Biosorption characteristics of uranium(VI) from aqueous solution by pummelo peel

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Abstract The biomass pummelo peel was chosen as a biosorbent for removal of uranium(VI) from aqueous solution. The feasibility of adsorption of U(VI) by Pummelo peel was studied with batch adsorption experiments. The effects of contact time, biosorbent dosage and pH on adsorption capacity were investigated in detail. The pummelo peel exhibited the highest U(VI) sorption capacity 270.71 mg/g at an initial pH of 5.5, concentration of 50 μg/mL, temperature 303 K and contacting time 7 h. The adsorption process of U(VI) was found to follow the pseudo-second-order kinetic equation. The adsorption isotherm study indicated that it followed both the Langmuir adsorption isotherm and the Freundlich adsorption isotherm. The thermodynamic parameters values calculated clearly indicated that the adsorption process was feasible, spontaneous and endothermic in nature. These properties show that the pummelo peel has potential application in the removal of the uranium(VI) from the radioactive waste water.

Keywords Pummelo peel · Biosorption · Uranium

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Introduction

With the rapid development of the global nuclear industry, there are more and more radioactive waste types and quantities. Uranium is a prominent element whose isotopes occur in various concentrations and oxidation states in radioactive waste. Uranium, like lead, cadmium, and arsenic, is deposited in the kidneys and cause irreparable damage to the main filtering mechanism of the body. Hence, its potential damage on human health and ecological environment is growing. Recently, removal of uranium from radioactive waste water has drawn increasing attentions. Several traditional methods including chemical clarification, precipitation, membrane filtration, and reverse osmosis are available for removing uranium from waste water. Biosorption has become a favorable method of choice, as it is economically and environmentally more viable [1].

Biomass possess a remarkable ability for taking up toxic and precious metals because cell walls of microbial biomass can offer electron donating functional groups or ligands such as carboxyl, hydroxyl, amide or phosphoryl groups for metal ion binding [2]. As a low-cost biosorbent, agricultural waste attracted people's attention in applying to treatment of heavy metals in wastewater because of several advantages: (1) rich sources and chemically stable; (2) a high surface area (porous); (3) high efficiency to treat low concentrations of heavy metals in wastewater; (4) easy to produce high concentrations of metal ion adsorption active groups; and (5) easy to make chemical modification.

Agricultural waste has unique chemical compositions, including hemicellulose, lignin, lipids, proteins, sugars, starch, etc., which contain different functional groups that will help remove heavy metal ions through the metal complex, especially the materials containing cellulose raw have high capacity on pronounced metal ion adsorption [3].

Studies have shown that a variety of agricultural waste can remove toxic heavy metal ions effectively, such as rice bran [4], rice husk [5], bark [6], peanut shells [7], coconut shell [8], wheat straw [9], waste tea leaves [10], bagasse [11], water hyacinth [12], coffee beans [13], a variety of plants, sawdust [14], etc. [15, 16].

Pummelo is a major fruit planting in many parts of the south of China. Pummelo peel accounted for 54–44 %, the quality of their internal white flocculent layer of the skin contains large amounts of cellulose. Discarding pummelo peel is usually not only resulted in waste, but polluted the environment. Currently, study of pummelo peel on how to extract the oil, pigment and pectin is primary. Saikaew and Kaewsarn [17] studied on simulated adsorption of cadmium ion by pummelo peel. The results showed that pummelo peel with the ability of adsorbed cadmium, and the absorption capacity can reach 21.83 mg/g at the pH of around 5. However, to our knowledge, there is few report has been appeared for the uranium adsorption with pummelo peel.

In this context, we have studied the adsorption characteristics of uranium from aqueous solution onto pummelo peel. The influence of experimental conditions, such as pH, initial metal ions concentration, biosorbent dosage and temperature on the biosorption features was investigated. The Langmuir and Freundlich were used to fit experimental data of the equilibrium isotherm. The biosorption rates were determined quantitatively and compared by pseudo-first and pseudo-second models. This study is a useful attempt to expand the recycling of agricultural waste, which not only saves cost, but also environmental friendly.

