Uranium biosorption from aqueous solution by the submerged aquatic plant *Hydrilla verticillata*
Zheng-ji Yi, Jun Yao, Mi-jia Zhu, Hui-lun Chen, Fei Wang and Xing Liu

**ABSTRACT**

The biosorption characteristics of U(VI) from aqueous solution onto a nonliving aquatic macrophyte, *Hydrilla verticillata* (dry powder), were investigated under various experimental conditions by using batch methods. Results showed that the adsorption reached equilibrium within 60 min and the experimental data were well fitted by the pseudo-first-order kinetic model. U(VI) adsorption was strongly \( \text{pH} \) dependent, and the optimum \( \text{pH} \) for U(VI) removal was 5.5. Isotherm adsorption data displayed good correlation with the Langmuir model, with a maximum monolayer adsorption capacity of 171.52 mg/g. Thermodynamic studies suggested that U(VI) adsorption onto *H. verticillata* was an exothermic and spontaneous process in nature. Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy indicated that the amino and hydroxyl groups on the algal surface played an important role in U(VI) adsorption. The mechanisms responsible for U(VI) adsorption could involve electrostatic attraction and ion exchange. In conclusion, *H. verticillata* biomass showed good potential as an adsorption material for the removal of uranium contaminants in aqueous solution.

**Key words** | biosorption, *Hydrilla verticillata*, isotherm, kinetics, uranium

**INTRODUCTION**

With the rapid development of the nuclear industry, uranium mining and milling operations for nuclear power generation and nuclear weapon manufacture have led to the production of excessive amounts of radioactive uranium-bearing wastewater. Being highly toxic and radioactive, uranium is undoubtedly one of the most dangerous heavy metals to the environment. Uranium released into the environment can enter the ecological food chain and eventually be ingested by human beings. Long-term exposure to uranium can lead to cancer, kidney and liver damage, and physical malformations (Yin *et al.* 2015). The maximum permitted level of uranium in drinking water proposed by the US Environmental Protection Agency is only 30 \( \mu \text{g}/\text{L} \) (USEPA 2012). The ecological pollution and toxicity associated with uranium prompted environmentalists to look for efficient and rapid methods for uranium removal.

Biosorption is a promising approach that can be adopted to remove poisonous metals and radionuclides from wastewater. Traditional methods for heavy metal removal include chemical precipitation (Mellah *et al.* 2007), coagulation (Volkova *et al.* 2011), ion exchange (Rahmati *et al.* 2012), electrode dialysis (Zaki 2002), solvent extraction (Rout *et al.* 2012), and membrane separation (Khedr 2013). Compared with these methods, biosorption offers shorter operation time, lower operation cost, higher efficiency at low metal concentration, higher adsorption selectivity, and secondary contamination absence.

In the past decades, much effort has been devoted to the biosorption of uranium by using the biomass of various algae or aquatic plant species, such as brown algae (Moghaddam *et al.* 2013), *Cystoseira indica* (Keshtkar *et al.* 2012), *Padina* sp. (Khani 2011), and water hyacinth (Blainsa & D’Souza 2001). *Hydrilla verticillata* is a submersed perennial aquatic macrophyte that commonly grows in freshwater lakes, ponds, rivers, impoundments, and canals in China. *H. verticillata* can tolerate a wide range of \( \text{pH} \), nutrient, and light levels; hence, *H. verticillata* propagates very fast and covers large areas of the water surface it invades, leading to the restriction of several water recreational activities, such as fishing, boating, and swimming. Utilization of these widely distributed and abundant *H. verticillata* plants for uranium removal can change waste into resources. Previous investigations have reported that *H. verticillata* might be a good adsorption
material because it contains substantial amounts of functional groups or binding sites that could sequester several heavy metals, such as Ni(II) and Cr(VI) (Pilli et al. 2012; Mishra et al. 2016), Cu(II) and Zn(II) (Li et al. 2016), Pb(II) (Chathuranga et al. 2014), and Cd(II) (Huang et al. 2016).

In the present study, nonliving biomass of *Hydrilla verticillata* was utilized to remove U(VI) from aqueous solution. The U(VI) adsorption behavior of *H. verticillata* was investigated with regard to contact time, pH, and initial U(VI) concentration in batch tests. These parameters were optimized, and the equilibrium adsorption isotherms, kinetics, and thermodynamics were studied. The interaction mechanisms between U(VI) and *H. verticillata* were investigated through scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), and X-ray photoelectron spectroscopy (XPS).

