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Insights into Kinetics, Equilibrium and Thermodynamics of Uranium Uptake onto Fir Sawdust

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Abstract

In this study, fir sawdust was used to adsorb U(VI) from uranium-bearing wastewater. Batch experiments showed that the optimal pH for removal was 4.5, and equilibrium was reached within 120 min. The kinetics conformed to the pseudo-second-order model, indicating chemical adsorption as the rate-controlling step. The adsorption data fit the Langmuir isotherm well with a monolayer capacity of 148.81 mg g⁻¹. FTIR, SEM-EDS, and XPS analyses revealed surface complexation and ion exchange as the dominant adsorption mechanisms, with hydroxyl, carboxyl, and carbonyl groups acting as the main active sites. Therefore, fir sawdust holds good uranium removal potential, serving as a promising biosorbent that

1 simultaneously achieves waste resource recycle and radioactive
2 wastewater treatment.

3 **Keywords**

4 Fir sawdust; U(VI); Adsorption; Ion-exchange and complexation
5 mechanisms

Introduction

With the sustained development of uranium mining, hydrometallurgy, and nuclear-related industries, large amounts of uranium-bearing wastewater is generated during the production process. Once released into rivers, uranium-containing wastewater not only contaminates surface water, groundwater and the ambient soil, but also severely threatens plant growth. Moreover, it can jeopardize human health through the enrichment effect of the food chain. Uranium in the wastewater usually occurs in the form of hexavalent uranium (U(VI)) or uranyl ions (UO_2^{2+}), which carry both radiation risks and chemical toxicity, resulting in serious damage to the human kidneys, hematopoietic organs, and nervous system [1]. Thus, harmless treatment of uranium-containing wastewater is becoming a critical problem that urgently requires to be solved in the areas of uranium mining and nuclear environmental protection.

Conventional methods for treating uranium-containing wastewater include chemical precipitation [2], biofilm technology [3], activated carbon adsorption [4], ion exchange [5], solvent extraction [6] and photocatalysis [7]. In actual fact, these traditional treatment processes have their own disadvantages such as high chemical dosage, considerable operating costs, substantial solid waste generation, and difficulty in regeneration, which limit extensive engineering applications. Therefore, seeking novel, low-cost, green and efficient adsorbent materials has gained significant research attention in the remediation of uranium-containing wastewater.

Agricultural and forestry waste, characterized by its wide availability, low cost and environmental friendliness, has become an extensively investigated material in heavy metal adsorption. Sawdust, a by-product of timber processing and generally regarded as waste, is

1 chiefly composed of cellulose, hemicellulose, and lignin (Fig. S1). The
2 raw material naturally carries polar functional groups such as
3 hydroxyl, carboxyl, phenolic hydroxyl and methoxy groups [8, 9]. In
4 addition, it has a loose and porous interior structure, enabling it to
5 sequester heavy metals in water bodies through physical
6 adsorption, ion exchange, surface complexation and other
7 mechanisms without requiring complex chemical modification. It is
8 commonly considered to be a promising biomass adsorbent material.

9 In recent years, various kinds of sawdust have been widely
10 adopted by researchers for the removal of diverse water contaminants,
11 including Cu(II) [10, 11], cadmium [12], Ni(II) [13], Cr(VI) [14],
12 precious metals [15], and organic dyes [16]. Nonetheless, systematic
13 study on the direct application of fir sawdust in the adsorption of
14 uranyl cations in aqueous solutions remains scarce. Firs are widely
15 cultivated across China, and their timber-processing industry
16 generates large quantities of sawdust waste every year (Fig. S2). Most
17 fir sawdust is either piled in the open air or incinerated on site, which
18 wastes biomass resources and causes dust and air pollution.
19 Unmodified raw fir sawdust may be directly used as a natural
20 adsorbent to dispose of uranium-polluted wastewater. The recycling
21 approach not only reuses discarded wood biomass and significantly
22 cuts the raw material expense of wastewater treatment, but also
23 prevents secondary contamination brought by chemical modifiers. The
24 treatment strategy fits well with the developmental principles of eco-
25 friendly water purification and solid waste reclamation.

26 Based on the above-mentioned background, this research selected
27 unmodified fir sawdust as the adsorbent material. Batch adsorption
28 experiments were carried out to explore the effects of environmental
29 factors such as adsorption time, solution pH, adsorption temperature,
30 and initial U(VI) concentration on the adsorption performance of

U(VI). Besides, various analytical approaches were adopted in this investigation, including adsorption kinetics, adsorption thermodynamics, adsorption isotherm model fitting, and characterization techniques of FTIR, SEM-EDS and XPS. On this basis, we clarified the adsorption mechanism and verified the feasibility of fir sawdust for removing uranyl ions in wastewater. The present work will provide a solid theoretical and experimental foundation for reusing agroforestry wastes to realize resource-based treatment of uranium-containing wastewater.

Experimental

Adsorbent treatment

The fir sawdust used in this study was obtained from a lumber mill in the suburbs of Hengyang, Hunan, Southern China. It was rinsed exhaustively with distilled water to get rid of particles and water-soluble substances attaching to its surface. After drying at 80 °C to constant weight, it was sieved through a 100-mesh sieve and placed inside a desiccator for further experiments (Fig. S2c).

Adsorbate solutions

To prepare a stock U(VI) solution, a total of 1.1792 g analytically pure U_3O_8 powder was accurately weighed and put into a beaker. Afterwards, 10 mL of concentrated hydrochloric acid ($\rho = 1.18 \text{ g mL}^{-1}$) and 2 mL of 30% hydrogen peroxide were added sequentially [17]. The mixture was heated on an electric hot plate until it was

nearly dry. The residue was dissolved with 10 mL of hydrochloric acid ($\rho=1.18 \text{ g mL}^{-1}$), then quantitatively transferred to a 1000 mL volumetric flask and diluted to the mark with thorough shaking. The final stock U(VI) standard solution has a mass concentration of 1000 mg L⁻¹. Working solutions with varying concentrations were obtained by diluting the stock U(VI) solution to appropriate volumes in terms of the experimental requirements. The pH was adjusted when required with either 0.5 mol L⁻¹ H₂SO₄ or 0.5 mol L⁻¹ NaOH.

Uranium biosorption experiments

In all adsorption experimental procedures, a specific amount of dried fir sawdust was separately added into 100 mL aliquots of U(VI) solution placed in multiple conical flasks. The resulting mixtures were then shaken on a rotary shaker at 140 rpm under set experimental conditions. After a designated incubation period, the suspension was collected, followed by centrifugation at 6000 × g for 10 min. The U(VI) concentration in the supernatant was measured by the Arsenazo III method at 652 nm using a UV-visible spectrophotometer [18]. The reported data represent the average of triplicate measurements. The U(VI) removal percentage and the U(VI) adsorption capacity of the fir sawdust were worked out using the following equations:

$$q = \frac{C_0 - C_t}{C_0} \cdot 100\% \quad (1)$$

$$R = \frac{C_0 - C_t}{C_0} \cdot 100\% \quad (2)$$

$$Q = \frac{(C_0 - C_t) \cdot V}{m} \quad (3)$$

where θ represents the U(VI) removal percentage (%), C_0 the initial U(VI) concentration (mg L^{-1}), C_t the U(VI) concentration at time t (mg L^{-1}), Q_t the U(VI) adsorption capacity at time t (min), Q_e the U(VI) adsorption capacity at equilibrium (mg g^{-1}), V the solution volume (L), and W the fir sawdust mass (g).

