

Research Article

Adsorption of Uranium(VI) from Aqueous Solution by Modified Rice Stem

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The biosorption is an effective and economical method to deal with the wastewater with low concentrations of uranium. In this study, we present a systematic investigation of the adsorption properties, such as the kinetics, thermodynamics, and mechanisms, of modified rice stems. The rice stems treated with 0.5 mol/L NaOH solutions show higher removal percentage of uranium than those unmodified under the conditions of initial pH (pH = 4.0), absorbent dosage (5–8 g/L), temperature ($T = 298$ K), and adsorption equilibrium time ($t = 180$ min). The removal percentage of uranium(VI) decreases with increasing initial concentration of uranium(VI). The Langmuir isotherm model, which suggests predominant monolayered sorption, is better than Freundlich and Temkin models to elucidate the adsorption isotherm of adsorbed uranium. Kinetic analyses indicate that the uranium(VI) adsorption of the modified rice stem is mainly controlled by surface adsorption. The pseudo-second-order kinetic model, with the correlation coefficient of $R^2 = 0.9992$, fits the adsorption process much better than other kinetic models (e.g., pseudo-second-order kinetic model, Elovich kinetic model, and intraparticle diffusion model). The thermodynamic parameters ΔG^0 , ΔH^0 , and ΔS^0 demonstrate that the adsorption of uranium(VI) is an endothermic and spontaneous process, which can be promoted by temperature. The adsorption of uranium can change the morphology and the structure characteristics of the modified rice stem through interaction with the adsorption sites, such as O-H, C=O, Si=O, and P-O on the surface.

1. Introduction

Uranium is a heavy metal with significant chemical toxicity and radioactivity. Since the leakage of radio nuclides in the Japan's Fukushima Daiichi nuclear plant, the uranium contamination has attracted more and more attentions. Large amounts of uranium released from aqueous solutions of natural deposits, uranium mill tailings, and ammunition have migrated into the environment [1, 2]. If uranium-containing wastewater is drained directly without appropriate treatment, the uranium would be absorbed by the humic and mineral materials and gradually enter the biological-geochemical circulation, finally breaking the organism's normal metabolism and even endangering human health and the ecosystem's safety. For example, the uranium leaking into the environment can cause extensive human

diseases (e.g., skin erythema, trichomadecis, nephritis, leukaemia, and bone cancer) and even deaths [3]. Therefore, it is critically important to prevent the uranium of wastewater from transporting into the environment.

Many methods, such as chemical precipitation-crystallizing, ion exchange, solvent extraction, and film separation [4–9], have so far been developed to deal with the uranium-containing wastewater. However, these methods are not effective and economical, especially when treating large amounts of wastewater containing the low contents of the radioactive ionic material [10]. Therefore, it is urgent to develop low-cost and easily obtained uranium sorbents for efficient treatment of uranium-containing wastewater. Biosorption has been considered to be a useful method as it utilizes various natural materials of biological origin, including bacteria, fungi yeast and algae, to remove metal ions

from solutions [11–14]. Compared with the traditional methods, the biosorption has the following advantages: (1) the fast sorption kinetic and high selectivity for removing low concentrations of heavy metals (e.g., uranium); (2) low energy consumption; (3) abundant sources of biosorbents; (4) simple operation; (5) wide operation ranges of pH and temperature; and (6) good reproduction of adsorbents.

The treatment of heavy metals through biosorption has been extensively studied in the past decades. The researches mainly focus on the selectivity of the biosorbents, the biosorption kinetics and thermodynamics, the biosorption mechanism, and large-scale experiments [15–18]. Currently, some potential biomaterials with higher adsorption capacity of heavy metals have been adopted to treat uranium-containing wastewater. From an economic point of view, researchers mainly use various disposed products from industries or agricultural farms as adsorbents. Thus, it is necessary to seek the most promising biosorbents from an extremely large pool of easily available and inexpensive biomaterials. Disposed agricultural products such as biosorbents are considered to be one of the most potential adsorbents [19]. Until now, various disposed agricultural biosorbents, such as wood powder, wheat straw, grapefruit peel, coir pith, and banyan leaves [19–22], have been investigated for the adsorption of uranium(VI). These biosorbents have been identified as an efficient kind of sorbent for adsorption of uranium.

There are abundant low-cost rice stems from agricultural wastes. At present, the world annual output amounts of the rice stem are over 17 billion tons. Large amounts of rice stem are burnt as fertilizer, resulting in environmental pollution and waste of resources. The rice stem, which is composed of rice hemicellulose, cellulose, lignin, and protein, can be used to efficiently solve the environmental pollution caused by metals in an economical and eco-friendly way because it has unique characteristics to remove the metal ion from aqueous solution. Some researchers have recognized the feasibility of rice stem for the treatment of wastewater. For example, Liu [23] and Amin et al. [24] suggested that rice stem had a great ability to enrich organic contaminants (e.g., methylene blue and phenol). However, while Sugashini [25] studied the sorption of heavy metal ions (Hg^{2+} , Cr^{3+} , and Mo^{3+}) by rice stem, very few studies have reported the rice stem as a biosorbent [26] for treatment of the wastewater with low contents of uranium.

