thermodynamics. Under different biomass concentrations, the experimental data fitted well with the D-R isotherm, which indicated the biosorption was a physical process. The maximum uranium adsorption obtained was 12.5 mg L$^{-1}$ for a fungal biomass of 0.029 g L$^{-1}$ at an initial uranium concentration of 0.75 mg L$^{-1}$. The calculated thermodynamic parameters $\Delta H$ and $\Delta S$ were given as 7.64 kJ mol$^{-1}$ and 37.66 J mol$^{-1}$ K$^{-1}$, respectively. All the values of $\Delta G^\circ$ were negative under different temperatures, indicating the spontaneous adsorption of uranium by $A. \text{niger}$. The SEM micrographs show that after biosorption, the $A. \text{niger}$ cell surfaces were uniformly covered with nano-particles of uranium precipitation. And the FTIR spectrum indicated that the functional groups of $-\text{CH}$, the amide II band, and the $-\text{COOH}$ and $\text{P=O}$ form of phosphate were taking part in the adsorption process. Hence, the fungal biomass of $A. \text{niger}$ direct from industrial production, without any chemical modification, is a promising biosorbent to remove uranium ions.

**(Figure 7(b) and 7(c)).** And it could be seen from the detail (Figure 7(d)) that the uranium precipitation was in the form of nano-particles sized from 20–50 nm.

For the FTIR spectrum, as reported in other articles (Schmitt & Flemming 1998; Wang et al. 2010), the peak at 2,925 cm$^{-1}$ was in conformity with the $-\text{CH}$ stretch, the adsorption band at 1,552 cm$^{-1}$ can be assigned to the amide II band of the amide bond, the peak at 1,251 cm$^{-1}$ can be assigned to the $-\text{COOH}$ and $\text{P=O}$ form of phosphate, and the peak at 1,151 cm$^{-1}$ may correspond to the C–O bond in carbohydrates and alcohols. As shown in Figure 8(b), after adsorption, the peaks around 2,925 cm$^{-1}$, 1,552 cm$^{-1}$ and 1,251 cm$^{-1}$ were obviously shifted to a lower adsorption band at 2,915 cm$^{-1}$, 1,545 cm$^{-1}$ and 1,245 cm$^{-1}$, respectively, indicating the $-\text{CH}$ group, the amide II band of the amide bond and the $-\text{COOH}$ and $\text{P=O}$ form of phosphate were taking part in the adsorption process. It cannot be ignored that after biosorption, the adsorption band at 1,151 cm$^{-1}$ disappeared, indicating that the carbohydrates and alcohols were involved in the adsorption. The most important part of the adsorption was the distinct peak at 916 cm$^{-1}$ that appeared (Figure 8(b)), which could be assigned to the asymmetric stretching vibration of $\text{UO}_2^{2+}$ (Liu et al. 2010).

**CONCLUSIONS**

The removal of low concentrations of uranium from aqueous solution by $A. \text{niger}$ was confirmed in equilibriums, and

**REFERENCES**


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