Adsorption kinetic models

Numerous classical kinetic models, such as the pseudo-first-order, pseudo-second-order and intraparticle diffusion equations, are extensively used to explore adsorption kinetics. Essentially, these tools enable investigators to determine the rate-controlling steps that govern mass transfer and physicochemical interactions during adsorption. This work utilizes all three models to identify the kinetic characteristics of U(VI) uptake by fir sawdust. The integrated expression of pseudo-first-order model can be written as follows [19]:

$$Q_t = Q_e(1 - e^{-k_1 t}) \quad (4)$$

where k_1 refers to the rate constant of the pseudo-first-order adsorption kinetics (min^{-1}).

The linear expression of the pseudo-second-order kinetic model can be shown below [20]:

$$(5)$$

where k_2 refers to the rate constant of pseudo-second-order adsorption kinetics ($\text{g mg}^{-1} \text{min}^{-1}$).

The mathematical expression of intraparticle diffusion kinetic model can be given as follows [21]:

$$Q_t = k_{\text{int}} t^{1/2} + C \quad (6)$$

where k_{int} ($\text{mg g}^{-1} \text{min}^{1/2}$) refers to the intraparticle diffusion rate constant and C refers to the boundary layer effect of adsorption.

Adsorption isotherm models

Langmuir, Freundlich and Temkin isotherm models were used to fit the experimental adsorption data. As an empirical fitting equation, Langmuir isotherm postulates single-layer adsorption onto homogeneous solid surfaces with finite identical adsorption sites, while neglecting any intermolecular lateral forces between adsorbed molecules [22]. The mathematical expression for the linearized Langmuir isotherm is given as follows:

$$(7)$$

where Q_{max} denotes monolayer saturated adsorption capacity (mg g^{-1}), and b denotes the Langmuir constant correlating with adsorption energy (L mg^{-1}).

Freundlich isotherm depicts adsorbate attachment to energetically irregular solid surfaces. This model presumes adsorption centers exhibit continuous energy distribution and possess unequal affinities [23]. The mathematical representation of its linearized form is as follows:

$$(8)$$

1 where K_F denotes a constant indicative of the adsorbent's adsorption
 2 capacity ($\text{mg}^{(1/n)} \text{g L}^{n-1}$), and n denotes a unitless Freundlich
 3 parameter reflecting adsorption strength.

4 Temkin isotherm operates on the premise that adsorption enthalpy
 5 undergoes a linear reduction with rising surface coverage, a
 6 phenomenon originating from repulsion among adsorbed molecules
 7 [24]. The mathematical expression for the Temkin isotherm is
 8 presented as follows:

$$9 \quad Q_e = a \ln K_T + a \ln C_e \quad (9)$$

10 where K_T denotes an equilibrium parameter linked to the maximal
 11 binding energy (L g^{-1}), and a denotes the unitless constant dependent
 12 on thermal conditions and adsorption medium.

13

14 Thermodynamic parameters of biosorption

15

16 The thermodynamic parameters associated with the adsorption
 17 behavior, including standard Gibbs free energy change (ΔG^0),
 18 standard enthalpy change (ΔH^0) and standard entropy change (ΔS^0),
 19 can be calculated by the following equations [25]:

$$20 \quad DG = -RT \ln K_d \quad (10)$$

$$21 \quad K_d = \frac{Q_e}{C_e} \quad (11)$$

$$22 \quad \ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (12)$$

where R is the molar gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), T is the thermodynamic absolute temperature (K), and K_d is the adsorption partition coefficient (mL g^{-1}). Based on the relationship expressed in Equation 12, the slope and intercept derived from linear fitting of $\ln K_d$ versus $1/T$ allow the respective estimation of ΔH^0 and ΔS^0 .

Instrumental analysis

0.1 g of fir sawdust biosorbent was added to 100 mL of U(VI) aqueous solution with an initial concentration of 100 mg L^{-1} . The pH of the mixture was subsequently adjusted to 4.5. The mixed suspension was shaken continuously at 140 rpm for a 120 min adsorption period. After the adsorption process was completed, the mixture was centrifuged at $6000 \times g$ for 10 min to separate the solid residues from the liquid phase, and the supernatant was then completely removed. The collected solid residues were subsequently treated with vacuum drying to remove residual moisture. Three distinct characterization methods were separately used to analyze raw fir sawdust and uranium-loaded adsorbent. Fourier-transform infrared (FTIR) spectra were obtained with a Thermo Scientific NICOLET iS10 spectrophotometer. Samples were prepared as KBr pellets, and spectral signals were collected in the wavenumber range from 400 to 4000 cm^{-1} . Preceding the SEM-EDS measurement with a Hitachi S-4800 instrument (Tokyo, Japan), all sawdust samples were coated with a thin gold layer via sparging under an argon atmosphere. The surface elemental distribution and uranium proportion on fir sawdust were determined by means of an XPS apparatus (Thermo ESCALAB 250, USA) equipped with monochromatic Al $K\alpha$ X-ray source running at an excitation energy of 1486.5 eV and an output power of 150 W. XPS data collection was carried out under fixed analyzer transmission

mode. The pass energy was set to 20 eV with a scanning step of 0.1 eV, and the full spectral collection process was conducted under ultrahigh vacuum of 8×10^{-9} Pa.

Results and discussion

Evaluation of biosorption kinetics

Investigation of adsorption kinetics through model fitting could be employed to describe the adsorption rate of U(VI) on fir sawdust and deduce its adsorption mechanism. Fig. S3 displayed the adsorption kinetic fitting curve of U(VI) onto fir sawdust, with the corresponding fitting parameters listed in Table 1. As shown in Fig. S3a, the adsorption process of U(VI) on fir sawdust proceeds via two distinct stages: rapid adsorption and slow adsorption. In the early stage of the reaction (0–30 min), the U(VI) adsorption capacity grows steeply with prolonged contact time. This is owing to the existence of many active binding sites on the surface of fir sawdust, where U(VI) fast adheres to the adsorbent's surface. As the binding sites are progressively occupied, the impedance to U(VI) mass transfer into the adsorbent intensifies, and the adsorption rate progressively slows down. Eventually, the adsorption system attained equilibrium at approximately 120 min, after which the U(VI) concentration stays constant without noticeable fluctuation.

As shown in Table 1, the correlation coefficients of the pseudo-first-order model ($R^2=0.843$) and intraparticle diffusion model ($R^2=0.656$) both deviate from 1.0, indicating a poor fitting performance. Notably, R^2 of the intraparticle diffusion adsorption model is very low, suggesting that diffusion within the adsorbent is

hard to take place. Hence the U(VI) uptake process of fir sawdust does not pertain to intraparticle diffusion adsorption.

By comparison, R^2 of the pseudo-second-order kinetic model reaches as high as 0.998, and the fitted equilibrium adsorption capacity (73.05 mg/g) closely matches the experimental value (69.46 mg/g). Accordingly, the results demonstrate that the pseudo-second-order kinetic model can better characterize the adsorption process of U(VI) on fir sawdust. Given that the pseudo-second-order kinetic model assumes chemical adsorption as its fundamental premise, we may infer from this that the rate-limiting step of U(VI) adsorption on fir sawdust is chiefly a chemisorption process.