Experimental

Solutions and reagents

All of the chemical reagents used in the experiments were of analytical grades. For the preparation of a stock uranium(VI) solution, 1.1792 g U_3O_8 was put into a 100 mL beaker, and 10 mL hydrochloric acid ($\rho = 1.18$ g/mL), 2 mL 30 % hydrogen peroxide were added. The solution was heated until it was nearly dry and then 10 mL hydrochloric acid ($\rho = 1.18$ g/mL) was added. The solution was transferred to a 1,000 mL volumetric flask and diluted to the mark with distilled water to produce a uranium(VI) stock solution (1 mg/mL). The uranium solutions were prepared by diluting the stock solution to appropriate volumes depending upon the experimental requirements.

Preparation and characterization of biosorbent

The pummelo peel used in this study was obtained from a local fruit market of Jiangxi in China. The preparing procedure of biosorbent was described as follows. The collected biomass was rinsed with distilled water, then soaked in 0.1 M sodium hydroxide for 4 h, washed with distilled water to neutral, and then dried in an oven at 60 °C for 48 h at last. Dry biomass was crushed into granules and used for the adsorption studies. Fourier transform infrared (FTIR) spectra were obtained using a Nicolet 380 spectrometer (USA) using KBr pellets of samples.

Adsorption studies

The batch sorption of uranium studies was performed in a reciprocating thermostated air bath shaker. A concussion agitation speed of 200 rpm was adopted for all experiments. In most of the experiments (except sorbent mass variation study), 0.01 g of sorbent was suspended in 100 mL solution of uranium. All experiments were performed in duplicates.

The concentration of uranium ions in solution was determined spectrophotometrically by Arsenazo-III method [18]. The adsorption amount q(mg/g) of uranium(VI) on adsorbent was calculated through the following equation:

$$q = \frac{(c_0 - c_e)V}{M} \tag{1}$$

where c_0 and c_e represent initial and equilibrium concentrations respectively (μg/mL). V is the volume of the solution in liter (L) and M is the mass of the adsorbent (g).

Statistical evaluation of the kinetic and isotherm parameters

In this work, the kinetic and equilibrium models were fitted employing the linear fitting method using the software Microcal Origin 7.0.

Results and discussion

Characterization of biosorbent

Figure 1 shows the FT-IR spectrum of the pummelo peel before and after uranium biosorption. Before the adsorption, the peak appeared at 3,400 cm^{-1} which was assigned to –OH and –NH stretching vibration [19], indicating a large presence of hydroxyl and amino in pummelo peel. The peak observed at 2,921 cm^{-1} was assigned to saturated hydrocarbon (C–H) [20], while the peak at 1,619 cm^{-1} was assigned to a carbonyl band (C=O). The above facts shows that the pummelo peel contains carbonyl, which likely to come from acid or ester because of that skin contains large amounts of pectin and cellulose [21]. The peak observed at
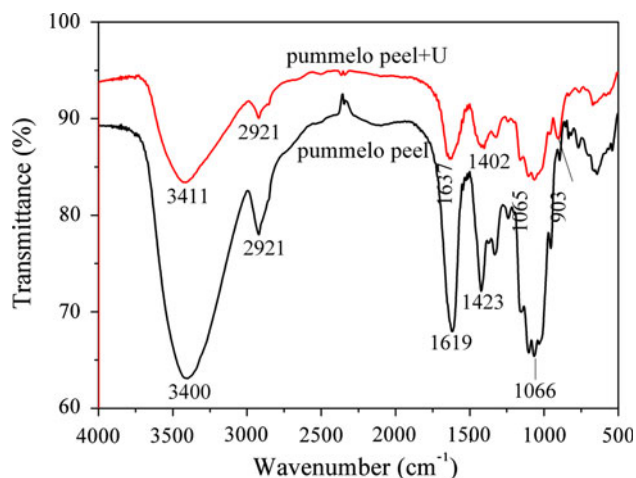
Fig. 1 FT-IR spectra for pummelo peel before and after uranium biosorption

Fig. 2 Effect of pH on U(VI) adsorption by pummelo peel

1,423 cm^{-1} was assigned to aromatic methyl, which is similar to the results of the literature [20].