In this study, the rice stem is chosen to deal with the wastewater with low contents of uranium. The main aim of this study is to investigate the effects of different experimental conditions, such as modified methods, pH, adsorbent dose, initial concentration, sorption equilibrium time, and temperature. In addition, the thermodynamics and mechanism of sorption were also systematically investigated based on the batch experiments of uranium(VI) ions adsorption. Our study suggests that the modified rice stem is a kind of promising biosorbent material to efficiently and economically remove uranium(VI) from the wastewater.

2. Materials and Methods

2.1. Materials. All the chemicals and reagents used in this study were analytically pure. The rice stem was supplied by

Hengyang County, Hunan Province. Uranium stock solution was prepared by dissolving a certain amount of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in distilled water, and the initial pH of the uranium(VI) solution was adjusted by addition of 10% HCl and 10% NaOH.

2.2. Preparation of Rice Stem. Rice stems were cut into 5 cm segments and then washed in running water twice and in distilled water once. The washed rice stems were dried in the oven at 80°C for 24 h. Then, the solids were ground into 60 mesh.

2.3. Batch Sorption Experiments. 40 mL uranium(VI) ion solution was put into a 250 mL Erlenmeyer flask. The pH of solution was adjusted by addition of HCl and NaOH in each experiment. A certain amount of rice stem was added into the Erlenmeyer flask placed in the constant temperature water bath oscillator. The experiment was carried out for 120 min. The suspension was separated by centrifuging at 4000 rpm for 10 min. Then, the supernatant liquid was filtered, and the filtrate was used to analyze the concentration of uranium by 5-Br-PADAP (used as a chromogenic agent in the spectrophotometric method). The uranium(VI) removal percentage R (%) and adsorption capacity Q_t (mg/g) were determined using the following equations, respectively:

$$R = \frac{(C_0 - C_t)}{C_0} \times 100\%, \quad (1)$$

$$Q_t = \frac{(C_0 - C_t)}{m} \times V,$$

where C_0 and C_t represent the initial concentration and concentration at time t , respectively, with the unit of mg/L; V is the volume of uranium solution (mL); and m is the mass of the sorbent (g).

3. Results and Discussion

3.1. Effect of the Modified Materials. 4 g of rice stem was added into 50 mL mixture of NaOH, HCl, H_2O_2 , ammonium hydroxide, and citric acid solutions and then stirred for 24 h. The resulted mixture was filtered and washed with distilled water at the same time, until the pH of the rice stem was close to neutral. Then, the modified rice stem was dried in the oven at 80°C for 24 h. The color changes of modified rice stem are shown in Figure 1. In this study, the effect of the modified materials on the adsorption capacity of rice stem is investigated using ion solutions of $10 \text{ mg} \cdot \text{L}^{-1}$ uranium(VI) at pH = 5. 0.2 g of different modified rice stems was added into aqueous solution containing $10 \text{ mg} \cdot \text{L}^{-1}$ of uranium(VI) at room temperature, where the reaction lasted for 120 min. The experimental results are given in Table 1.

Figure 1 shows the difference in color and texture of modified rice stem after modification through different ways. The NaOH-modified rice stems show lighter color and slimmer and softer texture. The rice stem treated with 0.5 mol/L NaOH has the highest uranium removal rate

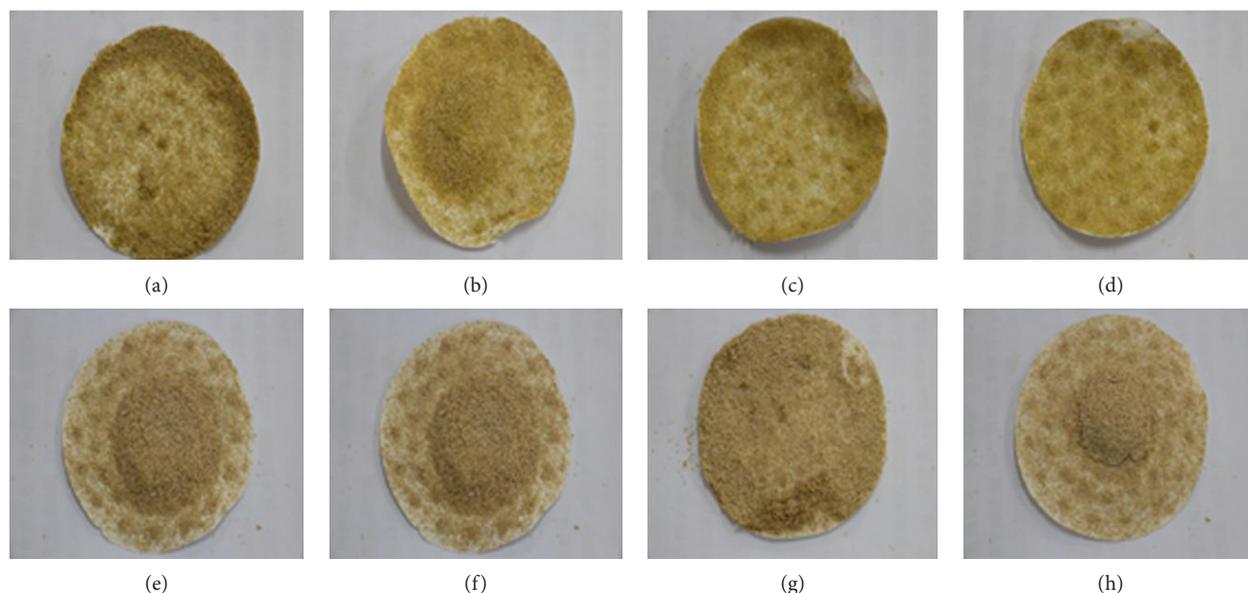


FIGURE 1: The hue changes of rice stem before and after modification by the modified materials: (a) 0.25 mol/L NaOH; (b) 0.5 mol/L NaOH; (c) 1.0 mol/L NaOH; (d) 1.5 mol/L NaOH; (e) HCl; (f) H₂O₂; (g) ammonium hydroxide; (h) citric acid.