Table 1 Kinetic parameters of U(VI) adsorption onto fir sawdust

Kinetical Model	Parameter	Value
Pseudo-first-order	k_1 (min^{-1})	0.078
	Q_e (mg g^{-1})	68.24
	R^2	0.843
Pseudo-second-order	k_2 ($\text{g mg}^{-1} \text{min}^{-1}$)	0.0018
	Q_e (mg g^{-1})	73.05
	R^2	0.998
	$Q_{e, \text{exp}}$ (mg g^{-1})	69.46
Intraparticle diffusion	k_{int} ($\text{mg g}^{-1} \text{min}^{1/2}$)	3.68
	C	30.65
	R^2	0.656

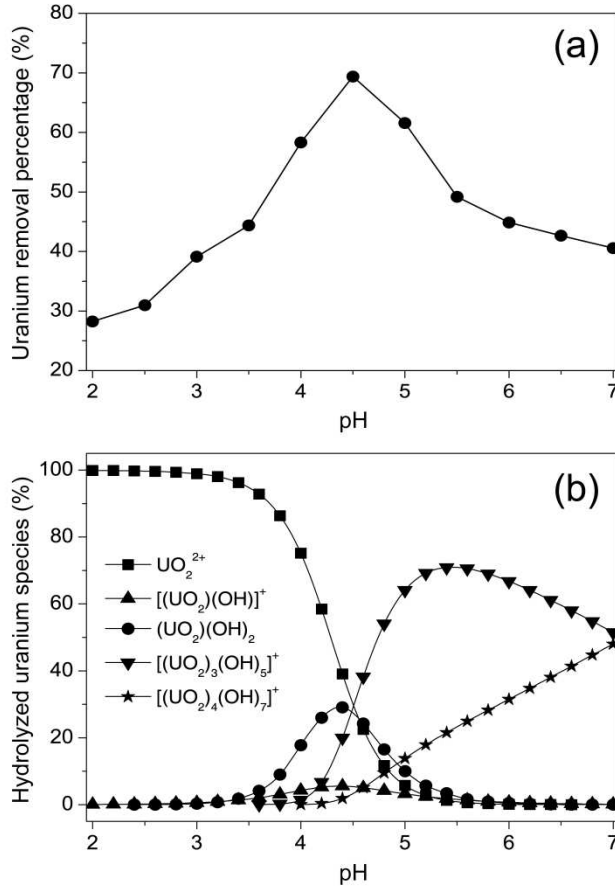
Influence of pH

The pH of the solution stands as one of the critical factors influencing the U(VI) adsorption performance of fir sawdust. The effect of initial pH (2.0–7.0) on adsorption performance was examined, and the results are exhibited in Fig. 1a. It is evident that the U(VI) removal percentage increased with increasing pH from 2.0 to 4.5, reached a maximum at pH 4.5, and declined within the pH interval of 4.5 to 7.0. To explain the pH-dependent behavior of uranium removal, we combined the experimental results with the U(VI) species distribution obtained via Visual MINTEQ 3.0 simulation (Fig. 1b).

The low U(VI) removal in the pH range of 2.0–4.0 can be attributed to the competitive occupation of surface active sites (e.g., hydroxyl and carboxyl groups) by H^+ , which exhibits a stronger binding affinity than UO_2^{2+} and thereby hinders complexation. This effect predominates despite the fact that uranium exists mainly as UO_2^{2+} at these pH values. When the pH is between 4.0 and 5.0, the dominant uranium species are positively charged mononuclear hydroxyl complexes, including UO_2^{2+} , $[UO_2(OH)]^+$, and $[(UO_2)(OH)_2]^{2+}$. These complexes possess strong attraction toward negatively charged functional groups on fir sawdust surface (e.g., unprotonated carboxyl and hydroxyl groups), thereby promoting the U(VI) adsorption process. When the pH exceeds 5.0, uranyl cations hydrolyze and condense, accompanied by agglomeration, and gradually convert into polynuclear complexes such as $[(UO_2)_3(OH)_5]^+$ and $[(UO_2)_4(OH)_7]^+$, or even precipitate as $4UO_3 \cdot 9H_2O$ [26]. Consequently, these resulting species are not readily captured by the adsorbent surface.

To sum up, the optimum pH for U(VI) adsorption by fir sawdust is 4.5. For some actual uranium-bearing wastewater with pH commonly

1 ranging from 3.0 to 5.0, fir sawdust has bright application outlooks
 2 and can realize efficient removal without remarkable pH adjustment.



3
 4 **Fig. 1** Variations in U(VI) removal percentage (a) and hydrolyzed
 5 uranyl speciation (b) as a function of solution pH ($C_0 = 100 \text{ mg L}^{-1}$, V
 6 $= 100 \text{ mL}$, $W = 0.1 \text{ g}$, $t = 120 \text{ min}$, $T = 298 \text{ K}$)

7 Effect of uranium concentration and adsorption isotherms

8
 9 The influence of initial U(VI) concentration on U(VI) adsorption
 10 capacity is given in Fig. S4a. At low initial U(VI) concentrations, the
 11 fir sawdust adsorbent is far from saturated and there are numerous
 12 residual adsorption sites that are not completely utilized, leading to a
 13 low adsorption capacity. When the initial U(VI) concentration rises,
 14 the concentration gradient between the solid and liquid phases

enhances, and the interaction between U(VI) and the adsorbent surface grows stronger, thereby resulting in a steady rise in U(VI) uptake. When the U(VI) concentration in the solution goes above 200 mg/L, the upward trend in adsorption capacity slows down considerably, and the change becomes insignificant. This demonstrates that the active sites on the surface of the adsorbent have been completely occupied by U(VI), and the adsorption achieves saturation, thus inhibiting further rises in U(VI) adsorption capacity. The isothermal adsorption behavior of U(VI) onto fir sawdust was subjected to fitting by using Langmuir, Freundlich and Temkin models (Fig. S4b, c & d), and the corresponding fitting parameters are presented in Table 2.

As documented in Table 2, the correlation coefficients (R^2) for the Langmuir, Freundlich, and Temkin models are 0.993, 0.924, and 0.968 in sequence. Among the three models, the R^2 of the Langmuir model is nearest to 1.0, suggesting that this model delivers the optimal description for the isothermal adsorption process of U(VI) on fir sawdust. This indicates that the adsorption process is governed by monolayer chemical adsorption, mainly taking place on the external surface of fir sawdust. In terms of Freundlich's theory, K_F stands for the unit adsorption capacity of the adsorbent, whereas $1/n$ reflects the adsorption intensity of the adsorbent. Generally, the greater the n value, the better the adsorption ability. When $1/n$ is between 0.1 and 0.5, it is easy for adsorption to proceed; while when $1/n$ is close to 1.0, it is difficult for adsorption to proceed [27]. In the present study, the value of $1/n$ falls in the range of 0.1–0.5, which reveals that U(VI) can be readily adsorbed onto fir sawdust.

For the Langmuir isotherm model, $Q_{\max}$ characterizes the maximum adsorption capacity of fir sawdust for U(VI). A higher $Q_{\max}$ value signifies a stronger adsorption performance. As shown in Table

3, the $Q_{\max}$ of fir sawdust toward U(VI) reaches 148.81 mg/g, which is greater than that of most alternative biomass adsorbents.

