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Biosorption of thorium(IV) from aqueous solution by living biomass of marine-derived fungus *Fusarium sp.* #ZZF51

S. K. Yang[1,2] · N. Tan[1] · W. L. Wu[2] · X. J. Hou[2] · K. X. Xiang[2] · Y. C. Lin[3]

Abstract The biosorption of Th(IV) by the marine-derived Fungus *Fusarium* sp. #ZZF51 was study. The Biosorption was found to be at a maximum (79.24 %), in a solution containing 50 mg Th/L, at pH 5.0, with 0.28 g dry biomass. The Temkin isotherm model and pseudo-second-order kinetic model was found to fit the data very well over the entire range of concentrations. The FTIR analysis reveals that the carboxyl, amino and hydroxyl groups on the cell wall of *Fusarium* sp. #ZZF51 play an important role in Th(IV) biosorption process.

Introduction

Thorium is a naturally radioactive element and it distributes widely in earth's crust with various forms. Tetravalent thorium(IV) is the main form in nature, and it is also useful as a tracer when studying environmentally important process [1–4]. The toxic nature of this radionuclide, even at trace level, has been a public health problem for many years. When thorium(IV) ions enter into the living organisms, it accumulates in lung, liver, spleen and marrow [5]. In the past few decades, although some techniques were available for the removal of thorium(IV) ions from aqueous solutions including chemical precipitation, electrofloatation, ion exchange, reverse osmosis and adsorption [6], they generally suffered from some disadvantages such as high operational cost, limited tolerance to pH change, incomplete metal removal, high cost of reagents, and energy requirements [7–9]. Therefore, the above methods have been restricted in application.

At present, biosorption by using microorganism especially for the living mycelium has been seen as a potential technology for removal of toxic heavy metals from industrial water, which main advantages are the reusability of biomaterial, low operating cost, easy fermentation cultivation, the improved selectivity for specific metals, short operation time, no toxic production of secondary compounds and so on [10–14]. It is well known that marine environment has its special properties such as high pressure, low temperature, less light, high salt and poor nutrition, which determine marine-derived microorganisms have theirs own special species and metabolic approaches beneficial to remove heavy metal ions. Mangrove endophytic fungus *Fusarium sp.* #ZZF51 was collected from South China Sea (Zhanjiang sea area). The initial work showed that the fungus could produce special metabolites and had strong ability to uptake copper(II), uranium(VI) and thorium(IV) ions by non-living biomass [15–17]. In order to systematically research the biosorption of the tested fungus so that it can be truly applied in practice in the future, this paper studies the adsorption models and the optimized conditions for thorium(IV) onto the living tested fungus, and the adsorption mechanism is also investigated.

✉ S. K. Yang
nhyangsk@163.com

1   School of Chemistry and Chemical Engineering, University of South China, Hengyang 421001, Hunan, China

2   School of Chemistry and Chemical Engineering, Hunan University of Medicine, Huaihua 418000, Hunan, China

3   School of Chemistry and Chemical Engineering, Sun Yat-sen University, Guangzhou 510275, Guangdong, China

Materials and methods

Materials

All used reagents are analytical grade unless otherwise stated. 1 g L^{-1} of thorium(IV) stock solution was prepared by dissolving 2.3795 g $Th(NO_3)_4 \cdot 4H_2O$ in 20 mL of 7 mol L^{-1} HCl and being diluted with distilled water to 1 L. The working solutions with different concentration were obtained by diluting the stock solution to appropriate volumes. Arsenazo-III solution was prepared by dissolving 0.1250 g arsenazo-III in 5 mL nitric acid with pH 3.0 and being diluted with distilled water to 250 mL, and the pH value was adjusted by 0.1 mol L^{-1} HCl and NaOH solutions.

Preparation of the biosorption materials

Fussarium sp. #ZZF51 was obtained from the South China Sea coast (Zhanjiang sea area) and deposited in school of chemistry and chemical engineering, Sun Yat-sen (Zhongshan) University, Guangzhou, China. At pH 7.0 and temperature 25 °C, the tested fungus was grown in liquid medium GPY that was consisted of glucose 10 g L^{-1}, sea salt 2 g L^{-1}, peptone 2 g L^{-1} and yeast extract 1 g L^{-1} [17]. 22 days later, the living biomass was harvested and washed two more times with distilled water, then it was spin-dried by high-speed centrifuge and promptly used in later experiments to ensure the tested mycelium live in the whole adsorption course.

