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REMOVAL OF URANIUM(VI)
FROM AQUEOUS SOLUTION BY RICE HUSK

Basic aspects of uranium adsorption by rice husk have been investigated. The influences of various experimental parameters such as pH, time, adsorbent dosage, rice husk size, temperature and various concentrations of uranium on uptake were evaluated. The thermodynamics and kinetics of adsorption were analyzed by FT-IR and SEM. The adsorption capacity for uranium on rice husk increased upon increasing initial concentration of uranium and temperature, while decreased with the increase of the amount of rice husk. Maximum uranium adsorption was observed at pH = 3 and particle size between 120 µm and 150 µm. Adsorption equilibrium was achieved within 60 min. At 25 °C, the saturated adsorption capacity q_{max} was up to 15.14 mg/g when the initial concentration of uranium ranged from 10 to 400 mg/dm^3. The adsorption of uranium followed Langmuir adsorption isotherm and according to quasi-second order kinetic equation. The calculated values of $\Delta H°$, $\Delta S°$, and $\Delta G°$ indicated that the biosorption process was endothermic and spontaneous. Based on FT-IR spectra it may be concluded that hydroxyl, carbonyl, P–O and Si=O groups are the main active sites.

1. INTRODUCTION

Uranium is one of the most important heavy metals displaying chemical toxicity and radioactivity. Excessive amounts of uranium have entered into the environment through several activities related to the nuclear industry [1]. Uranium disposed into the environment can eventually reach the top of the food chain and then be ingested by humans, causing severe kidney or liver damage and even death [2]. Uranium played a dangerous role in human's life, which has greatly prompted the development of various technologies for its removal from wastes produced from nuclear power programs

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and nuclear fuel reprocessing activities. At present, various microorganisms and related biopolymers for uranium biosorption are reported in the literature [3–5].Tu et al. [3] used *Rhodosporidium fluviale*, *Rhodotorula glutinis* as biosorbents for ^{137}Cs and uranium, which showed that the biosorption of ^{137}Cs on *Rhodosporidium fluviale* UA2 was a fast and pH-dependent process in the solution composed of *R. fluviale* strain UA2 (5 g/dm^3) and cesium (1 mg/dm^3). The maximum adsorption capacity of *Rhodotorula glutinis* was identified to be 149.4 mg/g (dry cell) at uranium concentration of 330 mg/dm^3. Comparison of the conventional treatment methods have indicated that these biomass-based systems are more acceptable being cost effective, dilute effluents, and minimizing the disposable sludge volume. They also offer the flexibility for developing non-destructive desorption techniques for biomass regeneration and quantitative metal recovery. Wang et al. [6] used wheat straw to adsorb uranium and showed that wheat straw could be regenerated by 1 M HCl. Amin et al. [7] used rice straw to adsorb phenol and found that adsorbed phenol could be desorbed with the help of 1 M NaOH.

For the last decade, biosorption of radionuclides on various biomasses such as side products of wool production, rice and tea leaves, straw, coco shaving, peat, etc., were increasingly studied due to the different type of functional groups that can take place in the biosorption reactions [6, 8, 9].The result of Wang et al. [6] showed that uranium--containing sites of wheat straw existed on the surface of the structure with hydroxyl, carbonyl, P–O and Si=O groups.

Rice husk, being of a high yield, is obtained from agriculture as a by-product. It contains abundant floristic fiber, protein, and some functional groups in its chemical structure such as carboxyl, hydroxyl, amidogen groups, etc., which enable the biosorption processes [10, 11]. In our work, we adopted the effective-accumulation rice husk to deal with the uranium-containing wastewater. The aim of our work was to study the possibility of the utilization of rice husk for removal of uranium(VI) from aqueous solutions in a batch system and to investigate its kinetic and thermodynamic mechanism thoroughly. The using of rice husk as a biosorbent material can lower both the cost of production and the processing expenses of the industrial residua. It will provide a reliable theoretical basis and technical support for its engineering practice.