TABLE 1: Effect of modified materials on adsorption of uranium(VI).

Modified methods	Removal rate (%)	Adsorption capacity (mg/g)
—	76.11	1.52
0.25 mol/L NaOH	92.00	1.84
0.5 mol/L NaOH	94.55	1.89
1 mol/L NaOH	93.84	1.88
1.5 mol/L NaOH	87.68	1.75
HCl	89.46	1.79
H ₂ O ₂	92.74	1.85
Ammonium hydroxide	91.98	1.84
Citric acid	79.09	1.58

(94.55%) because of many SiO₂ and nonaromatic esters in the surface of modified rice stem [27], which were dissolved out by NaOH. In this kind of modified rice stem, the cross-linked network structure among cellulose, hemicellulose, and lignin were broken and then exposed to the surface of sorbents [28]. Thus, the uranium removal percentage increases as a result of increasing specific surface area.

3.2. Effect of the Initial pH. The pH of solution has been considered as one of the most important parameters affecting uranium ion sorption because it can change the ionic forms of the uranyl ions. The effect of the initial pH on the adsorption capacity of modified rice stem is investigated using ion solutions of 10 mgL⁻¹ uranium(VI), where the pH values (pH = 1.4–7.0) are adjusted using HCl and NaOH at room temperature. The solutions were mixed with 0.2 g modified rice stem, where the reaction lasted for 120 min. The experimental results of the initial pH are shown in Figure 2, which indicates that uranium(VI) removal percentage and adsorption capacity reaches the maximum value (97.6% and

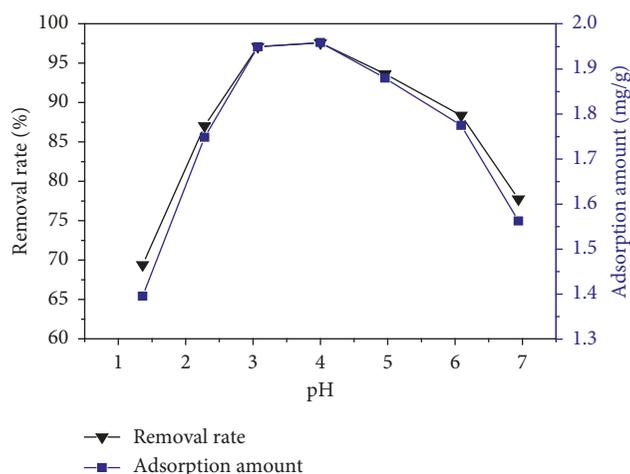


FIGURE 2: The effect of pH on adsorption of uranium(VI) by modified rice stem.

1.95 mg/g at pH = 4.0, respectively) with pH values increasing from 3.0 to 4.0. But the uranium removal percentage and adsorption capacity decrease when pH values increase from 4.0 to 7.0. The results demonstrate that pH = 4 is the most efficient pH value for removal of U(VI) by modified rice stem. It could explain the differences between the existence species of the uranium ion and the cell's surface activity sites at different pH values [29]. At lower pH values, H⁺ (or H₃O⁺) competed with UO₂²⁺ for the active sites on the surface of the modified rice stem [30]. Uranium can exist in many forms in different acid environments, such as UO₂²⁺, [UO₂(OH)]⁺, [(UO₂)₂(OH)₂]²⁺, and [(UO₂)₃(OH)₅]⁺ [2]. The rice stem modified by 0.5 mol/L NaOH has a high sorption capacity in the pH range of pH = 3–4. The adsorption capacity decreases with the increasing pH value (pH > 4), due to the formation of other forms or precipitation [22]. The main form of UO₂²⁺ in

solution is $\text{UO}_2(\text{OH})_2$, which deposited on the surface of banyan leaf cells and interfered with the enrichment of cells that cause the losing of absorbent efficacy. Therefore, $\text{pH} = 4$ is suggested as the best pH value for further sorption experiments.

3.3. Effect of the Contact Time. The effect of the contact time is investigated in the time range of 20–200 min. 0.2 g of modified rice stem was added into $10 \text{ mg}\cdot\text{L}^{-1}$ uranium(VI) solution. The results are shown in Figure 3, which indicates an increase in the removal of U(VI) by modified rice stem with the time up to 200 min. This increase is most pronounced during the first 180 min but becomes smaller with further increase in time, demonstrating that the sorption process almost reaches equilibrium at about 180 min. Thus, all the mixtures of the sorbent and the solution were shaken for at least 180 min to ensure full equilibrium in subsequent experiments.

3.4. Effect of the Adsorbent Dose. The effect of adsorbent dose is investigated in the dose range of $1.25\text{--}8.75 \text{ mg/L}$ at room temperature (Figure 4), where the solution was shaken for 180 min, and the initial concentration of the solution was $10 \text{ mg}\cdot\text{L}^{-1}$ at $\text{pH} = 4$.