After adsorption of uranium, the peak at 3,400 cm^{-1} weakened and shift to 3,411 cm^{-1}, which indicated hydroxyl and amino groups participated in the binding of U(VI); the changes of the peaks at 1619 and 1,423 cm^{-1} indicated that aromatic methyl and carbonyl were present in the binding of U(VI); 903 cm^{-1} appeared a new absorption peak for the uranyl ion stretching group. These results suggest that the hydroxyl, amino, carbonyl and aromatic methyl were involved in the process of adsorption uranium with the pummelo peel.

Effect of pH on sorption

Earlier studies on heavy metal biosorption have showed that pH is an important parameter affecting the biosorption process. It can influence the species of metal ions and ionization of surface functional groups [22]. The effect of pH on the adsorption of U(VI) onto the pummelo peel was carried out over the pH range 4.0–7.5 using 50 μg/mL initial uranium concentration at 308 K and the results were displayed in Fig. 2. As shown in Fig. 2, the adsorption amount of the biosorbent increased as the pH increased from 3.5 to 5.5 and reached a maximum 270 mg/g at the pH of 5.5, which was used in rest of the further studies. The adsorption amount was decreased as the pH rise from 5.5 to 7.5. This phenomenon may be because pummelo peel contains carboxyl and hydroxyl groups, the pH affect the electrical properties and electric quantity of these groups. The low sorption at lower pH values could be attributed to H$^+$ competition with uranium binding sites [23]. At low pH, the surface of the sorbent would be closely associated with protons (H$_3$O$^+$) which hindered the positively charged metal ions from reaching the binding sites of the sorbent.
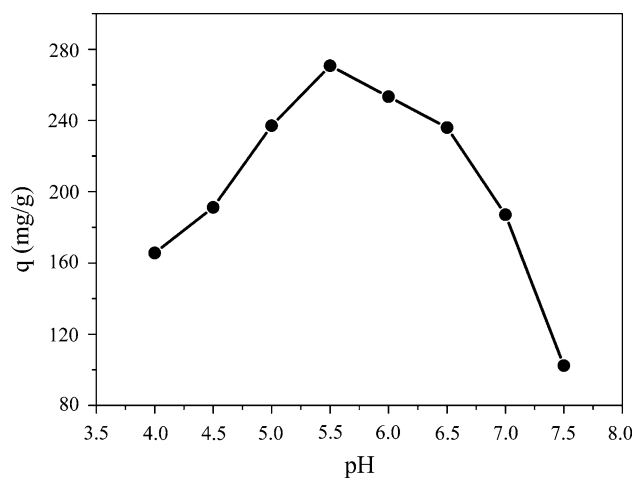
The extent of adsorption decreased as pH continued to rise from 6.0 to 7.5, which could be explained by the increase in the dissolved carbonate concentration with increasing pH. As dissolved carbonate and bicarbonate anions increased, they could compete adsorption sites with uranium(VI), thus resulting in a decrease in the adsorption amount continuously [24].