3

Table 2 Isotherm parameters for the adsorption of U(VI) onto fir sawdust

Isotherm	Parameter	Value
Langmuir	$Q_{\max}$ (mg g ⁻¹)	148.8
	b (L mg ⁻¹)	0.028
	R^2	0.993
Freundlich	K_F (mg ^{(1 -}	12.71
	n	2.02
	R^2	0.924
Temkin	K_T (L g ^{⊠1})	0.238
	a	35.01
	R^2	0.968

6

7

Table 3 Removal of U(VI) by various biosorbents and comparison of their maximum adsorption capacity

Adsorbent materials	$Q_{\max}$ (mg g ⁻¹)	pH	Referen ces
Rice husk	52.63	4. 0	[28]
Biochar from poplar catkins	71.85	5. 0	[29]
Sewage sludge biochar	149.15	4. 0	[30]
Citrus grandis	38.97	4. 0	[31]
Flax fiber	40.90	4. 0	[32]
Tribulus terrestris	43.56	6.	[33]

		0	
Ficus microcarpa aerial root	27.29	4. 0	[34]
Cotton stalk biochar	100.31	5. 0	[35]
Abies religiosa leaves	44.7	4. 4	[36]
Hedera helix leaves	3.86	3. 0	[37]
Cellulose from Musa paradisiaca leaves	24.70	4. 5	[38]
Waste bark from Aegle marmelos	58.14	7. 0	[39]
Hydrochars of Dendrocalamus	26.02	5. 0	[40]
Aerogel from chitosan and bayberry tannin	140	5. 0	[41]
Present work	148.81	4.	☒

Calculation of thermodynamic parameters

The thermodynamic fitting curves for U(VI) adsorption onto fir sawdust are displayed in Fig. S5, and the corresponding thermodynamic parameters are summarized in Table 4. According to the data in Table 4, ΔH is positive, indicating that fir sawdust adsorbs uranium in an endothermic manner. Moreover, the positive ΔS indicates that the entire system becomes more disordered after uranium adsorption compared with before adsorption. In contrast, the negativity of ΔG at all three temperatures suggests that the fir sawdust-mediated adsorption of uranium is capable of occurring spontaneously. When the temperature increases from 298 to 318 K, the absolute magnitude of ΔG exhibits an upward trend, indicating that increasing the temperature can further enhance the spontaneity

of the adsorption process. In another word, raising the reaction temperature favors the forward direction of U(VI) adsorption by fir sawdust.

Table 4 Thermodynamic parameters for adsorption onto fir sawdust

T (K)	ΔG^0 (kJ mol ⁻¹)	ΔH^0 (kJ mol ⁻¹)	ΔS^0 (J mol ⁻¹ K ⁻¹)
298	-2.06	10.35	41.63
308	-2.47		
318	-2.89		

FTIR spectra of fir sawdust

To elucidate the adsorption mechanism of U(VI) onto fir sawdust, FTIR spectroscopy was adopted to characterize fir sawdust before and after U(VI) adsorption, and the results are presented in Fig. 2 and Table 5. Before adsorption, a broad and strong absorption peak near 3424 cm⁻¹ was observed, which is attributed to the stretching vibrations of hydroxyl groups (-OH) in cellulose, hemicellulose, and lignin, thus confirming the abundance of aliphatic or phenolic hydroxyl groups on the sawdust surface. The weak peak positioned at approximately 2904 cm⁻¹ can be ascribed to the symmetric and asymmetric stretching vibrations of C-H bonds belonging to methyl (-CH₃) and methylene (-CH₂-) groups. The absorption peak at 1735 cm⁻¹ is primarily assigned to non-ionized carbonyl (C=O) stretching

vibrations of carboxyl and methyl ester groups ($-\text{COOH}$, $-\text{COOCH}_3$). By comparison, the signal at 1637 cm^{-1} is associated with the stretching vibration of asymmetric and symmetric COO^- derived from deprotonated carboxylate functional groups in cellulose. In addition, the absorption peak at approximately 1268 cm^{-1} is generally assigned to the stretching vibrations of C-O bonds in aromatic ethers. Meanwhile, the intense peak at roughly 1058 cm^{-1} can be attributed to the stretching vibration of C-O bonds in cellulose and hemicellulose, originating from numerous C-O-C glycosidic bonds and C-OH structures.

It is worth noting that significant changes were observed in the FTIR spectrum of sawdust after U(VI) adsorption (Fig. 2, Table 5). Firstly, the hydroxyl peak at 3424 cm^{-1} narrowed significantly and decreased in intensity, accompanied by a significant blue shift to higher wavenumbers. Such variations may arise from coordination and ion-exchange interactions between UO_2^{2+} and hydroxyl groups on sawdust surfaces, resulting in the generation of U-O bonds. Secondly, the peak located at 1735 cm^{-1} weakened in intensity after adsorption and shifted slightly to higher wavenumbers, whereas the peak at 1637 cm^{-1} weakened in intensity and shifted slightly to lower wavenumbers. This phenomenon can be attributed to the complexation of carbonyl and carboxyl groups with U(VI), which induces variations in the electron cloud density of the C=O bond. In particular, a new weak absorption peak emerged near 920 cm^{-1} after adsorption, which can be attributed to the asymmetric stretching vibration of $\text{O}=\text{U}=\text{O}$ within UO_2^{2+} . This observation directly verifies that uranyl ions were successfully adsorbed onto the sawdust surface.

According to the above FTIR analysis, the infrared characteristic peaks of oxygen-containing functional groups such as hydroxyl, carbonyl, and carboxyl groups have shifted and their peak intensities

1 have obviously changed after adsorption. Such spectral variations
2 demonstrate that these functional groups participate in the adsorption
3 of U(VI). This suggests that the adsorption behavior of fir sawdust
4 towards uranyl ions mainly depends on the large number of oxygen-
5 containing functional groups on its surface, where hydroxyl, carboxyl
6 and carbonyl groups act as core active sites. These groups enable
7 stable binding through complexation and ion exchange, ultimately
8 realizing good U(VI) adsorption performance.

