

Study on uranium(VI) biosorption of marine-derived fungus treated by cetyltrimethyl ammonium bromide

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Abstract *Fusarium* sp. #ZZF51 was chemically treated by cetyltrimethyl ammonium bromide to explore its potential for the removal of uranium(VI). The experimental results showed that the biosorption capacity and the removal efficiency for the modified mycelium under optimal conditions were 400.10 mg g⁻¹ and 96.02 %, respectively, which were more than those of the native biomass (21.42 mg g⁻¹ and 61.89 %). Lagergren's pseudo-second-order kinetic model and Langumir isotherm model showed the better agreement with the experimental data. SEM experiment indicated the mycelium could provide ready access and rich surface area for uranium binding, and FTIR analysis revealed that hydroxyl, carbonyl, especially for nitrogen groups played important roles in biosorption.

Keywords Uranium(VI) biosorption · Marine-derived fungus · *Fusarium* sp. #ZZF51 · Cetyltrimethyl ammonium bromide (CTAB) · Chemically treated

Introduction

With the development of ore mining and nuclear industry all over the world, some waste water containing uranium(VI) ions has been discharged into the natural environment [1]. The radioactive element uranium may be taken into human bodies through food chain, which can make humans more likely to get cancers, suffer some

chronic diseases, incur disability and even cause genetic defect due to its detrimental effects associated with toxicity and radioactivity [2]. Hence, the removal of uranium(VI) from waste water appears especially important not only for the development of nuclear industry, but also for the environment remediation [3, 4].

Biosorption can be used to bind and concentrate heavy metals and radionuclides from aqueous solution [5–7]. Compared with the conventional methods of removing toxic metals such as ion change, chemical precipitation, electrolysis and membrane filtration, the biosorption process offers several advantages, including low operation cost, short operation time, high efficiency at low metal concentration, selective adsorption and no secondary pollution [8, 9]. It is well known that marine environment has many special characteristics such as rich salt, high pressure, low temperature, less light, poor nutrition and so on, which determine marine-derived microorganisms have their own special species and metabolic approaches beneficial to remove heavy metal ions [10]. The marine-derived endophytic fungus *Fusarium* sp. #ZZF51, collected from the mangrove in Chinese Zhanjiang sea area. The initial work showed that the tested fungus could produce special metabolite bis(5-butyl-2-pyridinecarboxylato-N₁,O₂)-copper and had strong ability of uptaking copper(II), while the ability of removing uranium(VI) and thorium(IV) from waste water is not too excellent [11–13]. In order to enhance its removal efficiency for uranium(VI), cetyltrimethyl ammonium bromide (CTAB) was used to modify the mycelium of the tested fungus in this paper, and the influence factors such as initial solution pH, the ratio of solid/liquid (S/L), contact time, initial uranium(VI) concentration on biosorption were studied. Moreover, the adsorption models and mechanism were also explored.

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Materials and methods

Preparation of biomass

The fungus *Fusarium* sp. #ZZF51 used in this study was obtained from the South China Sea coast (Zhanjiang sea area), and deposited in the Department of Applied Chemistry and School of Life Sciences, Sun Yat-sen University, Guangzhou, China. A medium with 10 g L⁻¹ of glucose, 2 g L⁻¹ of peptone, 1 g L⁻¹ of yeast extract, and 2 g L⁻¹ of sea salt was used for the microorganism growth. After cultivating the tested fungus in the sterilized medium mentioned about at 30 °C for 5–7 days, the mycelium was aseptically transferred to 500 mL of erlenmeyer flask containing 300 mL sterilized liquid medium. The biomass was then incubated at room temperature. 22 days later, the mycelium was centrifuged at 5000 rpm for 10 min, washed thoroughly with distilled water, dried in an oven (60–80 °C, 10 h), and ground into 100 meshes. The biomass obtained by above procedure was referred as native biomass (NB) in the paper [14].

Preparation of uranium(VI) solution

Thousand milligram per litre of U(VI) stock solution was prepared by dissolving the required quantity of UO₂(CH₃COO)₂·2H₂O with a small amount of concentrated nitric acid and being diluted with distilled water to 1 L. The initial pH of uranium(VI) working solution was adjusted by 0.1 M HCl and 0.1 M NaOH [15].