2. MATERIALS AND METHODS

Main instruments. PHS-3C precision pH meters, a GB303 electronic balance, an SHC-C vertical temperature oscillators, a TG16-WS centrifuge, an 721 UV-Vis spectrophotometer, an JSM-6700F scanning electron microscope (SEM), and a PE-1710 Fourier transform infrared spectrometer (FT-IR) were used in the experiments.

Treatment of rice husk. The rice husk used in the present investigation was obtained from a local mill. The collected materials were washed with distilled water for several times and dried in an oven at 25 °C for a period of 24 h, and then ground and screened through a set of sieves to get different geometrical sizes and stored at room temperature in a sealed bottle.

Uranium solution. For the preparation of uranyl solutions, 1.1792 g uranous uranic oxide was put into a 100 cm^3 beaker and 10 cm^3 of hydrochloric acid (specific gravity 1.19 g/cm^3), 3 cm^3 of 30% hydrogen dioxide, and two drops of nitric acid (specific gravity 1.42 g/cm^3) were added. The beaker was covered and shaken for 3 min. After initiation of the reaction, the beaker was heated in a sand bath to completely dissolve solids and then cooled down. The solution was then transferred to a 1000 cm^3 flask, diluted with about 900 cm^3 of water, and shaken again to produce the initial uranium(VI) solution with a concentration of 1 g/dm^3.

Batch adsorption studies. Batch techniques to study the adsorption of uranium(VI) onto rice husk were conducted in flasks. 25 cm^3 of U(VI) standard solution was transferred into Erlenmeyer flask, and its pH was adjusted with HCl or NaOH. Some rice husk sample was added into the flask placed in a temperature controlled orbital shaker (4000 rpm for 10 min). The concentration of uranium in the feed solution as well as residual uranium in the filtrate was determined by UV-Vis spectrophotometry and the following parameters were calculated:

$$y = \frac{c_0 - c_t}{c_0} \times 100\% \tag{1}$$

$$q_t = \frac{(c_0 - c_t)V}{m} \tag{2}$$

where y is adsorption yield (%), q_t (mg/g) is the amount of U(VI) adsorbed per unit mass of the absorbent; c_0 and c_t (mg/dm^3) are the concentrations of U(VI) in the solution before and after biosorption, respectively. V (dm^3) is the volume of the aqueous solution and m (g) is the weight of the adsorbent.

The adsorption duration, pH, initial uranium(VI) concentration, adsorbent dosage, rice husk size and temperature were separately changed in the studies. The adsorption time were 10, 20, 30, 40, 50, 60, 70, 80, 100 and 120 min. pH of the U(VI) solution was changed in the range of 1–8. Initial uranium(VI) concentration ranged from 10 to 400 mg/dm^3. Adsorbent dosages were 2, 4, 6, 8, 10, 12 and 14 g/dm^3. Rice husk sizes ranged from 85 to 400 μm. Temperature was changed from 10 °C to 55 °C and amounted to 10, 15, 25, 35, 45 and 55 °C.

Adsorption isotherm. The Langmuir and Freundlich isotherms were used to simulate the adsorption capacity of uranium by rice husk [12–14]

- Langmuir isotherm

$$\frac{c_e}{q} = \frac{c_e}{q_{max}} + \frac{1}{q_{max}b} \tag{3}$$

- Freundlich isotherm

$$\lg q = \lg k + \frac{1}{n}\lg c_e \tag{4}$$

where q (mg/g) represents the equilibrium adsorption capacity, c_e (mg/dm^3) denotes the equilibrium concentration of the residual metal, q_{max} (mg/g) represents the maximum adsorption capacity, b is the ratio of the adsorption (dm^3/mg), k ((mg/g)(mg/dm^3)$^{-1/n}$) is a constant of adsorption and $1/n$ is the coefficient of intensity of adsorption.