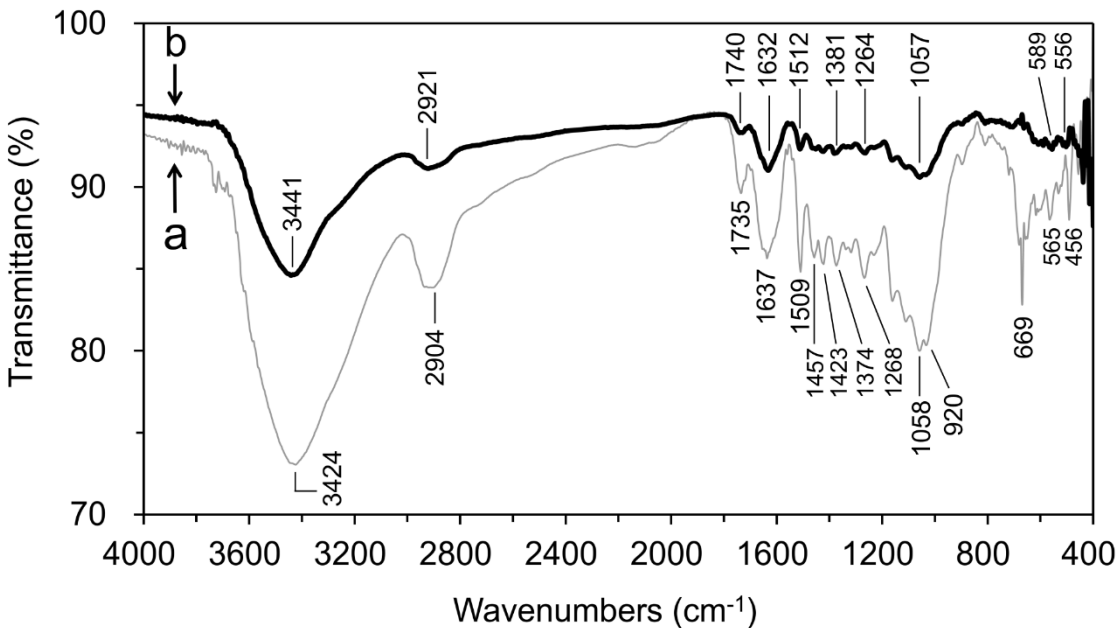


Fig. 2 FTIR spectra of fir sawdust before (a) and after (b) U(VI) adsorption

Table 5 Comparison of FTIR absorption peaks of raw sawdust before and after U(VI) biosorption

Wavenum ber	Before adsorption	After adsorption	Peak shift	Assignment
----------------	----------------------	---------------------	---------------	------------

range/Peak (cm ⁻¹)	(cm ⁻¹)	(cm ⁻¹)	(Δ , cm ⁻¹)	
3500–3200	3424	3441	+17	bonded hydroxyl groups (OH)
3000–2850	2904	2921	+17	C–H methyl and methylene groups
1750–1680	1735	1740	+5	C=O stretching of non-ionic carboxyl groups (COOH, $\overset{\curvearrowright}{\text{C}}\text{O}\text{O}\text{H}$)
1640–1500	1637	1632	–5	stretching vibration of the asymmetric and symmetric COO [–] (deprotonated carboxylate)
1500–1515	1509	1512	+3	aromatic ring C=C skeleton stretching
1470–1420	1457	absent	–	CH ₂ /CH ₃ asymmetric bending
1470–1420	1423	absent	–	scissoring bending of methylene
1380–1370	1374	absent	–	symmetric bending of methyl
1300–1000	1268	1264	–4	C–O stretching of aryl ether bond
1300–1000	1058	1057	–1	C–O stretching of C–O–C and C–OH
1000–900	absent	920	–	U=O asymmetric stretching of uranyl

SEM-EDS and XPS analyses of fir sawdust

Combined SEM-EDS and XPS characterization techniques were adopted to investigate variations in the micromorphology, elemental distribution, and surface functional groups of fir sawdust before and after U(VI) adsorption (Fig. 3 , Fig. S6), so as to elucidate the underlying adsorption mechanism. As shown in the SEM micrograph of raw fir sawdust prior to adsorption (inset of Fig. 3b, Fig. S6a & b), the sample surface displays folded and uneven textures. Such rough

morphological characteristics yield a large specific surface area, thereby facilitating the diffusion and enrichment of uranyl ions from aqueous solution onto the adsorbent surface via van der Waals force. The corresponding EDS spectrum displays only characteristic peaks for C and O (Fig. 3b), which accords with the elemental composition of lignocellulosic substrates, and uranium is not detected. Likewise, the XPS full spectrum of raw sawdust prior to adsorption exhibits largely identical elemental signals to the EDS spectrum, with an absence of uranium peaks (Fig. 3a).

Significant changes in the surface micromorphology of fir sawdust were observed after U(VI) adsorption (inset in Fig. 3d, Fig. S6c ☒ d). Numerous spherical nanoparticles emerged uniformly on the material surface, likely corresponding to chelating deposits formed through complexation of uranyl ions with surface functional groups. Distinct characteristic peaks of U element were observed in the EDS energy spectrum (Fig. 3d), confirming the effective immobilization of uranyl ions onto the sawdust surface. The full spectrum of XPS displayed new U4f characteristic peaks, and its high-resolution spectrum exhibited characteristic U(VI) doublet peaks at binding energies of 382.3 eV (U4f_{7/2}) and 392.9 eV (U4f_{5/2}) (Fig. 3c), further indicating that UO₂²⁺ was successfully loaded onto the surface of the sawdust.

Based on the above SEM-EDS, XPS and FTIR analysis, it can be inferred that the adsorption of UO₂²⁺ onto sawdust proceeds mainly via chemisorption. On the one hand, surface carboxyl (-COOH) and hydroxyl (-OH) groups of sawdust dissociate to release H⁺, which then participates in cation exchange with aqueous UO₂²⁺ to preliminarily bind and immobilize uranyl ions. On the other side, carboxylate and hydroxyl oxygen atoms chelate UO₂²⁺ via coordination interactions with its unoccupied outer orbitals to form stable organic-uranium

1 coordination complexes, representing another major mechanism
2 underlying uranyl removal.

3 Peak fitting was further performed on the high-resolution C1s and
4 O1s XPS spectra of sawdust samples collected before and after
5 adsorption to compare the binding energies of characteristic peaks
6 belonging to identical functional groups (Fig. S7, Table 6). The
7 binding energies of all C1s and O1s subpeaks showed only minor
8 fluctuations and no prominent overall shifts, suggesting little change
9 to the chemical environment of carbon-oxygen functional groups. This
10 result suggests that the cellulose-lignin skeleton structure of sawdust
11 remains intact, and oxygen-containing functional groups only bind to
12 uranyl through coordination and ion exchange, without breaking the
13 matrix chemical bonds or destroying its inherent skeleton structure.
14 In essence, fir sawdust relies on its surface active functional groups
15 as the dominant active sites to realize the stable adsorption of uranyl.