Surface modification

CTAB, as a surfactant, usually can combine with proteins or most polysaccharides except for acidic polysaccharides to form complexes, which may be beneficial to uranium(VI) ions biosorption. The chemical modification on the surface of the tested mycelium was as follows: 1.5 g of native biomass was suspended in 150 mL 5 % (w/v) of CTAB anhydrous methanol solution at 30 ± 2 °C, and the mixture was shaken on a rotary shaker for 24 h at 125 rpm. The suspension was then filtered, washed by sequential distilled water, and freeze-dried [16].

Analytical methods

Analysis of uranium(VI)

Uranium(VI) concentration in the solution was tested using the spectrographic method with Arsenazo III (0.05 %) as chromomeric reagent. The required quantity of uranium(VI)

solution and 500 μL 0.05 % Arsenazo III aqueous solution were added to a volumetric flask which was filled up to 10 mL by chloroacetic acid sodium acetate buffer solution (pH 2.50). The absorbance of the solution was analyzed at 650 nm by UV-721 spectrophotometer. The mixed solution with no uranium(VI) ions prepared in the same way was used as reference. Uranium(VI) concentrations were calculated from the calibration curve. The detection limits of this method was 0.0338 mg L⁻¹. The biosorption efficiency (*R*) and capacity (*q_e*) of uranium(VI) were calculated using the following equations:

$$\text{Removal efficiency : } R(\%) = \frac{c_0 - c_e}{c_0} \times 100 \% \quad (1)$$

$$\text{Biosorption capacity : } q_e(\text{mg g}^{-1}) = (C_0 - C_e)V/m \quad (2)$$

where *q_e* (mg g⁻¹) is the amount of uranium(VI) adsorbed by per gram of dry biomass (CTAB-B), *c₀* and *c_e* are the initial and the equilibrium uranium(VI) concentrations in the solution, *V* (L) is the volume of solution and *m*(g) is the weight of CTAB-B.

Scanning electron micrograph

The surface morphology of CTAB-B was analyzed using Hitachi S-4800 scanning electron microscope at an accelerating voltage of 5 kV and a working distance about 5 mm.

Fourier transforms infrared (FTIR) spectra experiments

FTIR spectra were used to analyze the functional groups on the surface of native biomass (NB), modified fungus mycelium (CTAB-B), and metal-loaded biomass (CTAB-B-U). The spectra were recorded with the wave number range from 4000–400 cm⁻¹ using a KBr window, and the KBr background was automatically subtracted from the sample spectra.

Results and discussion

Effect of pH on uranium biosorption

The effect of pH on uranium(VI) removal was analyzed with the initial pH range from 4.0 to 9.0 in 50 mL 50 mg L⁻¹ of uranium(VI) solution. The removal percentage and the adsorption capacity of uranium(VI) versus pH were plotted in Fig. 1. As it was seen, the removal percentage(*R*) and the adsorption capacity (*q*) varied with pH values and showed the same trend. When pH was 7.0,

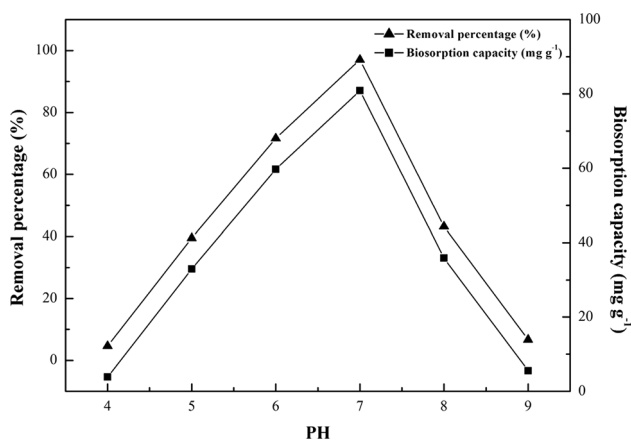


Fig. 1 Effect of pH on uranium(VI) adsorption by using CTAB-B (initial uranium(VI) concentration, 50 mg L⁻¹; S/L, 0.6 g L⁻¹; contact time, 60 min)