Effect of the amount of biosorbent on sorption

As it shown in Fig. 3, the adsorption capacity of uranium onto pummelo peel increased with the increase of the amount of pummelo peel. This is because the greater amount of pummelo peel can provide more surface functional groups and surface sites, which increased the adsorption capacity. When the adsorbent dosage is 0.05 g, and the concentration of uranium is 30 μg/mL, the removal rate can reach 97 % or more. When the adsorbent dosage is more than 0.03 g, the removal rate increases slowly and then tends to remain unchanged,
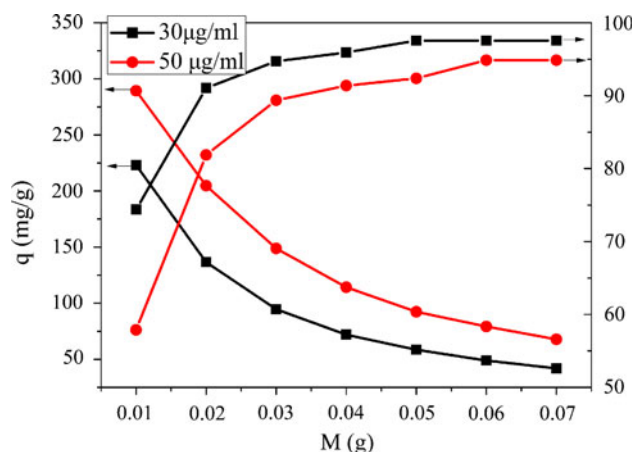
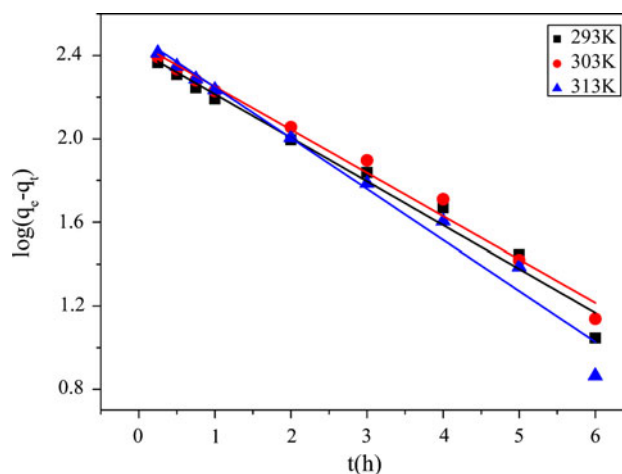Fig. 3 Effect of sorbent dose on the sorption of U(VI) onto pummelo peel
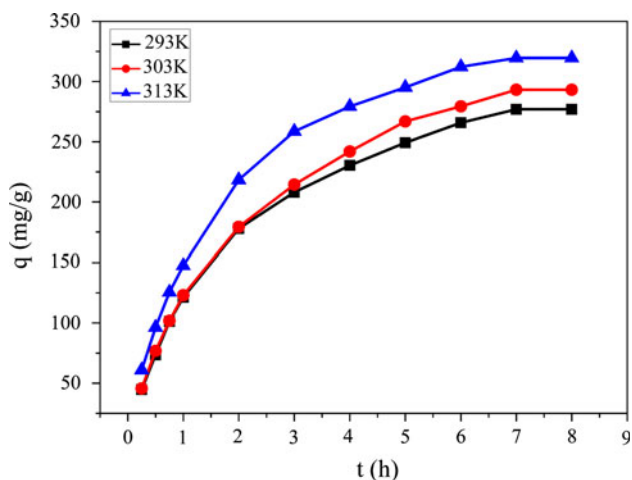
Fig. 4 Effect of contact time on U(VI) adsorption by pummelo peel

Fig. 5 Pseudo-first-order kinetic plot for the adsorption of U(VI) onto pummelo peel

which can be explained by that some active adsorption sites can not be exposed due to the skin aggregation or too much uranium in the remaining solution. Figure. 3 also shows that adsorption capacity of uranium on pummelo peel decreases while the amount of pummelo peel continues increasing. This is because the greater the amount of pummelo peel can provide more metal ion adsorption sites, so that pummelo peel binding sites can not be fully utilized, resulting in falling adsorption capacity of per unit mass.