**MATERIALS AND METHODS**

**Adsorbent, chemicals, and uranium standard solution**

*Hydrilla verticillata* biomass was provided by Honghu Liangshui Aquatic Plant Co. Ltd, Jingzhou, China. The fresh biomass without roots was extensively washed with running water to remove silt, sand, diatoms, and other epiphytic organisms. The biomass was first sun dried for 3 days and then oven dried at 80°C for 24 h (higher temperatures were not used to avoid possible degradation of organic matter). The dried biomass serving as the biosorbent was ground and allowed to pass through an 80-mesh sieve (i.e., pore size = 180 μm). The treated biomass was stored in a desiccator to be used in the biosorption experiments later.

A standard solution of U(VI) (1,000 mg/L) was obtained by dissolving 1.1792 g of U₃O₈ in a mixture of HCl and H₂O₂ (Zhang et al. 2014). U₃O₈ was supplied by the School of Nuclear Resources and Nuclear Fuel Engineering of the University of South China. Other desired concentrations (50–300 mg/L) were prepared by diluting the standard U(VI) solution with distilled water. All chemical reagents used were analytically pure without further treatment.

**Batch adsorption tests**

The adsorption experiments were carried out by batch tests in stoppered conical flasks of 250 mL. In brief, 0.12 g of the adsorbent was added in each flask containing 100 mL of uranium solution. The pH of the solutions was adjusted as needed with HCl (1.0 or 0.1 M) or NaOH (1.0 or 0.1 M) prior to each experiment. The adsorption equilibrium isotherm was obtained by varying the uranium ion concentration from 50 mg/L to 300 mg/L. Then, these flasks were placed on a reciprocal shaker at 140 r/min under the desired temperatures (298–318 K). The supernatants were sampled at appropriate time intervals, centrifuged at 5,000 × g for 5 min, and then used to determine residual U(VI) concentrations through standard spectrophotography (Chen & Zhao 1986). The uranium removal efficiency (Ad%) and uranium adsorption capacity (Q) were determined using the following equations:

\[
Ad\% = \frac{C_0 - C_t}{C_0} \times 100, 
\]

\[
Q_t = \frac{(C_0 - C_t) \times V}{W}, 
\]

\[
Q_e = \frac{(C_0 - C_e) \times V}{W}, 
\]

where Ad% represents the U(VI) removal efficiency; Qₜ and Qₑ represent the adsorption capacity (mg/g) at equilibrium and at time t (min), respectively; C₀, Cᵣ, and Cₑ represent the initial U(VI) concentration, liquid-phase U(VI) concentration at time t, and final equilibrium U(VI) concentration (mg/L), respectively; V represents the volume of the solution (L); and W represents the mass of the dried biomass (g). All experiments were carried out in triplicate. The arithmetic mean values of the calculations were then recorded. Control experiments were performed to ensure that no adsorption occurred on the walls of the glassware.

**Adsorption kinetics simulation**

Three common kinetic models, namely, pseudo-first-order, pseudo-second-order, and Elovich models, were chosen to fit the experimental data and to examine the controlling mechanism of the adsorption process.

The pseudo-first-order equation is a simple kinetic model to describe the kinetic process of a liquid-solid phase adsorption (Skodras et al. 2008), and its linear form can be expressed as follows:

\[
\ln (Q_e - Q_t) = \ln Q_e - k_1t, 
\]

where Qₑ is the equilibrium concentration (mg/g), Qₜ is the concentration at time t (mg/g), k₁ is the pseudo-first-order rate constant (min⁻¹), and t is time (min).
where \( k_1 \) is the rate constant of the pseudo-first-order sorption (min\(^{-1}\)). Obviously, \( k_1 \) can be derived from the slope of the plot of \( \ln (Q_e - Q_t) \) against \( t \).

The pseudo-second-order model based on the adsorption equilibrium capacity can be written as the following linear form (Wang & Li 2005):

\[
\frac{t}{Q_t} = \frac{t}{Q_e} + \frac{1}{k_2 Q_e^2},
\]

where \( k_2 \) is the rate constant of pseudo-second-order sorption (g mg\(^{-1}\) min\(^{-1}\)). Obviously, \( Q_e \) and \( k_2 \) can be obtained experimentally by plotting \( t/Q_t \) against \( t \) and by using further linear regression analysis.