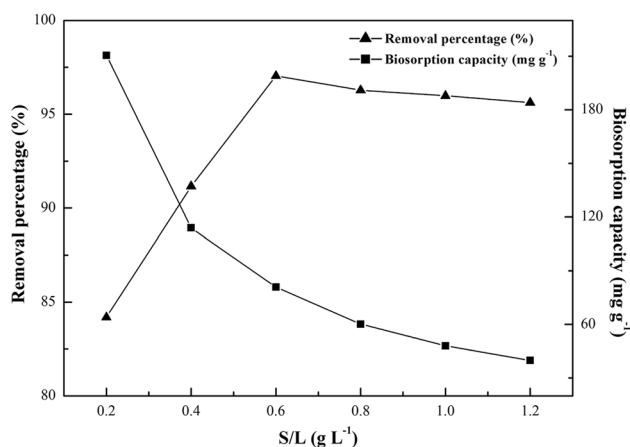


Fig. 2 Effect of S/L ratio on uranium(VI) biosorption by CTAB-B (initial pH 7.0; initial uranium concentration 50 mg L⁻¹; solution volume 50 mL; contact time 60 min)

they reached the maximum values, respectively. At low PH, the surface charge in the adsorbent was positive and uranium(VI) ions exist in solution mainly in the form of UO₂²⁺, inhibiting the combination of UO₂²⁺ and the binding sites, thus the uranium(VI) biosorption efficiency was very low. When pH in solution was around 7.0, the surface charge of the adsorbent was negative, and the uranium(VI) ions were in the forms of (UO₂)₂(OH)₂²⁺, (UO₂)₃(OH)⁵⁺, (UO₂)₄(OH)₇⁷⁺... in solution, which were easily attracted to the surface of the sorbent. With solution pH further increasing, the formation of UO₂O₇²⁻ had caused the competition with OH⁻, which led to the uranium(VI) removal efficiency of the sorbents decrease. It can be seen, metal ions transfer from the solution to the biosorbents while the H⁺ was in the opposite direction, which indicated that ion exchange mechanism was involved in the adsorption process [17, 18].

Compared with the uranium(VI) biosorption on the native biomass previous reported [12], the optimal solution pH has changed from 5.0 to 7.0, which was due to the enrichment of amino and imino groups on the surface of the CTAB-treated biomass in some degree. In consequence, the maximum biosorption capacity also showed the increase from 21.42 to 80.23 mg g⁻¹.

Effect of solid/liquid ratio on the removal of uranium(VI) ions

The effect of solid/liquid (S/L) on uranium(VI) biosorption was investigated at room temperature using its different range from 0.2 to 1.2 in the solution with pH 7.0 and initial uranium(VI) concentration 50 mg L⁻¹.

As shown in Fig. 2, it was quite clear that the uranium(VI) removal efficiency(R) increased sharply when S/L increased from 0.2 to 0.6, which mainly owed to the

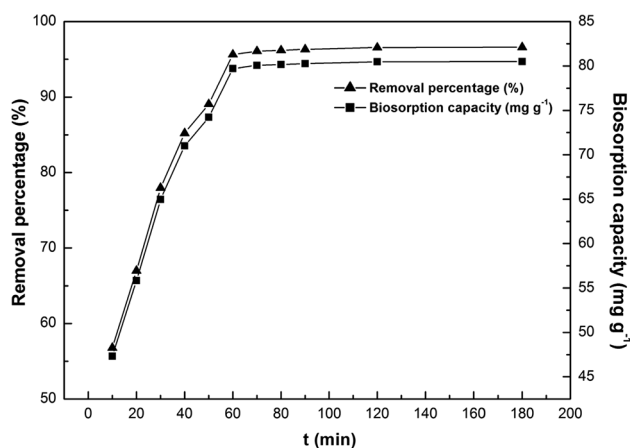


Fig. 3 Effect of time on uranium (VI) adsorption by CTAB-B (solution volume 50 mL; initial uranium concentration 50 mg L⁻¹; S/L 0.6 g L⁻¹; initial pH 7.0)