Figure 4 shows that the removal percentage increases, but the adsorption capacity of uranium(VI) decreases with the increasing adsorbent dose. It is worth noting that the removal percentage and the adsorption capacity of uranium(VI) are nearly constant when the adsorbent dose reaches $7.5 \text{ mg}\cdot\text{L}^{-1}$. This may be because the adsorption capacity of modified rice stem per unit area decreases as a result of the aggregation of excessive adsorbent [21].

3.5. Adsorption Kinetics. To assess the kinetic characteristics of uranium(VI) ions of the adsorption process, we adopted several kinetic models (i.e., pseudo-first-order kinetic model, pseudo-second-order kinetic model, Elovich kinetic model, and intraparticle diffusion model) to calculate the parameters [31, 32]. The expressions of models are shown in the following equations:

$$\text{pseudo first order kinetic model: } \ln(q_e - q_t) = \ln q_e - k_1 t,$$

$$\text{pseudo second order kinetic model: } \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e},$$

$$\text{Elovich kinetic model: } q_t = b + k_E \cdot \ln t,$$

$$\text{intraparticle diffusion model: } q_t = k_d t^{0.5} + C,$$

(2)

where k_1 (min^{-1}), k_2 ($\text{mg}/(\text{g}\cdot\text{min})$), k_E ($\text{mg}/(\text{g}\cdot\text{min})$), k_i (min^{-1}), and k_d ($\text{mg}/(\text{g}\cdot\text{min}^{0.5})$) are the adsorption rate constant; q_t (mg/g) is the amount of adsorbed uranium at time t ; q_e (mg/g) is the maximum adsorption capacity; and b and C are the constant.

The results of each kinetic model are given in Table 2, which shows that the correlative parameter R^2 of the

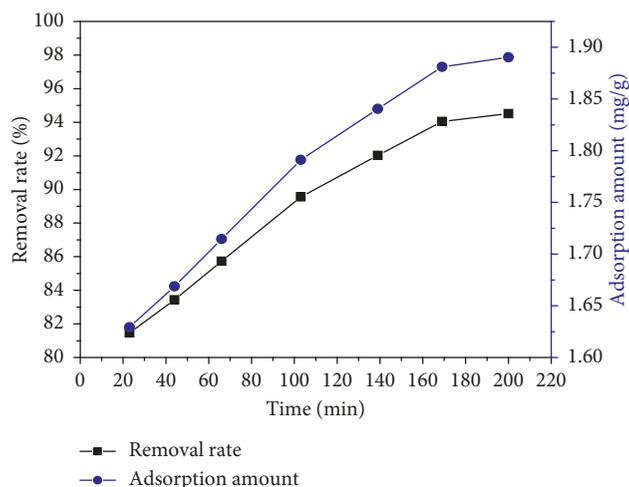


FIGURE 3: Effect of time on uranium adsorption by modified rice stem.

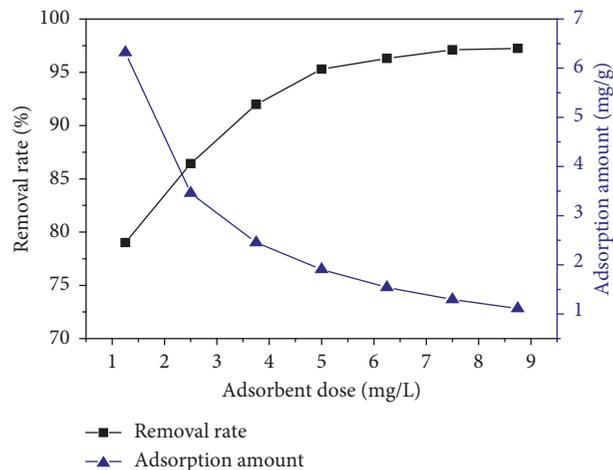


FIGURE 4: Effect of the adsorbent dose by modified rice stem.

TABLE 2: Adsorption kinetic parameters of uranium(VI) adsorption by modified rice stem.

	Adsorption kinetic parameters				R^2
	k	q	C	b	
Pseudo-first-order	0.00094	16.679	—	—	0.9673
Pseudo-second-order	0.0721	1.9467	—	—	0.9992
Intraparticle diffusion	0.0302	—	1.4779	—	0.9885
Elovich	0.1308	—	—	1.1923	0.9610

pseudo-second-order kinetic model is the best among the five kinetic models mentioned above, and the calculated equilibrium adsorption amount was 1.9467 mg/g , which was close to the experimental result of 1.8903 mg/g . This demonstrates that the pseudo-second-order kinetic model best fits the adsorption process of uranium(VI) ions. In addition to the physical and chemical processes, there may be other adsorption mechanisms of uranium(VI) by modified rice stem because the fitted curve of the intraparticle diffusion model does not pass across the origin of coordinate [28, 33].

3.6. Effect of the Initial Uranium(VI) Concentration. The effect of initial uranium ion concentration is investigated at room temperature under the conditions of the initial pH (pH = 4.0) and uranium contents (5–60 mg·L⁻¹), using 0.2 g modified rice stem, which was shaken for 180 min. The results about the effect of the initial uranium concentration are shown in Figure 5.