Thermodynamic studies. The thermodynamic functions for the sorption process were calculated as follows:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -RT \ln K, \qquad \ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{5}$$

where ΔH° is the standard enthalpy (kJ/mol), ΔS° is the standard entropy (kJ/(mol·K)), ΔG° is the standard Gibbs free energy (kJ/mol), K is the equilibrium constant, T is the absolute temperature (K), and R is the gas constant (8.314 kJ/(mol·K)).

Adsorption kinetics. The pseud-first and pseudo-second order models of Lagergren –Annadurai–Krishnan were used to describe the kinetic characteristics of uranium(VI) adsorbed by rice husk [15, 16].

- pseudo-first order kinetic model:

$$\lg(q_e - q_t) = \lg q_e - \frac{k_1 t}{2.303} \tag{6}$$

- pseudo-second order kinetic model:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{7}$$

where q_e (mg/g) denotes the equilibrium adsorption capacity, q_t (mg/g) – the adsorption capacity after time t, and k_1 (1/min) and k_2 (g/(mg·min)) – the adsorption rate constants for the first and second order models, respectively.

3. RESULTS AND DISCUSSION

Effect of adsorption duration on the adsorption efficiency. The effect of adsorption duration on uranium(VI) adsorption by rice husk was studied between 10 and 120 min at 25 °C, pH = 3, 150 µm using uranium(VI) of 100 mg/dm^3 initial concentration, 8 g/dm^3 adsorbent dosage.
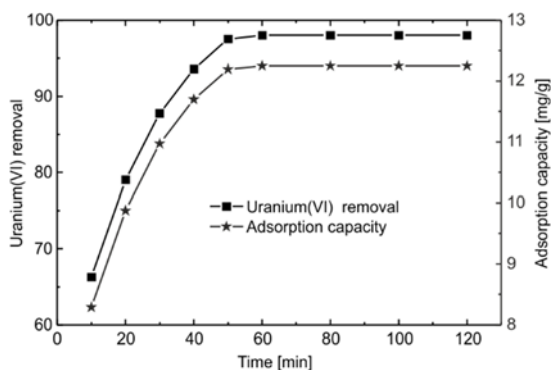

Fig. 1. Effect of duration on uranium biosorption by rice husk (adsorbent dose – 8 g/dm^3, pH = 3, T = 25 °C, rice husk size –150 µm, initial uranium concentration – 100 mg/dm^3)

Figure 1 shows that the U(VI) removal efficiency onto rice husk increases upon increasing adsorption duration. In the first 50 min, the biosorption proceeds very quickly and 97% of U(VI) adsorption takes place within 60 min; then it remains nearly constant after this period. According to Fig. 1, the practical adsorption duration to reach equilibrium should be 60 min.

Effect of solution pH on adsorption efficiency. The pH level of solution is one of the most important parameters on adsorption of metal ions from aqueous solutions. It influences both the speciation of U in the aqueous solution and the binding sites presenting on the surface of biomass. The effect of pH on uranium(VI) adsorption by rice husk was studied in the pH range of 1-8 at 25 °C for 60 min, 150 µm using 100 mg/dm^3 initial uranium(VI) concentration, 8 g/dm^3 adsorbent dosage. 10% HCl or NaOH solutions were used to adjust pH.

As is seen in Fig. 2, the percentage removal and the values of q increase upon pH increasing from 1 to 3, whereas in the range of pH from 3 to 8, the adsorption decreases sharply. Obviously, the maximum removal efficiency of U was obtained at pH = 3.0.