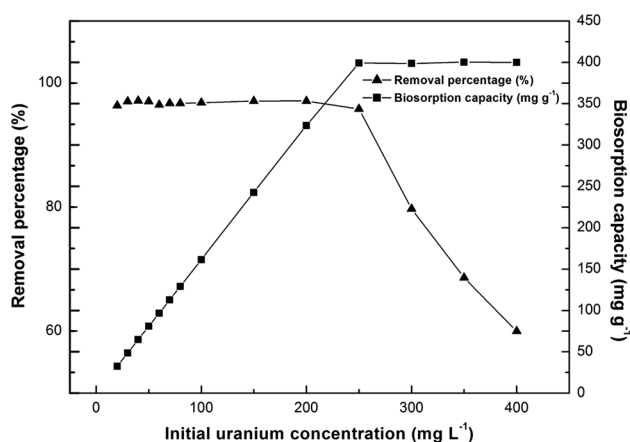


Fig. 4 Effect of initial uranium ion concentration on uranium biosorption by CTAB-B (solution volume 50 ml; initial pH 7.0; S/L 0.6 g L⁻¹; contact time 60 min)

increase of active sites in CTAB-B, so uranium(VI) ions could easily go onto the adsorption sites. When S/L exceeds 0.6, the removal percentage of uranium(VI) ions decreased, which could be illustrated that high dosage material produced a ‘screen effect’ on the cell wall [2]. Hence, the suitable ration of S/L was 0.6 g L^{-1} .

Effect of contact time on the removal of uranium(VI) ions

In order to establish the equilibration time for maximum uptake of the adsorption process, uranium(VI) biosorption on CTAB-B was investigated, and its results were shown in Fig. 3.

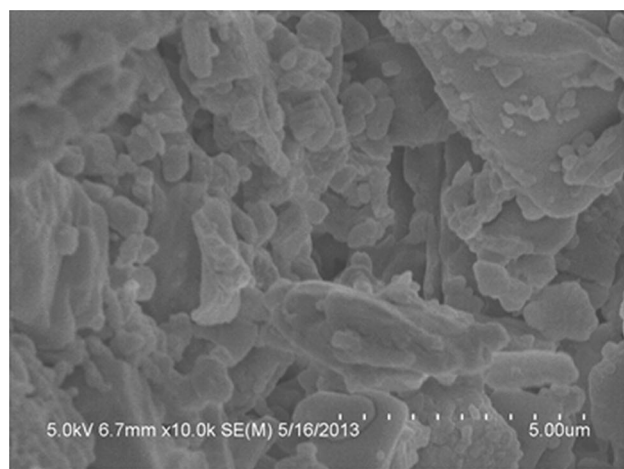
Figure 3 showed that the removal percentage and the biosorption capacity of uranium(VI) increased rapidly at the beginning of biosorption, this was because large amount of sorbent sites were unloaded and uranium(VI)

concentration gradient was high, which was greatly benefit to biosorption. 60 min latter, the change of sorption efficiency did not show notable, and this might be due to the gradual saturation of binding sites on the surface of CTAB-B. Based on the results, the contact time of 60 min can be selected as the equilibration time for the uranium(VI) biosorption process.

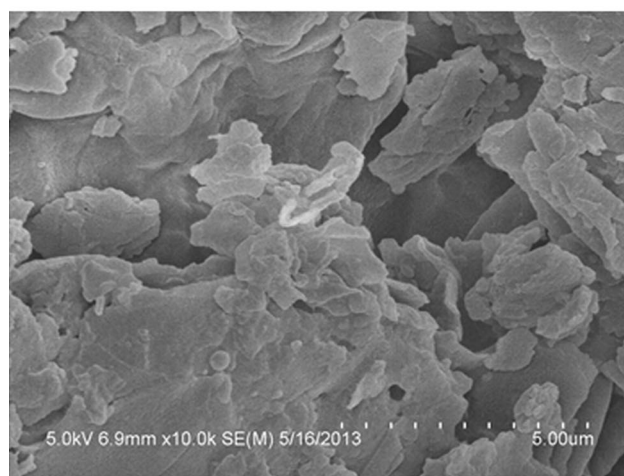
Effect of initial uranium(VI) concentration on the removal of uranium(VI) ions

The initial uranium(VI) concentration provides an important driving force to overcome all mass-transfer resistance of uranium(VI) between the aqueous and solid phase [19], and the uranium(VI) removal is clearly dependent on the initial metal ion concentration of the solution [20].