The Elovich model is commonly adopted not only to model reactions involving chemisorption of gases on a solid surface but also to characterize adsorption kinetics in an aqueous phase. The Elovich equation could be expressed as follows (Zare et al. 2015):

\[
Q_t = \frac{1}{\beta} \ln (\alpha \beta E) + \frac{1}{\beta} \ln (t),
\]

where \( \alpha \beta \) represents the initial adsorption rate (mg g\(^{-1}\) min\(^{-1}\)) and \( \beta \) is related to the occupied surface (g/mg).

**Equilibrium isotherm simulation**

Four extensively utilized adsorption isotherm models, namely, Langmuir, Freundlich, Dubinin–Radushkevich (D–R), and Temkin, were chosen to fit the experimental data and to characterize the adsorption isotherms precisely. The deviation between the experimentally observed and theoretically calculated data can be described through the square of the correlation coefficient \( (R^2) \).

The Langmuir model assumes adsorption homogeneity, such as uniformly energetic adsorption sites, monolayer surface coverage, and absence of interactions among adsorbate molecules in adjacent sites (Zhao et al. 2011). The linear Langmuir equation can be expressed as follows:

\[
\frac{C_e}{Q_e} = \frac{1}{Q_{max} C_e} + \frac{1}{bQ_{max}},
\]

where \( Q_{max} \) is the maximum amount of metals adsorbed per unit of weight of the adsorbent (mg/g) and \( b \) is a constant related to the appetency of adsorption sites for metals (L/mg). \( Q_{max} \) and \( b \) can be derived from the plot of \( C_e/Q_e \) against \( C_e \). On the basis of further analysis of the Langmuir equation, Langmuir adsorption isotherm can be described using an equilibrium parameter \( (R_L) \) calculated by using the following equation:

\[
R_L = \frac{1}{1 + b \times C_0},
\]

where \( R_L \) implies whether the adsorption process is irreversible \( (R_L = 0) \), favorable \( (0 < R_L < 1) \), linear \( (R_L = 1) \), or unfavorable \( (R_L > 1) \).

The Freundlich isotherm may be appropriate for non-ideal adsorption onto heterogeneous surfaces involving multilayer adsorption (Tan et al. 2008). The linear Freundlich equation can be written as follows:

\[
\ln Q_e = \ln K_F + \frac{1}{n} \ln C_e,
\]

where \( K_F \) is the Freundlich constant describing the adsorption capacity of the adsorbent \( ((mg/g)(L/mg)^{1/n}) \) and \( n \) is the Freundlich exponent depicting adsorption intensity (dimensionless). \( K_F \) and \( n \) can be obtained from the plot of \( \ln Q_e \) against \( \ln C_e \).

The Temkin isotherm considers the interaction between the adsorbent and the adsorbate, and assumes that the free energy of adsorption is a function of the surface coverage. Its linear form is expressed as follows (Adewuyi et al. 2016):

\[
Q_e = a \ln K_T + a \ln C_e,
\]

where \( K_T \) is an equilibrium parameter corresponding to the maximum binding energy \( (L/g) \) and \( a \) is a dimensionless constant related to the temperature and adsorption system.

The adsorption data were also correlated by the D–R model to distinguish between physical and chemical adsorption (Luo et al. 2016). The linear form of the D–R isotherm is expressed as follows:

\[
\ln Q_e = \ln Q_{DR} - \frac{b}{2} C_e^2,
\]

where \( Q_e \) is the adsorption capacity at equilibrium (mol/g), \( Q_{DR} \) is the theoretical D–R monolayer adsorption capacity (mol/g), \( b \) (mol\(^2\)/J\(^2\)) is a constant related to biosorption energy, and \( \varepsilon \) (J/mol) is the Polanyi potential related to the equilibrium concentration and can be written as follows:

\[
\varepsilon = RT \ln (1 + \frac{1}{C_e}).
\]
where R is the universal gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)) and T (K) is the absolute temperature. The mean biosorption energy, \(E\) (kJ/mol), which gives information about chemical and physical adsorption, can be calculated by using the following equation:

\[
E = \frac{1}{\sqrt{2\beta}}.
\] (13)

The \(E\) value is in the ranges of 0–8 and 8–16 kJ/mol, which indicate physical and chemical biosorption, respectively.