Sorption kinetics

Adsorption time is another factor affecting the adsorption of heavy metals. Figure 4 shows that adsorption time effect adsorption capacity greatly in the early adsorption. Therefore, at the temperature 293, 303 and 313 K the best times to reach adsorption equilibrium are 7 h. Adsorption rate of uranium is fast at the start, followed the adsorption process has become slow. This is because pummelo peel absorption of uranium is not saturated in a short time, the adsorption rate is higher; then the pummelo peel surface adsorbed a lot of uranium, resulting in the adsorption activity site that can be used has reduced and increasing the difficulty for interface elements to get into the micro-hole.

In order to characterize the biosorption kinetics, several kinetic models were applied to the experimental data. Pseudo-first-order and pseudo-second-order kinetic equations were

applied to describe the kinetic characteristic of uranium(VI) onto the pummelo peel.

The integrated linear form of Eq. (2) can be expressed as: [19]

$$\log(q_e - q_t) = \log q_e - k_1 t / 2.303 \qquad (2)$$

Where q_t q_e (mg g^{-1}) and k_1 (h^{-1}) are the amounts biosorbed at time t, equilibrium and the pseudo-first-order adsorption rate constant of the biosorption process, respectively.
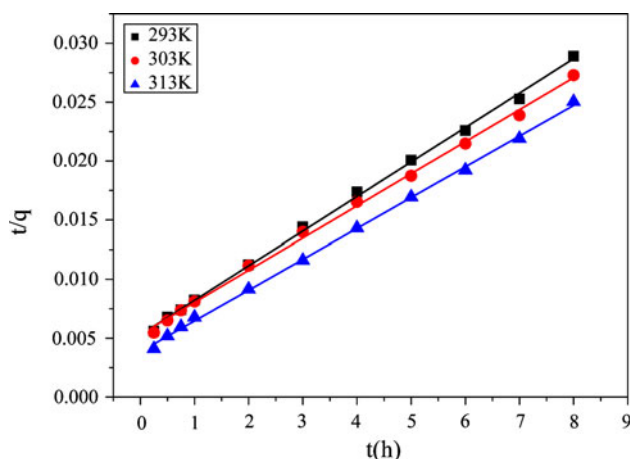
Using Eq. (2), a linear plot of $log(q_e - q_t)$ versus t was plotted (Fig. 5). The rate constants k_1 calculated equilibrium biosorption capacities $q_{e,cal}$ and correlation coefficient (R^2) at different temperatures obtained from the slopes and intercepts of the plots are given in Table 1. It was found that the correlation coefficients for the pseudo-first-order kinetic model were higher than 0.97 for all temperatures, moreover, the $q_{e,cal}$ values for the pseudo-first-order kinetic model also agree with the experimental data. These results suggest that the kinetic adsorption can be described by the pseudo-first-order kinetics very well.

The pseudo-second-order kinetic model has been considered to be the most appropriate in the last years. The pseudo-second-order equation can be expressed following Eq. (3)

$$t/q_t = 1/k_2 q_e^2 + t/q_e \qquad (3)$$

Table 1 The kinetic parameters of pummelo peel

Temperature (K)	Pseudo-first-order model			Pseudo-second-order model		
	k_1 (h^{-1})	$q_{e,cal}$ (mg g^{-1})	R^2	k_2 (g mg^{-1} h^{-1})	$q_{e,cal}$ (mg g^{-1})	R^2
293	0.4823	265.3	0.9790	0.001623	341.3	0.9986
303	0.4769	286.8	0.9871	0.001391	367.6	0.9977
313	0.5619	309.8	0.9737	0.001765	383.1	0.9989

Fig. 6 Pseudo-second-order kinetic plot for the adsorption of U(VI) onto pummelo peel