In this study, the effect of initial uranium(VI) concentration varied from 20 to 400 mg L^{-1} on the uptake of uranium(VI) by CTAB-B was conducted, and its results were shown in Fig. 4. The data revealed that the removal percentage decreased with the augment of uranium(VI) concentration, while the sorption capacity kept increasing with the increase of initial metal concentration until it reached the maximum value with the uranium concentration of 250 mg L^{-1} . The maximum biosorption capacity of CTAB-B for uranium(VI) was 400.10 mg g^{-1} , which was almost 18.7 times that of the native biomass (21.42 mg g^{-1}) [12]. From the sorption characteristic, it could be perceived that the surface saturation of sorbents was dependent on the concentration of initial uranium(VI) solution.



(a)



(b)

Fig. 5 Scanning electron micrographs for the pristine fungus biomass (a) and CTAB-B (b)

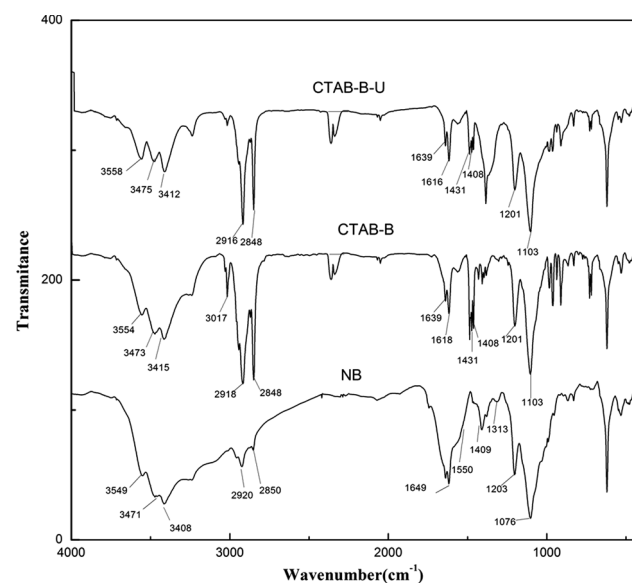


Fig. 6 Fourier transform infrared spectra of the sorbents: **a** native biomass NB, **b** modified biomass CTAB-B, **c** uranium-loaded biomass CTAB-B-U

In comparison with the maximum uranium(VI) biosorption capacities on other sorbents reported in recent years such as citric acid modified pine sawdust (only 71.59 mg g⁻¹) [21], methanol-treated *Rhodotorula glutinis* (129 mg g⁻¹), formaldehyde-treated *Rhodotorula glutinis* (110 mg g⁻¹) [22], it was obvious that the CTAB-B modified fungus was much greater, which revealed that

CTAB-B was a good ecological microorganism material in the field of removing uranium(VI) ions from wastewater.

Analysis of scanning electron microscopy (SEM) for the sorbents

SEM analysis was conducted to further investigate the mechanisms for the biosorption process. Results were shown in Fig. 5. It was clear that the surface of CTAB-B was rougher than that of the pristine fungus biomass, which could easily illustrate the increase of binding sites and interstitial space beneficial to uranium(VI) adsorption, thus CTAB-modified biomass had a better affinity to uranium(VI) ions.

FTIR analyses

Fourier transform infrared spectroscopy is usually used to identify the functional groups in the tested materials [23]. The FTIR spectra of native biomass (NB), modified biomass (CTAB-B) and uranium-loaded biomass (CTAB-B-U) were presented in Fig. 6.