**Thermodynamic studies**

The thermodynamic parameters could be calculated using the distribution coefficient \(K_d\) (\(Q_e/C_s\)), which is dependent on temperature. The standard free energy change (\(\Delta G^0\)), standard enthalpy change (\(\Delta H^0\)), and standard entropy change (\(\Delta S^0\)), which are all associated with the adsorption process, could be determined through the following equations (Sari et al. 2007):

\[
\Delta G = -RT \ln K_d,
\] (14)

\[
K_d = \frac{Q_e}{C_s},
\] (15)

\[
\ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT},
\] (16)

In terms of Equation (16), \(\Delta H^0\) and \(\Delta S^0\) could be obtained from the slope and intercept of the plot of \(\ln K_d\) versus \(1/T\).

**FTIR, SEM, and XPS analyses**

The dry powder of *H. verticillata* (0.12 g) with exposure to 100 mL of 150 mg/L U(VI) solution at pH 5.5 for 1 h was separated by centrifugation (4,000 g, 10 min) to discard the supernatants. Subsequently, the precipitate and the raw algal powder without exposure to U(VI) were dehydrated using vacuum freeze drying. The samples before and after U(VI) biosorption were characterized using FTIR, SEM, and XPS analyses. FTIR was carried out using NICOLET iS10 (Thermo Scientific) within 500–4,000 cm\(^{-1}\) and KBr pellets. The surface profile of *H. verticillata* was examined using a scanning electron microscope (Model S-4800, Hitachi, Tokyo, Japan). The samples were sputter coated with gold prior to SEM examination. XPS was obtained by a Thermo Fisher Scientific ESCALAB-250 spectrometer equipped with a monochromatic Al Ka X-ray excitation source (1,486.5 eV). The XPS spectra were recorded in the fixed analyzer transmission mode at a pass energy of 20 eV and a step size of 0.1 eV, and obtained at 8 × 10\(^9\) Pa.

**RESULTS AND DISCUSSION**

**Effect of contact time and adsorption kinetic studies**

The kinetic result of U(VI) adsorption by *H. verticillata* is shown in Figure S1 (available with the online version of this paper). U(VI) adsorption rapidly occurred during the first 20 min, after which the process slowed down and achieved an equilibrium state after 60 min (Figure S1(a)). The observed higher adsorption rate at the initial stage may be due to the considerable concentration gradient between the adsorbate on the surface of the adsorbent and the adsorbate in the solution. With time elapsed, this concentration gradient declined because of the binding of U(VI) ions to the vacant sites, which decreased the adsorption rate at the later stage. On the basis of the above analysis, the 60 min shaking time was suitable for maximum adsorption and was adopted in the subsequent biosorption experiments.

Moreover, kinetic adsorption data were fitted by using pseudo-first-order (Figure S1(b)), pseudo-second-order (Figure S1(c)), and Elovich kinetic equations (Figure S1(d)). The model parameters were calculated and are listed in Table 1. The correlation coefficient (\(R^2\)) of the Elovich model is less than 0.99, indicating that this model cannot be used to describe the kinetic profile because of the apparent lack of linear correlation. Notably, although the \(R^2\)

<table>
<thead>
<tr>
<th>Model</th>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pseudo first order</td>
<td>(k_1) (min(^{-1}))</td>
<td>0.0557</td>
</tr>
<tr>
<td></td>
<td>(Q_e) (mg/g)</td>
<td>106.39</td>
</tr>
<tr>
<td></td>
<td>(R^2)</td>
<td>0.996</td>
</tr>
<tr>
<td>Pseudo second order</td>
<td>(k_2) (g mg(^{-1}) min(^{-1}))</td>
<td>6.92 × 10(^{-4})</td>
</tr>
<tr>
<td></td>
<td>(Q_e) (mg/g)</td>
<td>116.41</td>
</tr>
<tr>
<td></td>
<td>(R^2)</td>
<td>0.996</td>
</tr>
<tr>
<td>Elovich</td>
<td>(q_e) (g mg(^{-1}))</td>
<td>20.60</td>
</tr>
<tr>
<td></td>
<td>(\beta_1) (g mg(^{-1}))</td>
<td>0.0419</td>
</tr>
<tr>
<td></td>
<td>(R^2)</td>
<td>0.9091</td>
</tr>
<tr>
<td></td>
<td>(Q_e) (mg/g)</td>
<td>ca. 105</td>
</tr>
</tbody>
</table>

Downloaded from https://iwaponline.com/wst/article-pdf/75/6/1332/454865/wst075061332.pdf by guest
values for the pseudo-first-order and pseudo-second-order models were both greater than 0.99, only the theoretical equilibrium adsorption capacity ($Q_e$) of the former approached the experimental equilibrium adsorption capacity ($Q_{e,exp}$). Therefore, the U(VI) adsorption onto *H. verticillata* could be best characterized by the pseudo-first-order kinetic model. This result indicates that the U(VI) biosorption process is controlled by the metal diffusion at the initial stage and that the adsorption rate constant is affected by the number of active sites on the algal surface.