As shown in Figure 5, the uranium(VI) removal percentage slightly decreases from 97.8% to 94.7% with the increasing initial uranium concentration from 5 mg/L to 60 mg/L, where the adsorption capacity, however, increases from 0.97 mg/g to 11.36 mg/g. This may be because most uranium(VI) ions interact with the sufficient surface active sites of modified rice stem, resulting in higher uranium(VI) removal percentages at lower uranium(VI) concentrations; however, the excessive uranium(VI) ions in the solutions increase with further increase in the uranium concentration, which would cause the increase of adsorption amount at higher uranium(VI) concentrations.

3.7. Equilibrium Adsorption Isotherms. Langmuir, Freundlich, and Temkin isotherms models are generally used to study the adsorption equilibrium [20]. The Langmuir isotherm model assumes that the sorption is monolayered, and the attractive force of the intermolecular sharply depresses with the increasing distance [34]. The Freundlich isotherm model is robust to elucidate the surface heterogeneity and the exponential distribution of active sites [35]. On the contrary, the Temkin isotherm model suggests that the adsorption heat decreases with the reduction of adsorption quantity [36]. The expressions of the Langmuir, Freundlich, and Temkin models are given by the following equations:

$$\text{Langmuir isotherms model: } \frac{c_e}{q_e} = \frac{c_e}{q_m} + \frac{1}{bq_m},$$

$$\text{Freundlich isotherms model: } \ln q_e = \frac{1}{n} \ln c_e + \ln K_f, \quad (3)$$

$$\text{Temkin isotherms model: } q_e = a \ln K_T + a \ln C_e,$$

where q_e is the amount of adsorbed metal ions, mg/g; c_e is the equilibrium concentration in solution, mg/L; q_m is the amount of maximum adsorbed metal ions, mg/g; b is the Langmuir adsorption model constant; K_f and n are the Freundlich adsorption model constants; and K_T and a are the Temkin adsorption model constants. With c_e/q_e as the ordinate and c_e as the abscissa, a straight line can be obtained, the slope of the line is $1/q_m$, and the vertical intercept of the line is $1/bq_m$. The parameters of the remaining two equations can be calculated in the same way. The parameters of the Langmuir, Freundlich, and Temkin isotherm models for the adsorption of uranium ions by rice stem are shown in Table 3.

Table 3 shows that the model parameters (e.g., q_m in the Langmuir model, K_f in the Freundlich model, and a and K_T in the Temkin model) increases slightly with increasing temperature, demonstrating that the uranium adsorption process by rice stem is endothermic. On the contrary, the

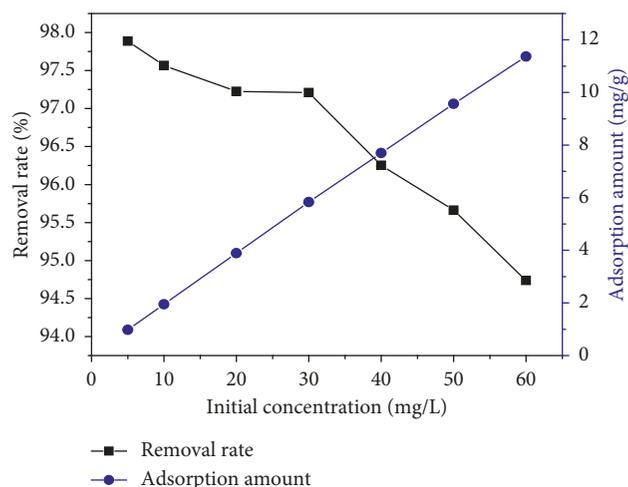


FIGURE 5: Effect of the initial uranium concentration by modified rice stem.

comparison between the correlation parameters R^2 of the three isotherm models (Langmuir, Freundlich, and Temkin) (Table 3) shows that the Langmuir model is better than Freundlich and Temkin models to elucidate the adsorption isotherm of adsorbed uranium. Therefore, it can be concluded that the predominant adsorption of uranium by modified rice stem is monolayered.

3.8. Effect of Temperature. The effect of temperature on adsorption properties of uranium is shown in Figure 6. As can be seen from Figure 6, the removal percentage of uranium increases slightly with temperature in the T range of 298–318 K, demonstrating that the adsorption reaction is more pronounced at higher temperature. This may be because (1) some new active sites are produced with heating and (2) the metal ions have stridden across the energy barrier to endure diffusion transmission or resist concentration gradient [28]. Thus, $T = 298$ K is suggested as the most appropriate temperature for adsorption experiments.

3.9. Adsorption Thermodynamics. The thermodynamic parameters of the sorption process are calculated according to the following equations at different temperatures [37]. The values of thermodynamic parameters are showed in Table 4:

$$\Delta G^0 = -RT \ln K_d,$$

$$\ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}, \quad (4)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0,$$

where ΔG^0 is the Gibbs free energy, kJ/mol; R is the ideal gas constant, with the value of 8.314 kJ/(mol·K); T is the absolute temperature; K_d is the thermodynamic stability constant; C_e is the equilibrium concentration, mg·L⁻¹; K_0 is the distribution coefficient; ΔS^0 is the standard entropy, kJ/(mol·K); and ΔH^0 is the enthalpy, kJ/mol.

TABLE 3: Parameters of different isothermal models of uranium(VI) adsorption by rice stem.