As seen in Fig. 6 (NB), the broad and strong band ranging from 3200 to 3600 cm⁻¹ should be attributed to the stretching vibration of O–H and N–H groups, and the band at 2920 cm⁻¹ was caused by symmetric or asymmetric C–H stretching vibration. The strong peak at 1649 cm⁻¹ was produced by –C=O stretching vibration, and the infrared peak at 1550 cm⁻¹ could be assigned to N–H in-plane bending vibration of secondary amide (amide II band). The band at 1076 cm⁻¹ was due to the stretching vibration of C–O and C–N in biomass. Compared with the FTIR spectrum of pristine biosorbent, the FTIR spectroscopy of CTAB-B in Fig. 6 displayed significant shifts in some peaks. The dramatic change was the appearance of the strong peaks at 2918 and 2848 cm⁻¹, which indirectly indicated CTAB had been grafted in mycelium. The curve CTAB-B-U in Fig. 6, in comparison with the FTIR spectrum of CTAB-B, was seen some changes of peak sites from 3412 to 3415 cm⁻¹, 3473 to 3475 cm⁻¹, 3554 to 3558 cm⁻¹ and 1616 to 1618 cm⁻¹, indicating the binding of uranium(VI) ions to hydroxyl, amine, imino, and carbonyl groups on the modified sorbents surface.

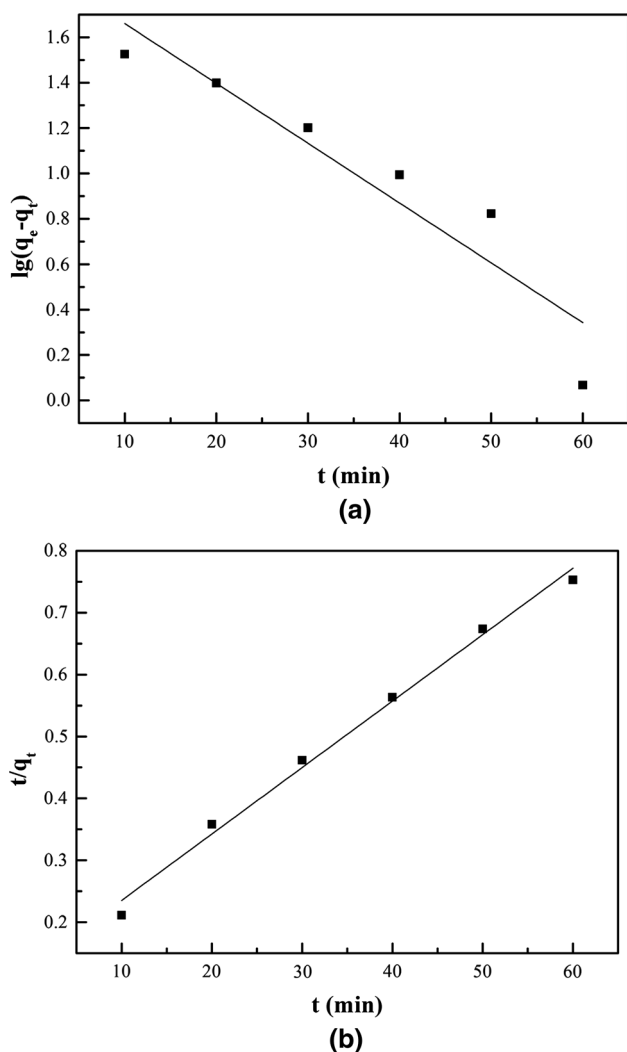


Fig. 7 Lagergren's pseudo-first-order kinetic model (a) and Lagergren's pseudo-second-order kinetic model (b) (initial uranium concentration 50 mg L⁻¹; pH 7.0; solution volume 50 mL; S/L 0.6 g L⁻¹)

Table 1 Comparison between adsorption rate constants, the estimated q_e and the coefficients of correlation associated with the Lagergren's pseudo-first-order kinetic model and the Lagergren's pseudo-second-order kinetic models at 25 °C

Sorbent	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model			$q_{exp}/\text{mg g}^{-1}$
	K_1/min^{-1}	$q_e/\text{mg g}^{-1}$	R^2	$K_2/\text{g mg}^{-1} \text{min}^{-1}$	q_e/mg	R^2	
CTAB-B	-0.0264	6.85	0.883	0.009	93.458	0.993	88.78