**Effect of pH**

Solution pH is a critical parameter affecting the adsorption performance of adsorbents because pH variation influences the speciation of metal and the adsorbent surface characteristics. The influence of pH on the U(VI) adsorption onto *H. verticillata* was examined at different pH values ranging from 1.0 to 7.0. The results are presented in Figure 1. Evidently, the U(VI) removal efficiency and adsorption capacity both increased with the increase in initial pH from 1.0 to 4.5. In other words, lower pH was unfavorable to U(VI) removal. In the pH range of 4.5–5.5, the maximum U(VI) removal efficiency (85.12%) and the maximum adsorption capacity (106.40 mg/g) were both achieved. As the pH was further increased from 5.5 to 7.0, U(VI) uptake slightly diminished. These findings can be also explained as follows.

On the one hand, under acidic pH values, some functional groups on the surface of *H. verticillata* will be protonized, which complicates the use of these groups for the sequestration of U(VI). In other words, a number of protonized, which complicates the use of these groups for the utilization groups on the surface of *H. verticillata* will be protonized, which complicates the use of these groups for the sequestration of U(VI). On the other hand, the speciation of different uranyl hydrolyzed products at varying pH values also had great effect on the U(VI) biosorption. The predominant forms of uranium ions as a function of pH were determined by using the Visual MINTEQ software, and the calculation results are shown in Figure S2 (available with the online version of this paper). When the pH level was changed from 1.0 to 7.0 for a fixed concentration of 150 mg/L U(VI), the species distribution of uranium varied considerably. When the pH was lower than 4.0, U(VI) occurs chiefly in the form of uranyl cations (UO$_2^{2+}$) in acidic solutions. Uranyl cations (UO$_2^{2+}$) account for the highest percentage of uranium species, which could be sequestered through the binding sites on the surface of *H. verticillata*. Meanwhile, in the acidic environment with a pH level lower than 4.0, an increase in pH may lead to a decrease in free uranyl level because of the formation of various hydrolyzed hydroxo complexes of U(VI), such as UO$_2$(OH)$_2$,$^+$, (UO$_2$)$_2$(OH)$_3^{2+}$, and (UO$_2$)$_3$(OH)$_4^2-$, which could consequently weaken the competition between H$^+$ and UO$_2^{2+}$ for binding sites on the *H. verticillata* surface and enhance the uranium uptake. Therefore, the U(VI) uptake increased with increasing pH to a certain extent (pH < 4.5).

However, when the pH level was greater than 5.5, the schoepite precipitate (4UO$_2$·9H$_2$O) was produced, and the dissolved U(VI) concentration decreased in the solution, which consequently decreased U(VI) uptake (Khani 2011). In terms of this experimental result, the solution pH of 5.5 was used as the optimum pH in further experiments of U(VI) adsorption onto *H. verticillata*.

**Adsorption isotherm**

The isotherm parameters of U(VI) adsorption onto *H. verticillata* were calculated using the Langmuir, Freundlich, D–R, and Temkin models (Figure S3, available with the online version of this paper), and the results are shown in Table 2. Evidently, the $R^2$ value of the Langmuir model was not only close to 1.0 but was also higher than those of the three other models. On the basis of the comparison of $R^2$ values, the U(VI) adsorption onto *H. verticillata* could be well described by the Langmuir isotherm parameter. These results indicate that U(VI) biosorption is very close to a homogenous and monolayer adsorption system.