Fig. 7 Effect of initial uranium concentration on U(VI) adsorption by pummelo peel

where k_2 (g mg^{-1} h^{-1}) is the pseudo-second-order rate constant. Using Eq. (3), linear plot of $log(q_e-q_t)$ versus t was plotted (Fig. 6). The rate constants k_2 and calculated equilibrium biosorption capacities q$_{e,\text{cal}}$ obtained from the intercepts and slopes of the plots are given in Table 1. Though the correlation coefficient values R^2 were higher than 0.99 for all temperatures, the $q_{e,\text{cal}}$ calculated values and the experimental values $q_{e,\text{exp}}$, are not close, showing that the biosorption kinetics for the entire process did not follow the pseudo-second-order model. These results suggest that the kinetic adsorption can be described by the pseudo-first-order kinetics very well.

Biosorption isotherm

The adsorption isotherm was carried out at different temperatures 293, 303 and 313 K with initial concentration of uranium(VI) varying from 30 to 80 μg/mL. To ensure full equilibration, a shaking time of 7 h was used for all concentrations of uranium(VI) in this study. As shown in Fig. 7, the biosorption capacities of pummelo peel for uranium(VI) is increasing with increasing temperature from 293 to 313 K. This could be due to higher probability of collision between metal ions and the adsorbent surface and stronger driving force, which lessened the mass transfer resistance. Since the biosorption increased with temperature, therefore, the system is endothermic.

Adsorption isotherms describe how solute interacts with the adsorbent under equilibrium conditions, and so, is one of the most important data to understand the mechanism of the adsorption systems. Two biosorption isotherm models, namely Langmuir and Freundlich isotherm models were used to fit the biosorption experimental data in this study. The Langmuir model is based on assumptions of adsorption homogeneity such as equally available adsorption sites,
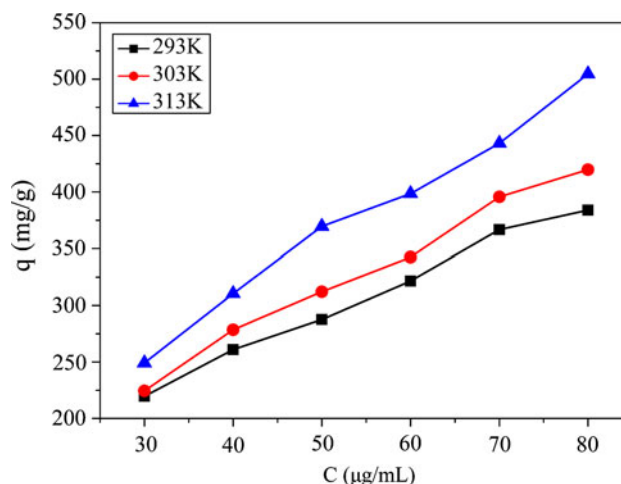
monolayer surface coverage, and no interaction between adsorbed species [25] and can be described by the linearized form [26].

$$C_e/q_e = 1/Q_0 K_L + C_e/Q_0 \qquad (4)$$

where q_e is the amount of solute per unit weight of sorbent (mg/g), C_e is the equilibrium concentration (μg/mL), Q_0 is the saturated monolayer sorption capacity (mg/g) and K_L is the Langmuir isotherm constant that relates to the energy of adsorption (L/mg).

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter R_L, [27] which is defined as:

$$R_L = 1/(1 + K_L C_0) \qquad (5)$$

where K_L is Langmuir constant (L/mg), C_0 is the initial concentration (μg/mL). The value of R_L indicates the type of isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$).

The Freundlich model can be applied to nonideal sorption on heterogeneous surfaces as well as multilayer sorption [28]. The empirical Freundlich equation [29] can also be transformed into linear form:

$$\log q_e = \log K_f + \log C_e/n \qquad (6)$$

where q_e is the amount of solute sorbed per unit weight of sorbent (mg/g), C_e is the equilibrium concentration (μg/mL), K_f and n are the Freundlich constants related to the adsorption amount and adsorption intensity of the sorbent, respectively.