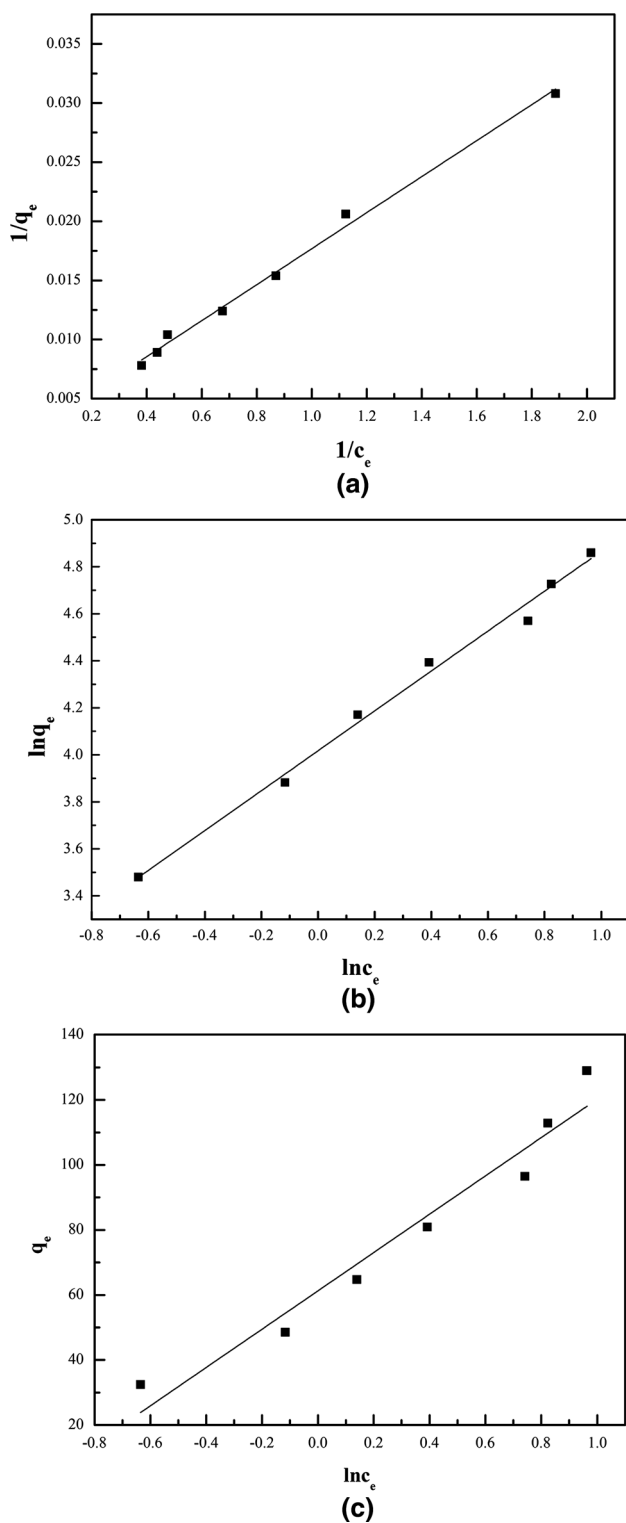


Fig. 8 Uranium(VI) adsorption isotherms within the concentration range of 20–80 mg L⁻¹: Langmuir isotherm (a), Freundlich isotherm (b), Temkin isotherm (c)

Kinetic study

Kinetic parameters derived from different models are tools of engineering significance and are needed for optimizing the metal removal process [20]. Kinetic model equations describe the quick kinetics of mass-transfer processes both between fluid phase and solid sorbent phase and in both phases. Different kinetic models have been used to fit the experimental data of heavy metal sorption. In this paper, two kinetic models namely Lagergren's pseudo-first-order and pseudo-second-order kinetic models were applied, and the adsorption kinetics describe the relationship of the adsorption capacity and the adsorption time, the equation are expressed as following:

$$\ln \frac{q_e - q_t}{q_e} = -K_1 t \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