Biosorption experiments

The batch biosorption experiments were carried out at different pH values, initial metal concentration and contact time under the same conditions of temperature 25 °C, living biomass dosage 3.0 g in 50 mL solution and agitation rate 150 rpm. In fact, 3.0 g living biomass dosage could become 0.28 g dry non-living mycelium after the disposal process of being dried at 120 °C for 5 h. In the batch adsorption experiments, 3.0 g living biomass dosage was added to 50 mL thorium(IV) solution in 250 mL flask which pH value was controlled within 2.0–10.0 and concentration 20–60 mg L^{-1}. The flask was shaken for different time (0–24 h), then the aqueous sample was centrifuged for 10 min at 4000 rpm. The thorium(IV) concentration in supernatant was determined by UV visible spectrophotometer at 660 nm through the thorium(IV) arsenazo(III) complex method [18]. All the experiments were carried out independently in triplicate. The biosorption capacity and thorium(IV) removal efficiency by mycelium were respectively calculated by using the following equations [Eqs. (1) and (2)]:

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

Removal efficiency: $R\ (\%) = (C_0 - C_e) \times 100\ \%$ (2)

where C_0 and C_e are the initial and equilibrium thorium(IV) concentrations (mg L^{-1}), respectively. m (g) is the mass of mycelium, and V(L) is the volume of solution.

SEM and FTIR spectroscopy analysis

The surface characters of *Fusarium sp.* #ZZF51 biomass including before and after loaded by thorium(IV) ions were analyzed using scanning electron microscopy (SEM). The timed *Fusarium sp.* #ZZF51 myceliums were placed on cover slip and air-dried, then the samples were fixed in a 2.5 % glutaraldehyde solution for 7 h, and they were dehydrated 20 min in the graded ethanol series (30, 50, 70, 95 and 100 % ethanol). Finally, the samples were air-dried and sputter-coated with 4 nm of gold particles before using [19].

Fourier transformed infrared (FTIR) spectrometry were used to probe the functional groups in the mycelium of the tested fungus. Sample disks were made by mixing 5 mg of dry non-living mycelium with 150 mg of KBr. Data analysis was focused on the 400–4000 cm^{-1} region.