The characteristic Langmuir isotherm parameter that indicates the type of the isotherm is the dimensionless
factor $R_L$. As shown in Table 2, the $R_L$ values for all initial concentrations were in the range of $0 < R_L < 1$, indicating that the adsorption of uranium ion by *H. verticillata* is favorable. The $Q_{\text{max}}$ (maximum uranium adsorption capacity) of *H. verticillata* was 171.52 mg/g. Comparisons between the maximum uptake capacity of *H. verticillata* and that of the other adsorbents for U(VI) in previous studies show that the adsorption of uranium ion by *H. verticillata* was feasible and spontaneous. The positive value of $\Delta G^0$ demonstrated that the degree of freedom or randomness at the solid–liquid interface increased during U(VI) adsorption and confirmed the excellent affinity of U(VI) ions toward the algal surface. To sum up, both enthalpy and entropy were the driving force of biosorption from the thermodynamic point of view.

### Characterization of *H. verticillata*

**FTIR spectra of *H. verticillata***

Figure 2 shows the FTIR spectra of *H. verticillata* before and after U(VI) biosorption in the 500–4,000 cm$^{-1}$ region. Before U(VI) adsorption, a broad band observed at 3,290 cm$^{-1}$ was assigned to the O–H and N–H stretching vibrations, suggesting that hydroxyl (–OH) and amino (–NH$_2$) groups were existent on the surface of *H. verticillata*. The two absorption peaks at 2,920 and 1,420 cm$^{-1}$ corresponded to the C–H stretching vibration and C–H scissor bending vibration of CH$_2$ (methylene) in the carbon chain, respectively. The absorption peak observed at 1,620 cm$^{-1}$ could be attributed to the N–H bending vibration of the amino group. Meanwhile, the absorption peak at 1,020 cm$^{-1}$ could be associated with the C–O stretching vibration of the primary hydroxyl groups (–CH$_2$OH), which could be considered as the characteristic absorption peaks of structural polysaccharides in the algal cell wall.

### Thermodynamic and kinetic parameters of biosorption

The values of $\Delta H^0$, $\Delta S^0$, and $\Delta G^0$ were calculated using the plot of $\ln K_d$ against $1/T$ (Figure S4, available with the online version of this paper), and the results are shown in Table 4. The negative values of $\Delta G^0$ indicate that the adsorption of U(VI) ions onto *H. verticillata* was feasible and spontaneous. The $\Delta G^0$ decreased and became more negative with increasing temperature, indicating better adsorption at high temperatures. The negative value of $\Delta H^0$ signifies the exothermic nature of the adsorption process. The positive value of $\Delta S^0$ demonstrated that the degree of freedom or randomness at the solid–liquid interface increased during U(VI) adsorption and confirmed the excellent affinity of U(VI) ions toward the algal surface.

### Table 2 | Isotherm parameters for the adsorption of U(VI) onto *H. verticillata*

<table>
<thead>
<tr>
<th>Model</th>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>$Q_{\text{max}}$ (mg/g)</td>
<td>171.52</td>
</tr>
<tr>
<td></td>
<td>$b$</td>
<td>0.069</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.998</td>
</tr>
<tr>
<td></td>
<td>$R_L$</td>
<td>0.046–0.224</td>
</tr>
<tr>
<td>Freundlich</td>
<td>$K_F$ (mg$^{(1-n)}$·g L$^{-1}$)</td>
<td>25.18</td>
</tr>
<tr>
<td></td>
<td>$n$</td>
<td>2.442</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.915</td>
</tr>
<tr>
<td>Temkin</td>
<td>$K_T$</td>
<td>0.7735</td>
</tr>
<tr>
<td></td>
<td>$a$</td>
<td>35.27</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.979</td>
</tr>
<tr>
<td>D–R</td>
<td>$Q_{DR}$ (mol/g)</td>
<td>$1.671 \times 10^{-3}$</td>
</tr>
<tr>
<td></td>
<td>$\beta$ (mol$^2$/J$^2$)</td>
<td>$4.857 \times 10^{-9}$</td>
</tr>
<tr>
<td></td>
<td>$E_{DR}$ (J/mol)</td>
<td>$1.015 \times 10^4$</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.9528</td>
</tr>
</tbody>
</table>