These phenomena may be explained by competition of H$^+$ ions with uranium binding sites at lower pH and the formation of extractable uranium species at higher pH. At lower pH, the concentration of H$^+$ ions is high, which compete with other ions (uranyl) for the binding sites on the surface of the biomass [17] resulting in a decrease in biosorption of uranium. At the maximum adsorption (pH = 3), the predominant uranium ions in the adsorption medium are UO_2^{2+}, $[UO_2(OH)]^+$, $[(UO_2)_2(OH)_2]^{2+}$, and

$[(UO_2)_3(OH)_5]^+$ [18]. When pH is exceeding 3, precipitation starts due to the formation of complexes in aqueous solution and adsorption decreases [19].
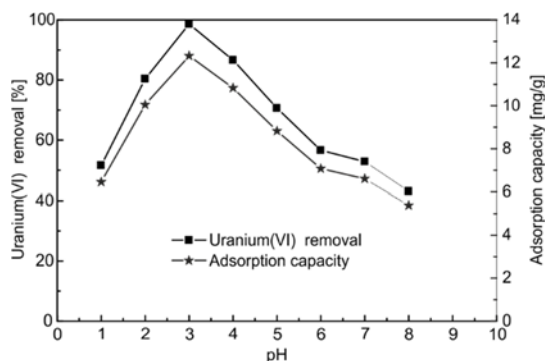

Fig. 2. Effect of pH on uranium biosorption by rice husk (adsorbent dose – 8 g/dm^3, t = 60 min, T = 25 °C, rice husk size – 150 μm, initial uranium concentration – 100 mg/dm^3)

Effect of initial uranium(VI) concentration. Several experiments were taken to study the effect of the initial uranium ions on the UO_2^{2+} ions removal from the solution. The effect of initial uranium(VI) concentration was studied for the range of 10–400 mg/dm^3 at 25 °C, pH = 3, 60 min, 150 μm with the 8 g/dm^3 adsorbent dosage.
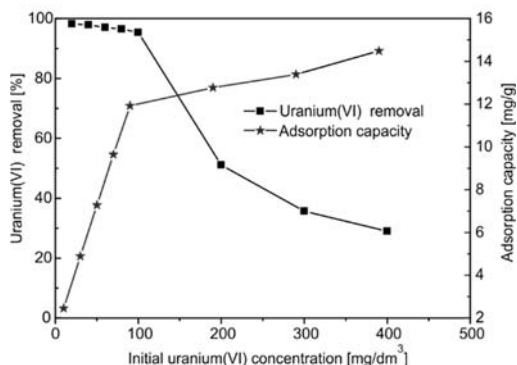

Fig. 3. Effect of initial uranium concentration on uranium biosorption by rice husk (adsorbent dose – 8 g/dm^3, pH = 3, t = 60 min, T = 25 °C, rice husk size – 150 μm)

For all samples, the data shows that the metal uptake increases and adsorption percentage of UO_2^{2+} ions decreases with the increase of initial UO_2^{2+} ion concentration (Fig. 3). The removal efficiency exceeds 95% when the initial concentration of uranium ions is below 100 mg/dm^3. At low UO_2^{2+} concentrations, the ratio of surface active sites to the total UO_2^{2+} ions in the solution is relatively high and almost all UO_2^{2+} ions may interact with the adsorbent and be removed from the solution. However, the amount of UO_2^{2+} ions adsorbed per unit weight of adsorbent is higher at high concentrations. As a result, the rice husk adsorbent is more efficient for the wastewaters of low UO_2^{2+} ions

concentrations and the purification yield can be increased by diluting the wastewaters containing high UO_2^{2+} ions concentrations.

Effect of adsorbent dosage on adsorption efficiency. The effect of adsorbent dosage was studied for the range of 2–14 g/dm^3 at 25 °C, pH = 3, 60 min, 150 µm using 100 mg/dm^3 initial uranium(VI) concentration.
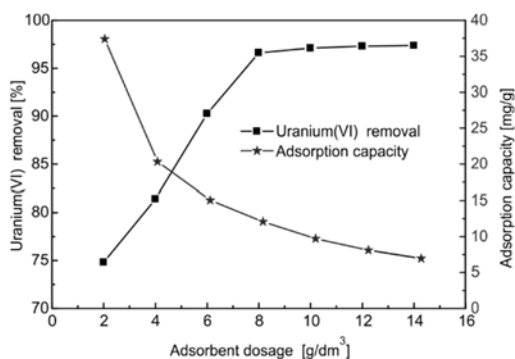