T (K)	Langmuir model			Freundlich model			Temkin model		
	q_m	b	R^2	K_f	n	R^2	a	K_T	R^2
298	18.0857	0.5200	0.9854	5.0343	1.3550	0.9934	3.0980	7.8284	0.9309
308	18.2883	0.5107	0.9899	5.5823	1.3651	0.9844	3.11	8.991	0.9450
318	18.9753	0.5012	0.9903	6.3818	1.3254	0.9767	3.2576	9.818	0.9583

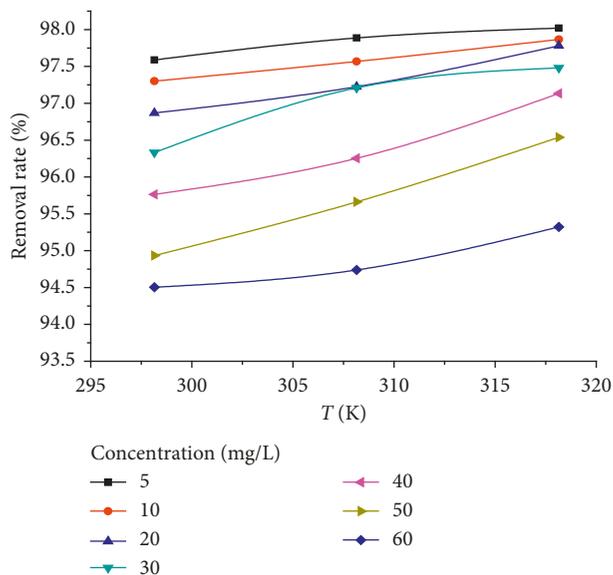


FIGURE 6: Effect of temperature on adsorption properties.

TABLE 4: Thermodynamic parameters of uranium(VI) adsorption by modified rice stem.

T (K)	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 [J/(mol·K)]
298	-1.4883	9.4533	49.9505
308	-1.5383		
318	-1.5882		

For the initial mass concentration, with $\ln K_d$ as the ordinate and $1000/T$ as the abscissa, a straight line can be obtained, the slope of the line is $-\Delta H^0/R$, and the vertical intercept of the line is S_0/R .

As showed in Table 4, the negative free energy ΔG^0 is less than zero, and ΔG^0 decreases with the increasing temperature, indicating that the uranium adsorption process by rice stem is spontaneous, where the reaction is promoted by temperature. The enthalpy change ($\Delta H^0 = 9.4533$) indicates an endothermic uranium adsorption. The positive entropy ΔS^0 reflects the inconvertible process of adsorption uranium and little possibility of desorption. The three parameters illustrate that the adsorption process is a physical and chemical reaction.

3.10. Adsorption Mechanism

3.10.1. FT-IR Analysis. FT-IR spectra of samples are measured by Fourier infrared spectrum instrument which collects and analyzes scattered IR energy [38] (Figure 7). FT-IR spectra record the presence of different typical peaks which

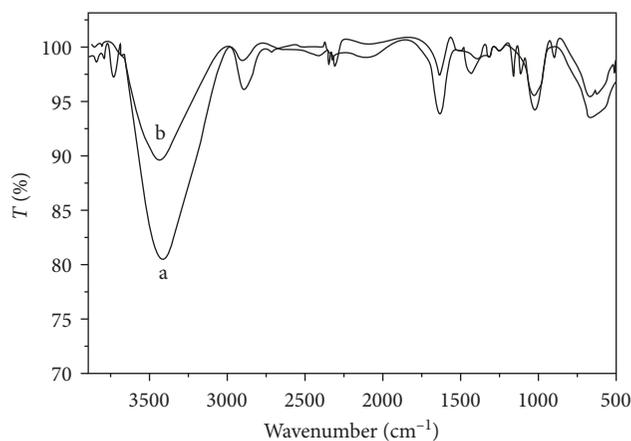


FIGURE 7: FT-IR spectra of modified rice stem: (a) before adsorption of uranium(VI); (b) after adsorption of uranium(VI).

correspond to functional groups and surface properties. The curve a in Figure 7 shows the FT-IR spectrum of modified rice stem before adsorption of uranium. The widely strong peak observed at 3431 cm^{-1} is due to O-H stretching vibration [28]. The band at 2912 cm^{-1} is formed as a result of C-H asymmetric stretching vibration of methyl and methylene groups in cellulose [4], whereas that at 2312 cm^{-1} is produced due to overtone or combination band of amino acids. The peak located at 1635 cm^{-1} indicates the stretching vibration of carbonyl groups from carboxylates and ketones [5]. The peak at 1433 cm^{-1} is due to C-H bending vibration in lignin [39], while that at about 1026 cm^{-1} is attributed to C-O-C and asymmetric stretching vibrations of phosphate and silicate groups [39].

The curve b in Figure 7 illustrates the FT-IR spectrum of modified rice stem after adsorption of uranium, which shows a slight shift. None of new bands appear, but the transmittance is reduced. It can be inferred that the structure of rice stem does not change after adsorption of uranium. The peaks at 3431 , 2912 , 2312 , 1635 , 1433 , and 675 cm^{-1} are shifted to 3429 , 2900 , 2310 , 1633 , 1381 , and 686 cm^{-1} after the adsorption of uranium, respectively, implying the replacement of some H^+ by UO_2^{2+} , which causes the decrease of the vibration strength and the absorption peak wavenumber [40, 41]. The observed FT-IR spectra show that O-H, C=O, Si=O, and P-O are the main adsorption sites in the uranium adsorption process.