16

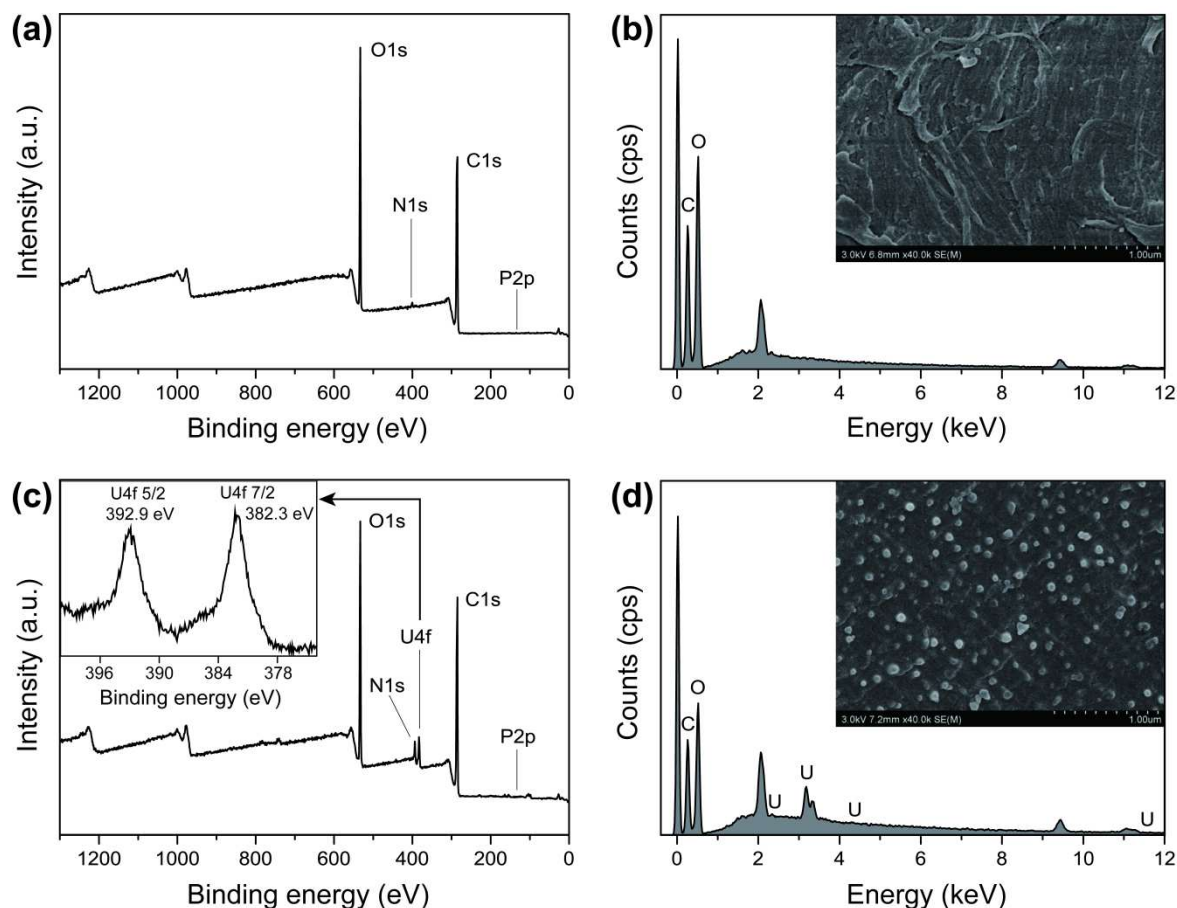


Fig. 3 XPS of fir sawdust before (a) and after (c) U(VI) adsorption; Scanning electron microscopic (SEM) and chemical analysis analysis of fir sawdust before (b) and after (d) U(VI) adsorption

Table 6 XPS peak fitting parameters of C1s and O1s for fir sawdust before and after adsorption

Atom orbitals	Functional group assignment	Binding energy before adsorption (eV)	Binding energy after adsorption (eV)
	C-C、C-H	284.8	284.8
C1s	C-O-H、 C-O-C	286.4	286.3
	C=O、O-C=O	287.5	287.5

1		C=O、O-C=O	531.5	531.5	
2	O1s	C-O-H、 C-O-C	532.9	532.8	
3		adsorbed water	534	534	

Conclusions

The adsorption of U(VI) onto fir sawdust in batch systems depends on contact time, pH, temperature, and initial uranium concentration. Among these, pH exerts the most pronounced effect, with maximum U(VI) uptake by fir sawdust achieved at pH 4.5. The U(VI) adsorption kinetics can be better described by the pseudo-second-order model, indicative of chemical adsorption as the rate-limiting step. The adsorption isotherm data fit the Langmuir model well, which suggests monolayer adsorption occurs on the adsorbent surface. The maximum U(VI) adsorption capacity of fir sawdust was calculated to be 148.81 mg/g from Langmuir model. Thermodynamic data indicate that the process of U(VI) adsorption is spontaneous and endothermic. The FTIR, SEM-EDS, and XPS analyses confirm that the adsorption of U(VI) onto fir sawdust is governed by the synergistic effects of surface complexation and ion exchange. The hydroxyl, carboxyl, and ketone groups on the material surface were the main active functional groups involved in the adsorption reaction. These findings demonstrate that fir sawdust is a highly effective adsorbent for uranium removal from radioactive wastewater.

Acknowledgements

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- 8

Supplementary information

Insights into Kinetics, Equilibrium and Thermodynamics of Uranium Uptake onto Fir Sawdust

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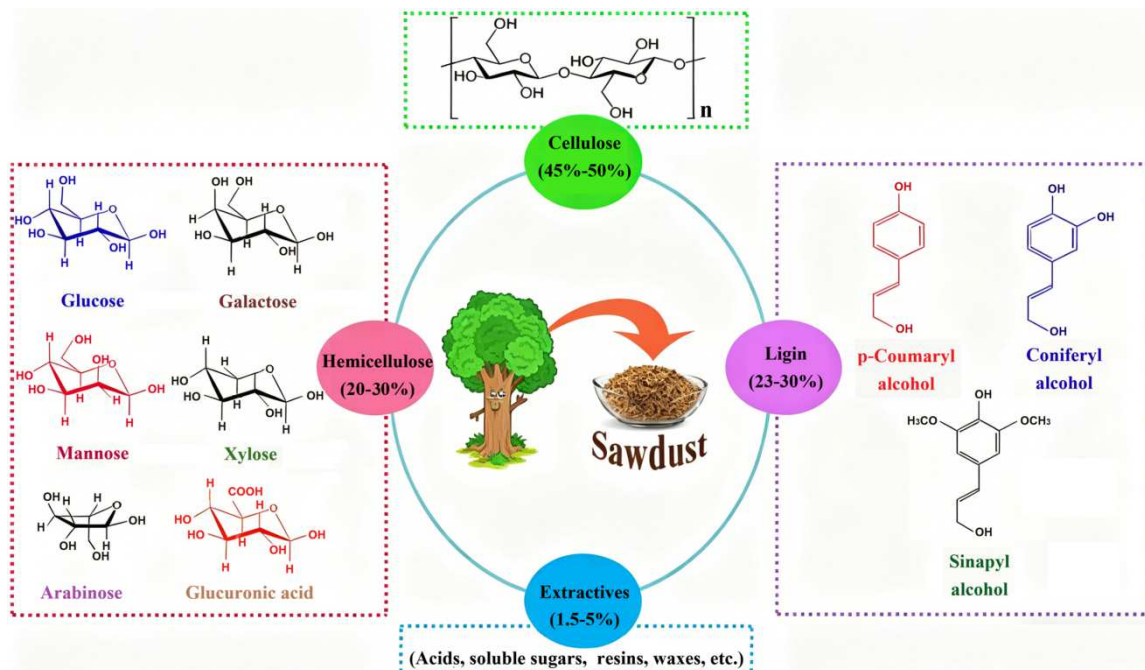