Fig. 4. Effect of adsorbent dosage on uranium biosorption by rice husk (pH = 3, t = 60 min, T = 25 °C, rice husk size – 150 µm, initial uranium(VI) concentration – 100 mg/dm^3)

The removal of UO_2^{2+} ions is dependent on the adsorbent dose (Fig. 4). Upon increasing the adsorbent dose, the amount of UO_2^{2+} ions adsorbed per unit weight of adsorbent decreases. Remarkably, the higher the concentration of adsorbent dose is, the better the removal of uranium. There is a very fast adsorption enhancement onto the rice husk at higher adsorbent concentration [20]. Thus, the adsorption capacity decreases or the removal percentage increases with the increase of adsorbent dose.

Effect of rice husk size on adsorption efficiency. The effect of rice husk size was studied for the range of 85–400 µm at 25 °C, pH = 3, 60 min, 100 mg/dm^3 initial uranium(VI) concentration, 8 g/dm^3 adsorbent dosage.
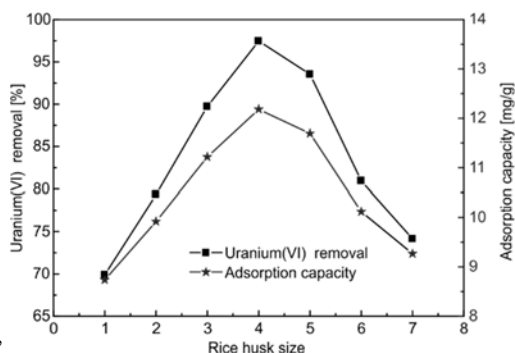

Fig. 5. Effect of rice husk size (in µm) on uranium biosorption: 1) 250–380, 2) 80–250, 3)150–180, 4)120–150, 5)109–120, 6) 96 –109, 7) 80–96 (adsorbent dose – 8 g/dm^3, pH = 3, t = 60 min, T =25 °C, initial uranium(VI) concentration – 100 mg/dm^3)

For the particle size between 125 and 150 μm, the removal efficiency is optimal (Fig. 5), the adsorption capacity of UO_2^{2+} by rice husk reaches the maximum as well. These results suggest that surface area of rice husk plays an important role on the sorption of UO_2^{2+} ions.

Effect of temperature on adsorption efficiency. The effect of temperature was studied in the range between 10 and 55 °C at pH=3, 60 min, 150 μm using 100 mg/dm^3 initial uranium(VI) concentration, 8 g/dm^{3}adsorbent dosage.
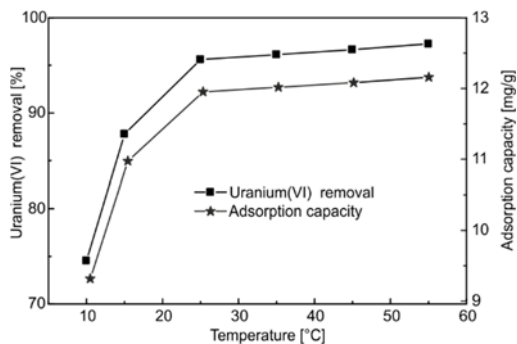

Fig. 6. Effect of temperature on uranium biosorption by rice husk (adsorbent dose – 8 g/dm^3, pH = 3, t = 60 min, rice husk size –150 μm, initial uranium concentration – 100 mg/dm^3)

Batch experiments were performed under the temperature range 10–60 °C. The results are presented in Fig. 6. The increase of temperature greatly enhances the U(VI) removal rate and the adsorption capacity, which is beneficial for the adsorption process. These results may indicate that some new activity sites are generated during heating or that the ions get over the energy barrier to resist concentration gradient or endure diffusion transmission [6].