3.10.2. EDS Analysis. The EDS can detect the difference in excited X-ray energies when the surface atoms of sample are bombard by the electron beam. The EDS images of modified rice stem before and after adsorption are shown in Figure 8.

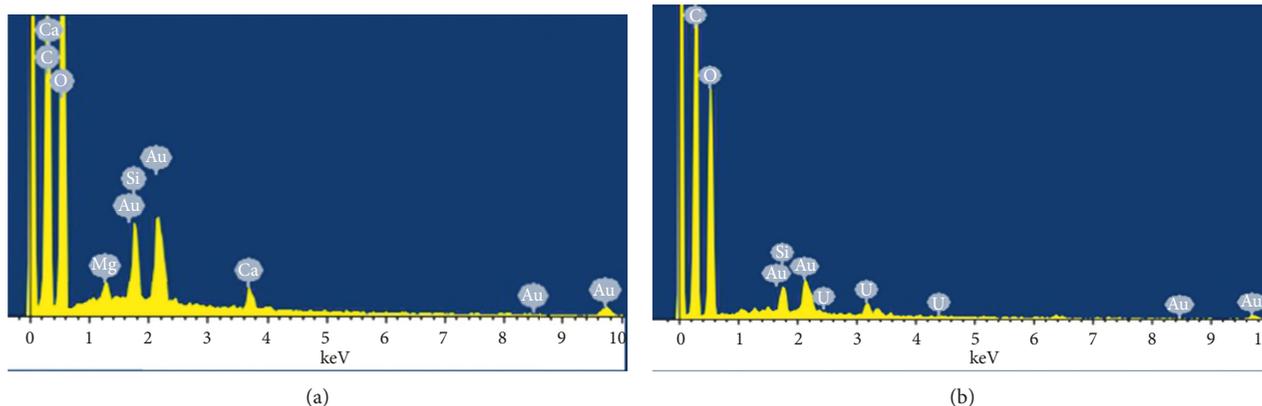


FIGURE 8: EDS analyses of modified rice stem: (a) before adsorption of uranium(VI); (b) after adsorption of uranium(VI).

The EDS images before adsorption of uranium (Figure 8(a)) show that the modified stem is composed of C, O, Ca, Si, and Mg elements. On the contrary, the EDS images after adsorption of uranium (Figure 8(b)) show the appearance of the U element and the decrease in the amounts of Si and Ca elements. These results indicate that the interaction of active groups of modified rice stem with uranium(VI) can cause a good adsorption of uranium(VI).

3.10.3. SEM Analysis. The SEM images of modified rice stem before and after adsorption of UO_2^{2+} are shown in Figure 9, which indicates the variation in morphology of modified rice stem. For example, the images before adsorption show a rough surface of modified rice stem, with many voids in the distribution (Figure 9(a)). However, the distributed interstices and voids in the surface obviously decrease after adsorption, indicating a significant change in the surface morphology of rice stem (Figure 9(b)). This means that a large amount of UO_2^{2+} is adsorbed by the rice stem in the adsorption process. The reason for this phenomenon may be because of (1) the interaction of UO_2^{2+} with the functional organic groups (e.g., the hydroxyl group, carbonyl group, silicon oxygen bond (Si-O), and P-O) of the cell walls of rice stem [28, 37]; (2) the exchange of H^+ on the surface with UO_2^{2+} ; and (3) diffusion of free UO_2^{2+} into the void of the stem.

3.10.4. XRD Analysis. The XRD images of the modified rice stem before and after adsorption of uranium(VI) are shown in Figure 10. The XRD result of the rice stem before adsorption represented by the curve a shows diffraction peaks at $2\theta = 15.64$, 22.08 , and 29.17 , whereas that after adsorption shown in curve b illustrates the weaker diffraction peak at $2\theta = 15.64$, and 22.08 , and even disappearance of the peak at $2\theta = 29.17^\circ$, implying that new crystals are not formed, and that the number of the crystal structure decreases in the adsorption process. This may be due to the adsorption of uranium(VI) by modified rice stem, which causes part of the molecule structures change from crystal to amorphous [21, 42].

3.11. Adsorption Process. Based on the results of FT-IR, SEM, EDS, and XRD mentioned above, we suggest that the adsorption process may be divided into the following 3 stages (Figure 11):

- (1) UO_2^{2+} migrates to the cell wall surface in solution
- (2) UO_2^{2+} reacts with active sites of the cell wall of rice stem
- (3) UO_2^{2+} deposits on the surface of the rice stem cell wall

4. Conclusions

This study presents a systematic investigation of the adsorption properties, such as the kinetics, thermodynamics, and mechanisms of modified rice stem. The following conclusions can be drawn:

- (1) The rice stem treated with 0.5 mol/L NaOH solutions can effectively remove uranium(VI) from aqueous solution. pH = 4.0 is the best pH condition to remove uranium(VI). The removal percentage of uranium(VI) decreases with increasing initial concentration of uranium(VI).
- (2) The sorption mode calculations using Langmuir, Freundlich, and Temkin isotherm models show that the maximum adsorption capacity of uranium by modified rice stem increases with temperature. Langmuir model, which indicates predominant monolayered adsorption of uranium, is better than Freundlich and Temkin models to describe the adsorption isotherm of uranium.
- (3) The thermodynamic parameters ΔG^0 , ΔH^0 , and ΔS^0 show that the adsorption of uranium(VI) is an endothermic and spontaneous process, where the temperature promotes the process. It is also suggested that the adsorption process is a physical and chemical reaction.
- (4) The pseudo-second-order kinetic model, with the correlation coefficient of $R^2 = 0.9992$, fits the adsorption process of uranium(VI) much better than other kinetic models (e.g., pseudo-first-order kinetic