The linearized form of Langmuir and Freundlich adsorption isotherms obtained at 293, 303 and 313 K were presented in Figs. 8 and 9, respectively, whereas the adsorption constants evaluated from the isotherms with the
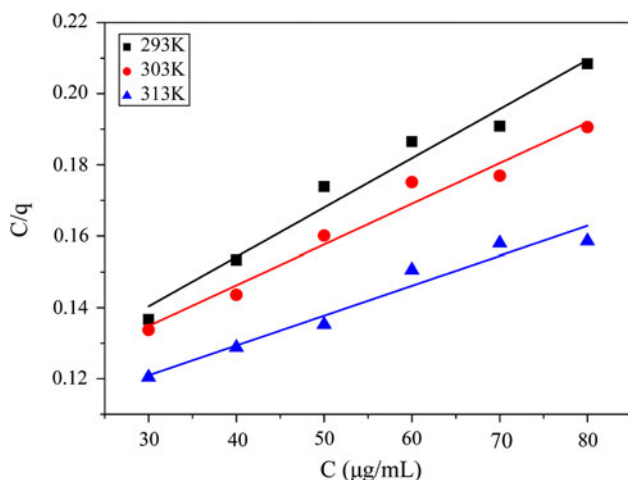
Fig. 8 Langmuir isotherm of sorption U(VI) on pummelo peel
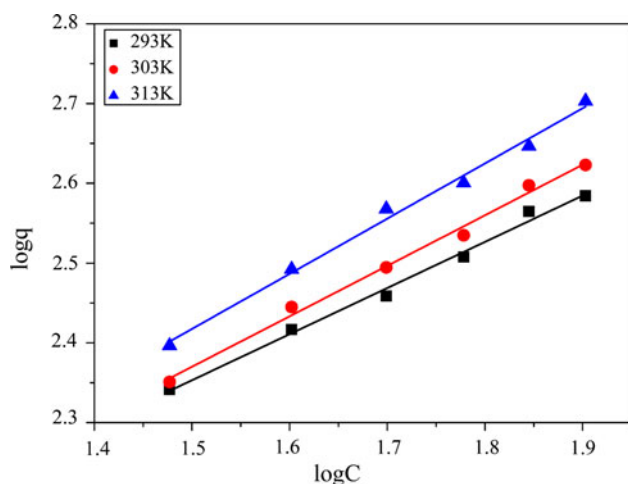
Fig. 9 Freundlich isotherm of sorption U(VI) on pummelo peel

correlation coefficients were given in Table 2. The results show that Langmuir and Freundlich isotherm models fitted well for the adsorption studies ($R^2 > 0.94$); however, Freundlich isotherm had a better fitting model than Langmuir isotherm ($R^2 > 0.99$). Langmuir constant, Q_0, represents the maximum monolayer adsorption amount of the biosorbent. The values are 724.6, 877.2 and 1192.321 mg/g at 293, 303 and 313 K, respectively. It was also found that the R_L values calculated are in the range of $0 < R_L < 1$, which indicates that the adsorption of U(VI) on the pummelo peel is favorable. As seen from Table 2, the values of the

Freundlich constant (n and K_f) showed rapid uptake of the uranium from solution with high adsorptive capacity of pummelo peel.

Thermodynamic parameters

Thermodynamic behavior of the biosorption of pummelo peel biomasses is evaluated by the thermodynamic parameters including the change of Gibbs free energy (ΔG), enthalpy (ΔH) and entropy (ΔS). The thermodynamic data at various temperatures were calculated using the following equations [30].

$$K_d = (C_0 - C_e)V/(C_e m) \tag{7}$$

Where the distribution coefficient, K_d (mL/g), was used to compute the apparent thermodynamic parameters, C_0 and C_e are the concentration of the initial solution and equilibrium, V is the volume of the solution (mL) and m is the weight of the sorbent (g).