where q_t and q_e are the amounts of uranium(VI) (mg g⁻¹) adsorbed at time t (min) and at equilibrium, and K_1 (min⁻¹) and K_2 (g mg⁻¹ min⁻¹) are the rate constants for the pseudo-first-order and pseudo-second-order adsorption process. The least-squares method for non-linear regression was used to fit the time-dependent data and the parameters of two kinetic models were obtained. The experimental data and the kinetic curves were presented in Fig. 7, and the corresponding model parameters were tabulated in Table 1. It was clear that the value of the correlation coefficient (R^2) for the pseudo-second-order model (0.993) was greater than that of the pseudo-first-order adsorption model (0.883), and the calculated value of q_e (93.458 mg g⁻¹) for the pseudo-second-order was also closer to the experimental value (88.78 mg g⁻¹). So Lagergren's pseudo-second-order kinetic model can adequately fit the adsorption data better for the CTAB modified biomass.

Thermodynamic study

Langmuir, Freundlich, and Temkin models are usually applied to depict the adsorption thermodynamics, and they may be expressed respectively as:

$$q_e = \frac{q_m K_L c_e}{1 + K_L c_e} \quad (5)$$

$$\ln q_e = \ln K_f + \frac{1}{n} \ln c_e \quad (6)$$

$$q_e = \frac{RT}{B_T} \ln(A_T c_e) \quad (7)$$

Table 2 A comparison of Langmuir, Freundlich, and Temkin models regression constants for biosorption of uranium(VI) on CTAB-B

Sorbent	Langmuir			Freundlich			Temkin		
	$K_L/L \text{ mg}^{-1}$	$q_m/\text{mg g}^{-1}$	R^2	$K_f/(\text{mg g}^{-1})/(\text{mg L}^{-1})^{1/n}$	n	R^2	B_T	$A_T/L \text{ g}^{-1}$	R^2
CTAB-B	0.055	357.14	0.995	18.42	1.1091	0.992	42.47	0.846	0.952

where c_e (mg L^{-1}) is the equilibrium concentration of uranium(VI) in the solution, and q_e (mg g^{-1}) denotes the biosorption capacity at equilibrium. In Eq. (5), K_L (L mg^{-1}) is the Langmuir adsorption equilibrium constant, q_m (mg g^{-1}) represents the maximum amount of metal biosorption. In Eq. (6), K_f is the Freundlich equilibrium binding constant corresponding to the maximum binding energy, n is Freundlich constant depicting the sorption intensity, which values (>1) show the favorable nature of adsorption [23]. In Eq. (7), B_T and A_T are the Temkin isotherm constants, T (K) denotes the thermodynamic temperature, and R is the ideal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$).

The relative uranium(VI) sorption isotherms by CTAB-B were shown in Fig. 8. The experimental data were modeled according to Langmuir, Freundlich, and Temkin isotherms, and the evaluated constants were given in Table 2. It could be observed that the coefficients of association of Langmuir (0.995) and Freundlich (0.992) were close to each other, and they were greater than that of Temkin (0.952) seen in Table 2, which represented that the monolayer and the multilayer sorption were both involved in the sorption process. What's more, it could easily find that the calculated maximum uranium(VI) sorption capacity for CTAB-B was 357.14 mg g^{-1} , which was closer to the experimental data (400.10 mg g^{-1}).

Conclusion

By the single factor analysis method, uranium(VI) ions in waste water onto CTAB-B (mycelium) were optimized at pH 7.0, equilibrium time 60 min, uranium(VI) initial concentration 250 mg L^{-1} and the ratio of solid/liquid 0.6 g L^{-1} with 96.02 % of removal efficiency and 400.10 mg g^{-1} of sorption capacity, which had greatly surpassed those (21.42 mg g^{-1} and 61.89 %) of the native biomass for uranium(VI) biosorption under its optimized condition. SEM analysis illustrated CTAB-modified biomass had a better affinity for uranium(VI) ions, and FTIR spectra of NB, CTAB-B and CTAB-B-U indicated hydroxyl, carbonyl, especially for nitrogen groups played important roles in uranium(VI) biosorption procedure. Kinetic study revealed that the pseudo-second-order model

well described the sorption process, which showed the physical–chemical interactions between CTAB-B and metal ions. The data of thermodynamic study were in good agreement with Langmuir and Freundlich models, and this suggested the monolayer and the multilayer sorption character existed in the biosorption process.

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