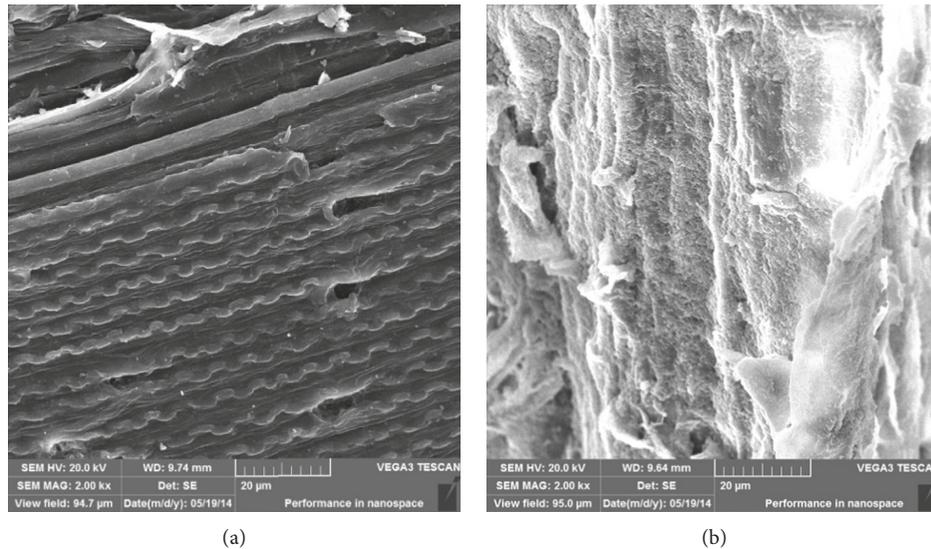


FIGURE 9: SEM images of modified rice stem: (a) before adsorption of uranium(VI) (2000x); (b) after adsorption of uranium(VI) (2000x).

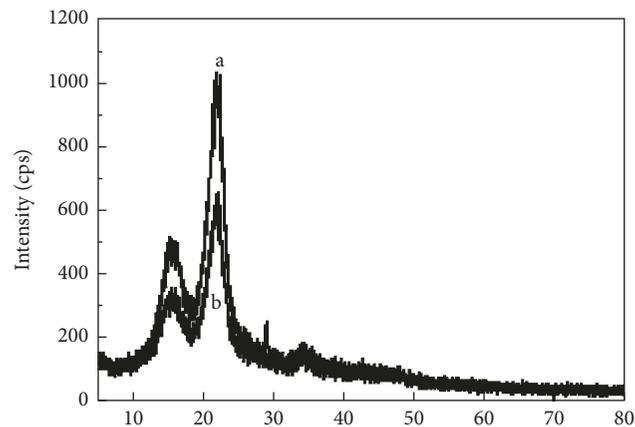


FIGURE 10: XRD images of modified rice stem: (a) before adsorption of uranium(VI); (b) after adsorption of uranium(VI).

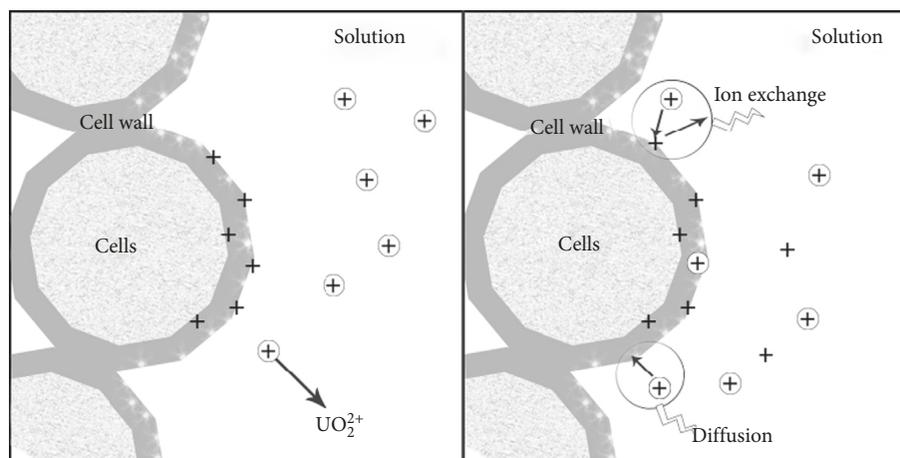


FIGURE 11: Adsorption process of uranium(VI) by modified rice stem.

model, pseudo-second-order kinetic model, Elovich kinetic model, and intraparticle diffusion model). (5) FT-IR and EDS analyses show that the interaction of

the main adsorption sites (O-H, C=O, Si=O, and P-O) of modified rice stem with uranium(VI) can cause a good adsorption of uranium(VI). SEM and

XRD analyses show that the surface morphology and the crystal structure of rice stem treated with NaOH solutions have significantly changed during the adsorption process.

Data Availability

This is a research article, and the data are from the experiment. All the data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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