Fig. S1 Sawdust and its chemical structural components



Fig. S2 Images of (a) fir tree, (b) tree trunk, and (c) fir sawdust

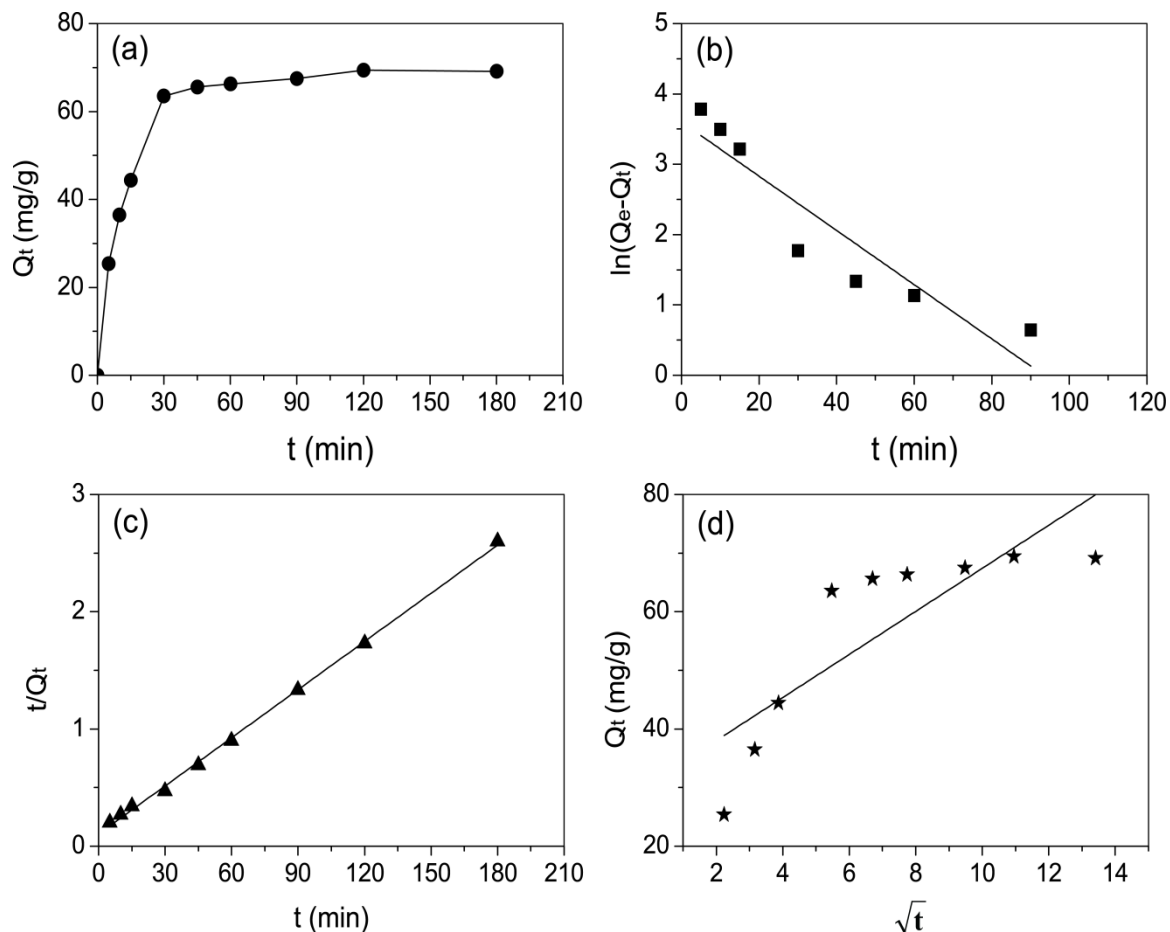


Fig. S3 Kinetic model fitting curves for uranium biosorption: (a) pseudo-first-order, (b) pseudo-second-order, and (c) intraparticle diffusion ($T = 298$ K, $\text{pH} = 4.5$, $C_0 = 100$ mg L⁻¹, $W = 0.1$ g, $V = 100$ mL)

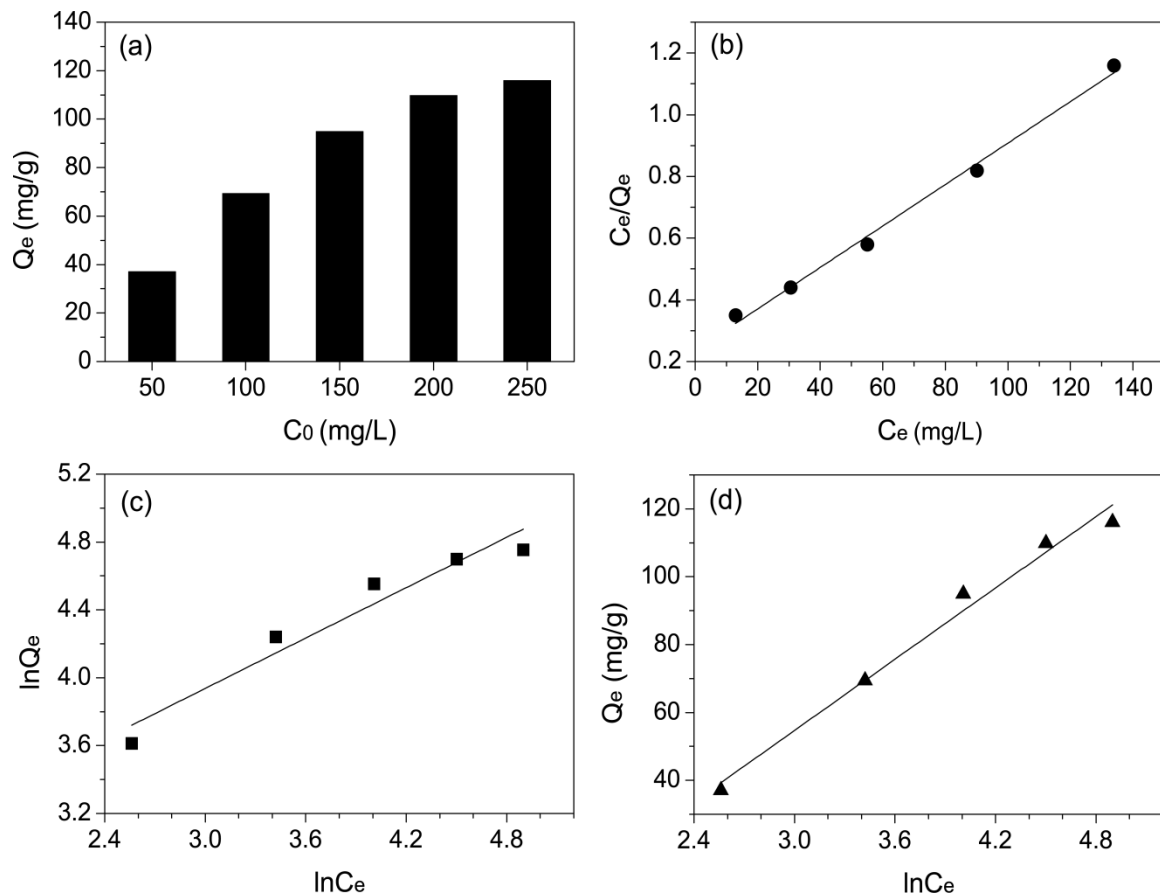


Fig. S4 (a) Effect of initial U(VI) concentration on the U(VI) adsorption capacity at equilibrium; (b) Langmuir fitting; (c) Freundlich fitting; (d) Temkin fitting ($T = 298$ K, $t = 120$ min, $\text{pH} = 4.5$, $C_0 = 50 \times 250$ mg L⁻¹, $W = 0.1$ g, $V = 100$ mL)