Equilibrium modeling. The Langmuir and Freundlich isotherm plots for the U(VI) biosorption onto rice husk are presented in Figs. 7 and 8. The correlation coefficient R^2 for both models were 0.99549 and 0.66595, respectively. The Langmuir isotherm model better describes the experimental data than Freundlich model. The Langmuir and Freundlich isotherm parameters at 298 K calculated based on the literature data (Table 1) show that rice husk, as an abundant low cost biomaterial with a high U(VI) uptake capacity (q_{max} = 14.8588 mg/g), should be seriously considered for the disposal of uranium from wastewater.

T a b l e   1

Uranium biosorption isotherm constants by rice husk

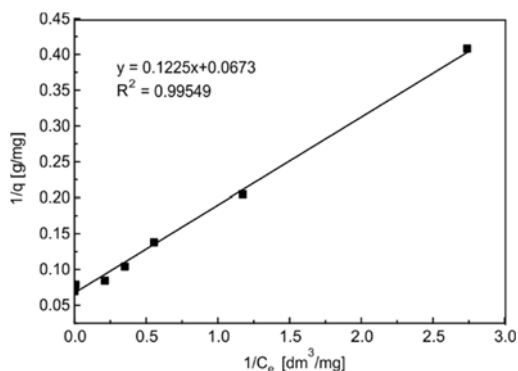| Langmuir model			Freundlich model		
q_{max} [mg/g]	b [dm^3/g]	R^2	k [(mg/g)(mg/dm^3)$^{-1/n}$]	n	R^2
14.8588	0.5494	0.9955	6.9759	7.2993	0.6660

Fig. 7. Langmuir isotherm of uranium
biosorption on rice husk
(adsorbent dose – 8 g/dm^3, pH = 3,
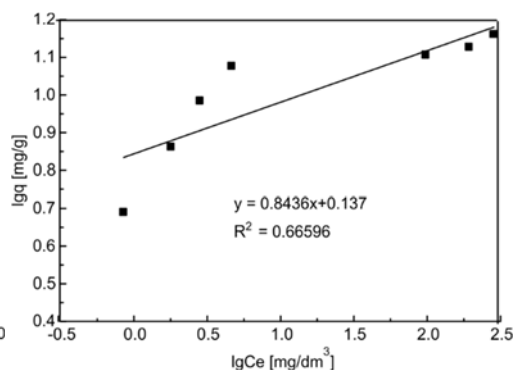t = 60 min, T = 298 K, rice husk size – 150 μm)

Fig. 8. Freundlich isotherm of uranium
biosorption on rice husk
(adsorbent dose – 8 g/dm^3, pH = 3,
t = 60 min, T = 298 K, rice husk size – 150 μm)

Thermodynamic studies. The experiments were carried out at 298–328 K and uranium(VI) concentration of 100 mg/dm^3. The values of $\Delta H°$ and $\Delta S°$ were calculated from the slopes and intercepts of linear regression of ln$K$ versus $1/T$. The values of $\Delta G°$ were calculated Eq. (5). The values of $\Delta H°$, $\Delta G°$, and $\Delta S°$ at various temperatures are given in Table 2.

Table 2

Thermodynamic parameters for uranium biosorption by rice husk

T [K]	$\Delta G°$ [kJ/mol]	$\Delta H°$ [kJ/mol]	$\Delta S°$ [kJ/(mol·K)]
298	−53.93		
308	−63.61	365.6	1.4
318	−76.32		
328	−96.83		

The positive value of $\Delta H°$ demonstrates the endothermic nature of the adsorption process and negative free energy $\Delta G°$ indicates the feasibility of the process. Besides, the adsorption process takes place spontaneously without any induction period.