The values of $\Delta H°$ and $\Delta S°$ were calculated from the slope and intercept of the linear variation of $\ln K_d$ with reciprocal temperature (Fig. 10) by the equation:

$$InK_d = \Delta S°/R - \Delta H°/RT \tag{8}$$

where K_d is distribution coefficient, R is the gas constant (8.314 J/mol·K) and T is the absolute temperature in Kelvin (K). The change of Gibbs free energy, $\Delta G°$, can be calculated by:

$$\Delta G° = \Delta H° - T\Delta S° \tag{9}$$

The values of thermodynamic parameters for the sorption of U(VI) at different temperature were given in Table 3. The values of $\Delta G°$ were found to be −23.17, −24.47 and −25.77 kJ/mol at 293, 303 and 313 K, respectively. The negative values of $\Delta G°$ at different temperatures confirm the feasibility and spontaneous nature of adsorption process. Further, the decrease in the values of $\Delta G°$ with the increasing temperature indicates that higher temperature favors the sorption process. The value of $\Delta H°$ 14.95 kJ/mol suggests that the adsorption of uranium (VI) is endothermic and hydrogen bonding process [31]. The positive value of $\Delta S°$ reflects the affinity of the biosorbent for uranium(VI) and confirms the increased randomness at the solid solution interface during adsorption.

Table 2 Isotherm parameters for the adsorption of U(VI) on pummelo peel at different temperatures

Temperature (K)	Langmuir isotherm			Freundlich isotherm		
	K_L (L mg^{-1})	Q_0 (mg g^{-1})	R^2	K_f	n	R^2
293	0.01395	724.6	0.9654	30.5774	1.7289	0.9913
303	0.01133	877.2	0.9653	26.3330	1.5798	0.9917
313	0.00876	1192.3	0.9446	24.0049	1.4463	0.9911
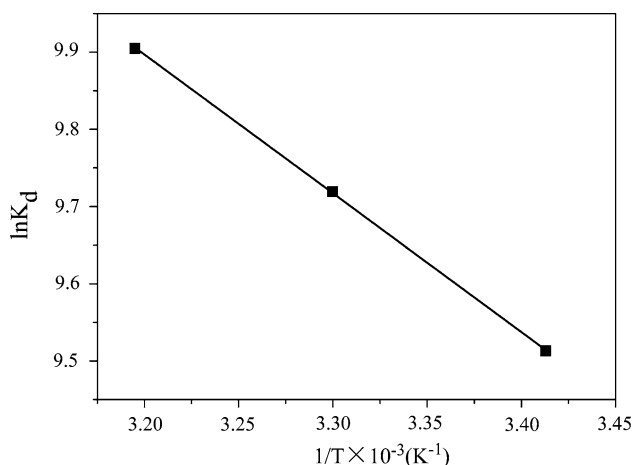
Fig. 10 The diagram of $\ln K_d$-$\frac{1}{T}$ of pummelo peel

Table 3 Thermodynamic parameters for the sorption U(VI) on pummelo peel

ΔH° (kJ mol^{-1})	ΔS° (J mol^{-1} K^{-1})	ΔG° (kJ mol^{-1})		
		293 K	303 K	313 k
14.95	130.11	−23.17	−24.47	−25.77

Conclusions

The present study focuses on the biosorption of uranium from aqueous solution using the pummelo peel as a low-cost biosorbent. The biosorption characteristics have been examined at different temperature, initial concentration, and contact time. The maximum capacity was observed at the pH value of 5.5 and at 7 h. Kinetic studies on sorption of uranium by the biosorbent revealed that the experimental data showed better fit to the pseudo-first-order kinetic model. The experimental data were evaluated by Langmuir, Freundlich isotherms. Equilibrium data were well fitted to Freundlich isotherm model. The thermodynamic calculations indicated the feasibility, endothermic and spontaneous nature of the biosorption process.

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