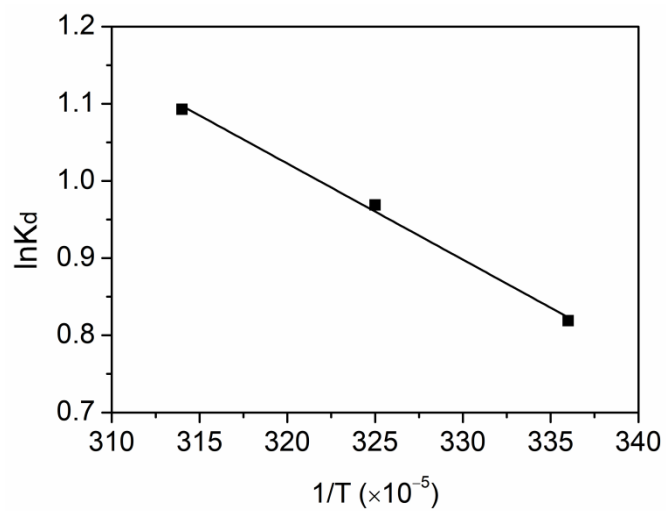
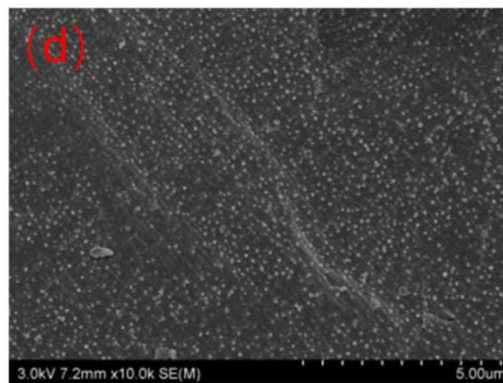
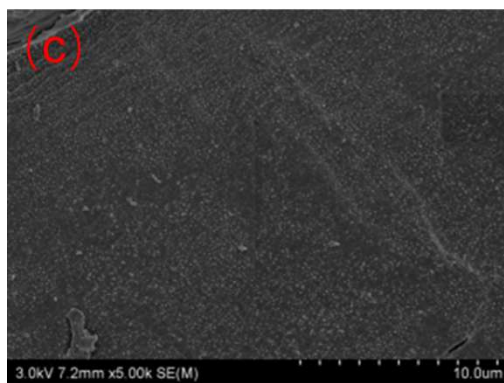
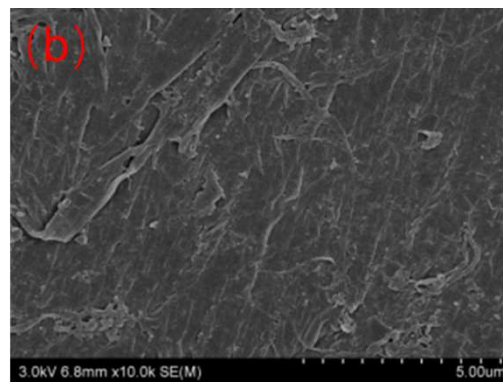
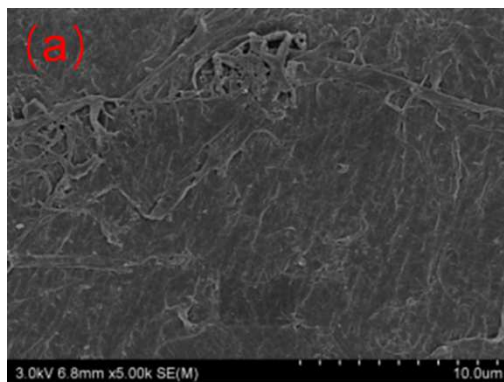
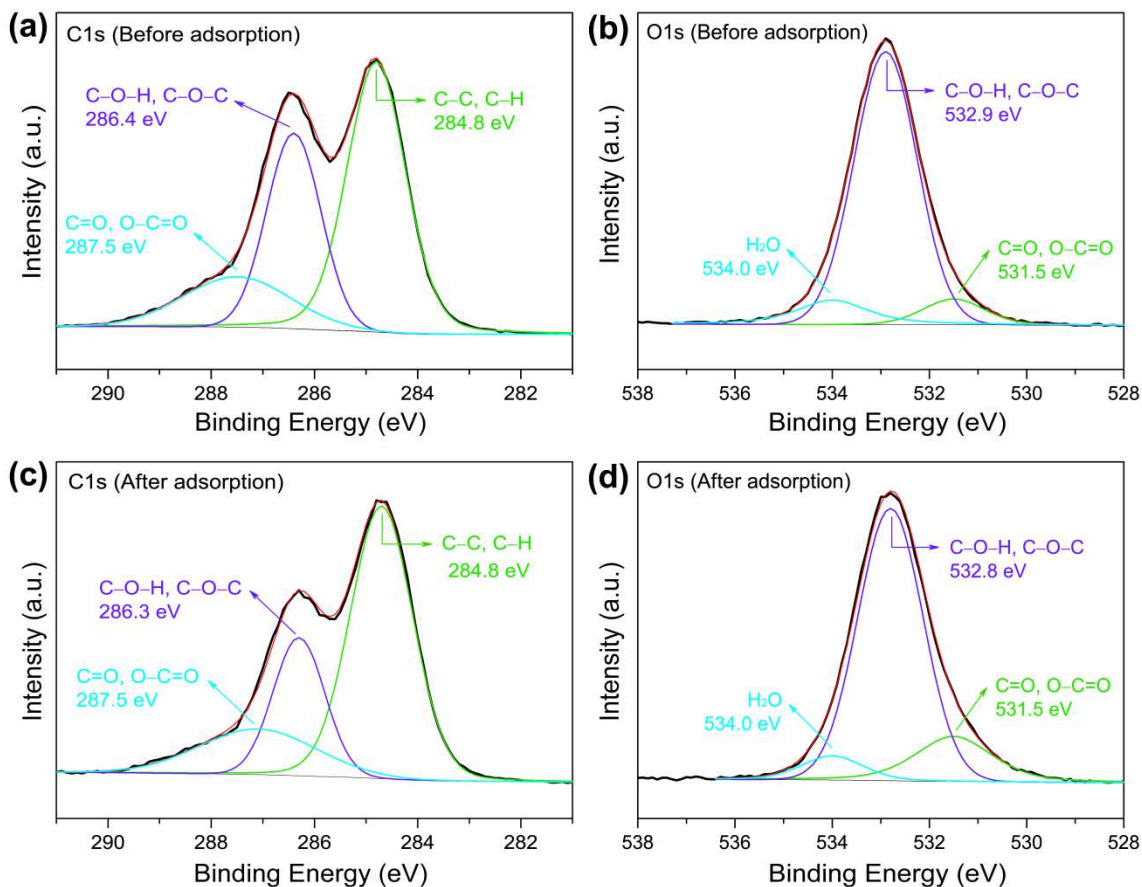


Fig. S5 Plot of $\ln K_d$ against $1/T$ for the calculation of thermodynamic parameters



1 **Fig. S6** SEM images of fir sawdust before (a and b) and after U(VI)
2 adsorption (c and d)

3



4

5 **Fig. S7** C1s XPS spectra of fir sawdust before and after U(VI)
6 adsorption (a and c); O1s XPS spectra of fir sawdust before and after
7 U(VI) adsorption (b and d)