### Table 3 | Comparison of the U(VI) adsorption capacity with other adsorbents

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>$Q_{\text{max}}$ (mg/g)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuCl$_2$ –modified giant kelp biomass</td>
<td>156</td>
<td>[Zhou et al. (2016)]</td>
</tr>
<tr>
<td>Brown algae <em>Dictyopteris polymodioides</em></td>
<td>62.5</td>
<td>[Bampaiti et al. (2016)]</td>
</tr>
<tr>
<td>AgOH–multiwalled carbon nanotubes nanoparticles</td>
<td>140</td>
<td>[Zare et al. (2015)]</td>
</tr>
<tr>
<td>Brown algae <em>Laminaria japonica</em></td>
<td>96.4</td>
<td>[Lee et al. (2014)]</td>
</tr>
<tr>
<td>Polyvinyl alcohol (PVA)/titanium oxide (TiO$_2$) nanofiber</td>
<td>196.1</td>
<td>[Abbasizadeh et al. (2015)]</td>
</tr>
<tr>
<td>PVA-g-amidoxime</td>
<td>42.84</td>
<td>[Chi et al. (2015)]</td>
</tr>
<tr>
<td>Magnetic Mg-Al layered double hydroxide intercalated with citrate</td>
<td>180</td>
<td>[Zhang et al. (2012)]</td>
</tr>
<tr>
<td>Conventional activated carbon</td>
<td>45.24</td>
<td>[Morsy &amp; Hussein (2011)]</td>
</tr>
<tr>
<td>Chitosan impregnated with magnetite nanoparticles</td>
<td>42</td>
<td>[Stopa &amp; Yamaura (2010)]</td>
</tr>
<tr>
<td><em>H. verticillata</em> (L.f.) Royle</td>
<td>78</td>
<td>[Srivastava et al. (2010)]</td>
</tr>
<tr>
<td><em>H. verticillata</em></td>
<td>171.52</td>
<td>This research</td>
</tr>
</tbody>
</table>

### Table 4 | Thermodynamic parameters and corresponding correlation coefficient values for uranium biosorption onto *H. verticillata*

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$\Delta H^0$ (kJ mol$^{-1}$)</th>
<th>$\Delta S^0$ (kJ mol$^{-1}$ K$^{-1}$)</th>
<th>$\Delta G^0$ (kJ mol$^{-1}$)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>$-20.97$</td>
<td>$-10.14$</td>
<td>$36.39$</td>
<td>0.967</td>
</tr>
<tr>
<td>305</td>
<td>$-21.22$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>312</td>
<td>$-21.52$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>318</td>
<td>$-21.67$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
However, obvious changes were found in the FTIR absorption bands for *H. verticillata* after U(VI) biosorption. The absorption peaks at 3,290, 1,620, and 1,020 cm\(^{-1}\) shifted to 3,300, 1,630, and 1,010 cm\(^{-1}\), respectively. However, all of the three infrared absorption peaks decreased in intensity after U(VI) biosorption. These findings implied that the –OH and –NH\(_2\) groups played a significant role in U(VI) biosorption. Other related research on U(VI) biosorption onto a brown alga (giant kelp) also suggested that the –OH and –NH\(_2\) groups are responsible for this adsorption process (Zhou et al. 2016). They conjectured that the O atom in –OH and the N atom in –NH\(_2\) on the kelp surface adopt sp\(^3\) hybridization to participate in bonding with the H atom. Moreover, two lone pairs of electrons located on the O atom and one lone pair of electrons on the N atom might fill the empty orbital of positively charged U(VI) ions and thus form U ← O and U ← N coordination bonds, which could promote chemisorption. In the present study, whether the complexation between U(VI) ions and functional groups (hydroxyl and amino) on the *H. verticillata* surface occurred requires further in-depth study. Notably, the absorption peak intensity of CH\(_2\) decreased or even disappeared after the adsorption of U(VI), although the absorption peak position of C–H stretching vibration and C–H scissor bending vibration of CH\(_2\) remain unchanged. The former suggested that CH\(_2\) could not bond with U(VI) and minimally contributed to U(VI) adsorption, whereas the latter suggested that the CH\(_2\) of the bone chain originally present on the algal surface could enter and hide inside during U(VI) adsorption, thus decreasing surface CH\(_2\) density.

**SEM images of *H. verticillata***

SEM is a powerful diagnostic tool for morphological research. The morphology of *H. verticillata* before and after exposure to U(VI) was observed using SEM (Figure 3). In general, the surface of raw *H. verticillata* was relatively smooth and showed a special texture, where a series of stripe ribbons with the width ranging from 15 \(\mu\)m to 25 \(\mu\)m was juxtaposed (Figure 3(a)).