Kinetic modeling. According to Figs. 9 and 10, the higher value of the correlation coefficient r for the pseudo-second order kinetic model than for the pseudo-first order model indicates that the former one better describes the kinetics of the process and the adsorption rate is proportional to the number of unoccupied sites.
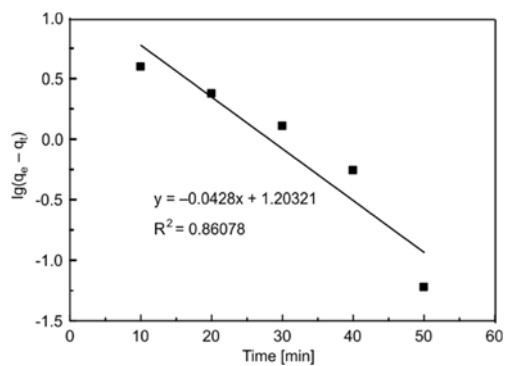
Fig. 9. Pseudo-first order model (adsorbent dose – 8 g/dm³, pH = 3, T = 298 K, rice husk size – 150 μm, initial uranium(VI) concentration – 100 mg/dm³)
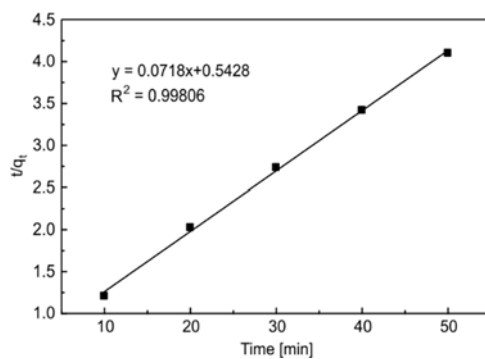
Fig. 10. Pseudo-second order model (adsorbent dose – 8 g/dm³, pH = 3, T = 298 K, rice husk size – 150 μm, initial uranium(VI) concentration – 100 mg/dm³)

FT-IR images before and after adsorption. Figure 11a shows the FT-IR spectroscopy of rice husk before adsorption of uranium. The broad band observed at 3280 cm⁻¹
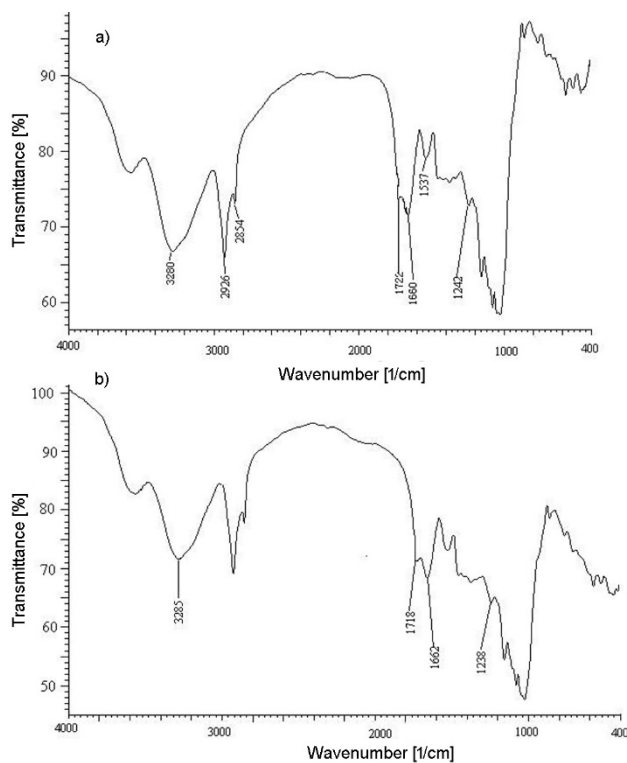

Fig. 11. FT-IR of rice husk before (a) and after (b) adsorption of uranium

is due to O–H stretching vibration. The band at 2926 cm^{-1} is assigned to C–H asymmetric stretching mode of methyl and methylene groups on the surface and 2854 cm^{-1} to methylene C–H symmetric stretching vibration. The peaks located at 1722 and 1660 cm^{-1} are characteristic stretching vibrations of carbonyl groups of carboxylates and ketones. The peak near 1456 cm^{-1} is attributed to the asymmetric bending stretching mode of CH_2, and 1377 cm^{-1} is the symmetric bending stretching mode of CH_3. The peak at 1157 cm^{-1} is assigned to C–O stretching vibration in phenols. The band around 1047 cm^{-1} can be assigned to phosphate and silicate groups. As is seen, the main rice husk cells contain –OH, C=O, P–O, Si=O, and other active groups.

The absorbance spectrum of rice husk loaded with UO_2^{2+} ions is shown in Fig. 11b. After adsorption of uranium, some peaks slightly shift with no new bands appearing, which indicates that the rice husk structure does not change after adsorption of uranium. The peaks at 3280, 1722, 1660 and 1242 cm^{-1} are shifted to 3285, 1718, 1662, and 1238 cm^{-1}, respectively, which demonstrates that some H$^+$ ions are replaced by UO_2^{2+}. It may result in the decrease of the C=O bond strength and of the wavenumber of the maximum absorption peak. The spectrum shows that the main adsorption active sites of the rice husk are associated with –OH, C=O, P–O and Si=O bonds.

Scanning electron microscopy (SEM) images before and after adsorption. The morphology of rice husk before and after adsorption observed by SEM are shown in Fig. 12.
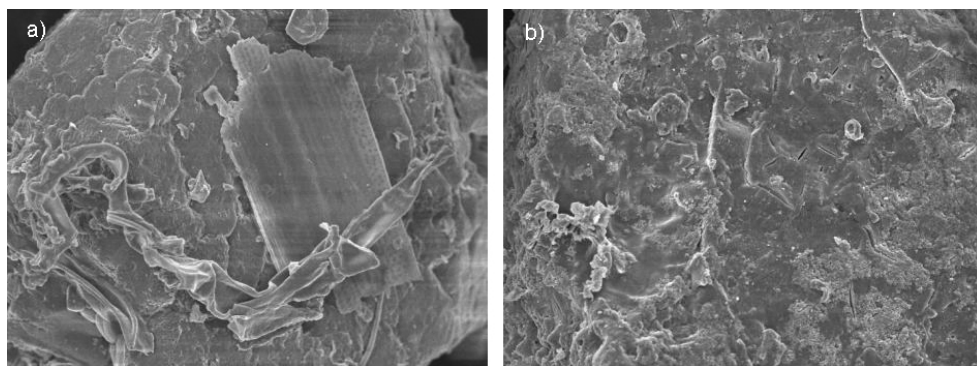

Fig. 12. SEM of rice husk before (a), after (b) biosorption of uranium

Before adsorption, the surface of rice husk is slippery with numerous interstices and cavities while after adsorption, the distribution density of interstices and cavities decreases and a great deal of opaque crystals adheres to the surface, which indicates that rice husk adsorbs a certain amount of UO_2^{2+}. The cell walls of rice husk consist of carbohydrates, xylogens, and celluloses which can provide a great deal of organic groups

as ligands interaction with UO_2^{2+} with unoccupied orbitals. Consequently, the SEM image of the surface of rice husk after adsorption fundamentally changes.

4. CONCLUSION

The adsorption capacity for uranium on rice husk increases with the increase of initial concentration of uranium and temperature, while decreases with the increase of the amount of rice husk. The rice husk exhibits the highest uptake capacity for uranium at 60 min, pH = 3 and the particle size of 125–150 μm. The adsorption of uranium on rice husk follows Langmuir adsorption isotherm according to quasi-second order kinetic equation. The thermodynamic functions $\Delta S°$, and of The process is endothermic ($\Delta H° > 0$), and adsorption rate is higher at higher temperatures. The positive entropy value demonstrate the affinity of rice husk to uranium. The positive value of $\Delta G°$ indicated that the adsorption is possible and takes place spontaneously. FT-IR micrographs before and after rice husk adsorption of uranium indicate that the activated sites of the rice husk are mainly composed of hydroxyl, carbonyl, P–O and Si=O groups, and the main way of adsorption of uranium is the ion exchange or surface complexation. The SEM images show that the rice husk surface changed after adsorption, which indicates the adsorption of a certain amount of UO_2^{2+} by rice husk.

ACKNOWLEDGEMENT

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