After the U(VI) biosorption, the algae had an uneven surface and assumed an abundant irregular rectangular structure with a side length of about 30–60 \(\mu\)m (Figure 3(b)). Moreover, several concave grooves appeared among the neighboring rectangles. Comparing Figure 3(a) with 3(b), we determined that *H. verticillata* could adjust its surface structure to ensure the uptake of U(VI). In other words, its grooved and rough surface could be beneficial in creating a high-affinity adsorption toward adsorbate molecules.
XPS spectra of H. verticillata

XPS provides quantitative elemental and chemical state as well as functional group information from the surface of materials. The XPS wide-scan spectra for the raw H. sample as well as that taken after U(VI) uptake are shown in Figure 4(a) and 4(b). The figures also provide details about the types and atomic concentrations of all elements. The U4f narrow-scan spectrum for the H. verticillata sample collected after U(VI) uptake is shown in Figure S5 (available with the online version of this paper).

For the raw H. verticillata sample, C, O, N, and Si constituted the main nonmetal elements of the algae, whereas Ca and Al constituted the main metal elements of the algae (Figure 4(a)). In addition, the chemical composition of the algae contained no uranium, which could indicate that uranium is nonexistent or negligible in the environment for its propagation. For the H. verticillata sample collected after U(VI) uptake, the uranium peaks were observed in the XPS wide-scan spectrum (Figure 4(b)). In addition, the high-resolution XPS spectrum of H. verticillata collected after U(VI) biosorption showed the appearance of U4f5/2 and U4f7/2 peaks at 393.18 and 382.58 eV, respectively (Figure S5). Previous studies found the U4f5/2 and U4f7/2 peaks of U(VI) at 392.9 ± 0.3 and 382.2 ± 0.3 eV, respectively, and the U4f5/2 and U4f7/2 peaks of U(IV) at 391.5 ± 0.3 and 380.4 ± 0.3 eV, respectively (Kushwaha et al. 2012). Therefore, uranium remained unchanged in the hexavalent state throughout the biosorption.

Notably, the atomic concentrations of Ca and Al dropped below their detection limits after U(VI) biosorption, suggesting that ion exchange occurred between U and Ca/Al. The discussion of the pH effect in combination with instrumental XPS and FTIR analyses suggests that the mechanisms responsible for U(VI) biosorption could involve electrostatic attraction and ion exchange.

CONCLUSIONS

The present study investigated the adsorption of U(VI) onto the dry powder of H. verticillata under various experimental conditions and examined the effect of these parameters on U(VI) adsorption. The optimum pH for U(VI) biosorption was 5.5. The adsorption of U(VI) by H. verticillata followed Langmuir adsorption isotherm. The adsorption kinetics for H. verticillata could be described by the pseudo-first-order model. The thermodynamic parameter values indicated that the U(VI) adsorption onto H. verticillata is exothermic and spontaneous. The possible adsorption mechanism could involve electrostatic attraction and ion exchange. The results of this study demonstrated that H. verticillata could be used as an efficient adsorbent for U(VI) removal.

ACKNOWLEDGEMENTS

This work is supported in part by grants from Key Project from National Natural Science Foundation of China (41430106), National Natural Science Foundation of China (41273131, 41273092 & 41573080), Public Welfare Project of Chinese Ministry of Environmental Protection (201509049), Aid Programs for Science and Technology Innovative Research Team in Higher Educational
Institutions of Hunan Province and the Key Discipline of Hunan Province.

REFERENCES


Kushwaha, S., Sreedhar, B. & Padmaja, P. 2012 XPS, EXAFS, and FTIR as tools to probe the unexpected adsorption-coupled reduction of U(VI) to U(V) and U(IV) on Borassus flabellifer-based adsorbents. Langmuir 28 (46), 16038–16048.


Li, G. X., Li, Q. S., Zhang, D. D. & Wang, L. 2016 Biosorption of Cu(II) and Zn(II) ions from aqueous solution by a new sorbent prepared from Hydrilla verticillata and Fe3O4 nanoparticles: one-component and binary systems. Desal. Water Treat. 57 (18), 8480–8493.


USEPA, United States Environmental Protection Agency 2012 2012 Edition of the Drinking Water Standards and Health Advisories, EPA 822-S-12-001, Office of Water, US.
Environmental Protection Agency, Washington, DC, p. 9.

Volkova, T. S., Medvedev, V. P. & Fedorova, O. V. 2011


First received 2 July 2016; accepted in revised form 5 December 2016. Available online 23 December 2016.