Results and discussion

FTIR spectra characterization of biomass

FTIR spectra are helpful to identify functional groups in the tested materials [20]. The FTIR spectra of the virgin and thorium(IV)-loaded biosorbents are respectively shown in Fig. 1a, b. As seen in Fig. 1a, the broad and strong band ranging from 3200 to 3600 cm^{-1} may be attributed to –OH groups and $–NH_2$ groups, and the band at 2924 cm^{-1} is due to C–H stretching vibrations. The strong peak at 1639 cm^{-1} is produced by –C=O stretching vibration. Compared with FTIR spectrum of virgin biosorbent, FTIR spectrum of thorium(IV)-loaded roots in Fig. 1b displays significant shifts in some peaks. The FTIR spectroscopic analysis of thorium(IV)-loaded biosorbents indicates absorption peak site and intensity shift for asymmetrical stretching band at 3278 cm^{-1} (indicative of –OH and –NH groups) when compared with that of unloaded biomass which shows the same type of absorption at 3462 cm^{-1}. This is a typical red shift phenomenon as the result of thorium(IV) ions bonding the related functional groups in the tested biomass. Another shift of the peak from 1639 to 1654 cm^{-1} reflects the change in the stretching frequency of carboxylate when linking thorium(IV) ions. Above
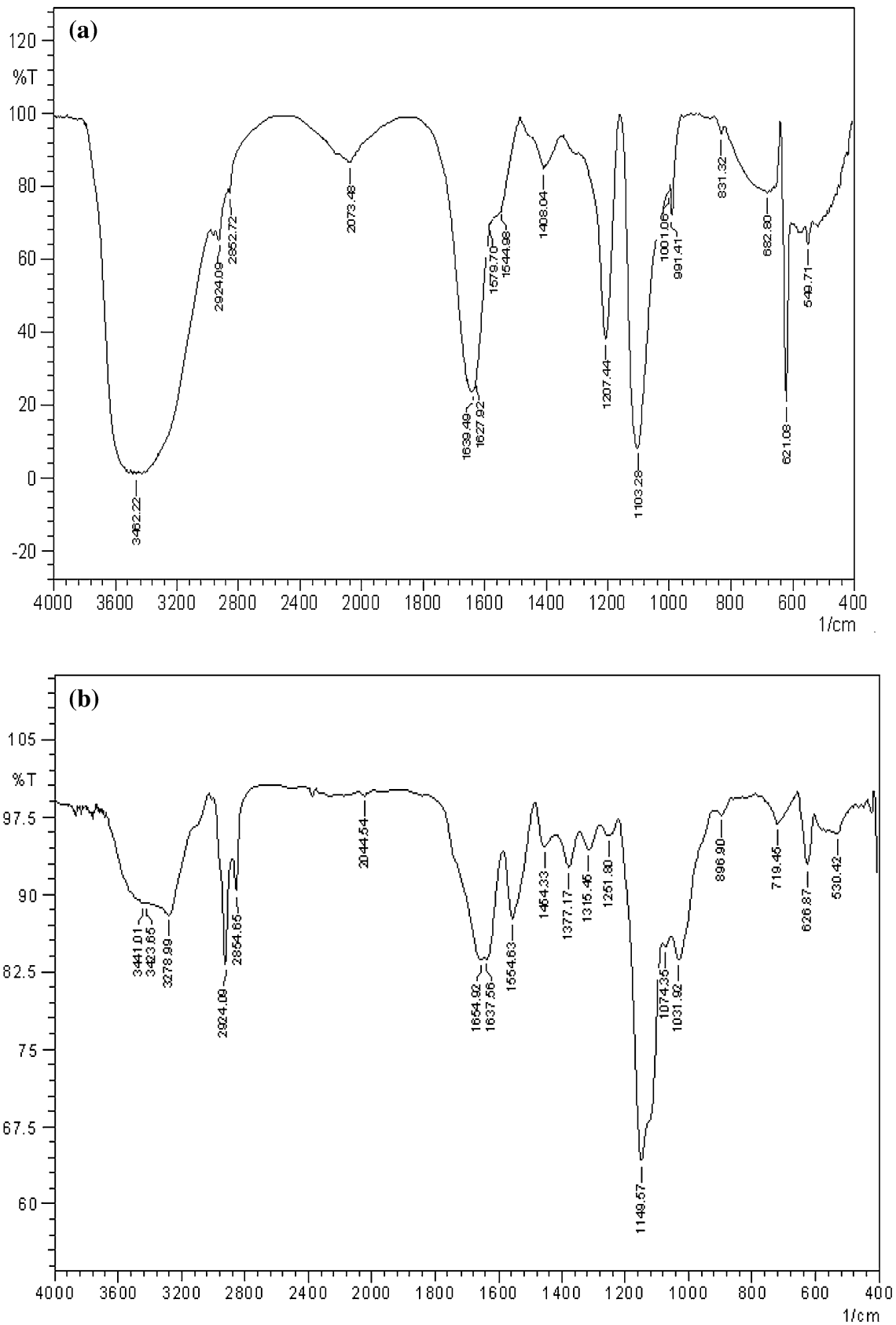
Fig. 1 FTIR spectra for fungus *Fusarium sp.* #ZZF51 biomass before (**a**) and after (**b**) loaded with thorium(IV)

observations indicate the involvement of functional groups –OH, –NH, and –C=O in the whole biosorption process.

Scanning electron microscopy (SEM)

To further investigate the adsorption process, the native and thorium(IV)-loaded biomass are observed under the Scanning electron microscopy, and the SEM images of the tested biomass are shown in Fig. 2. The image of the virgin biomass (Fig. 2a) shows a regular symmetry structure in the material surface, and amounts of small pores can be also seen, which indicates that this material presents good characteristics to be employed as a natural adsorbent for metallic ions uptake, as previously reported [21], while the surface of thorium(IV)-loaded biomass appears a rough asymmetry structure as seen in Fig. 2b. These observations denote that the tested sample especially in the virgin
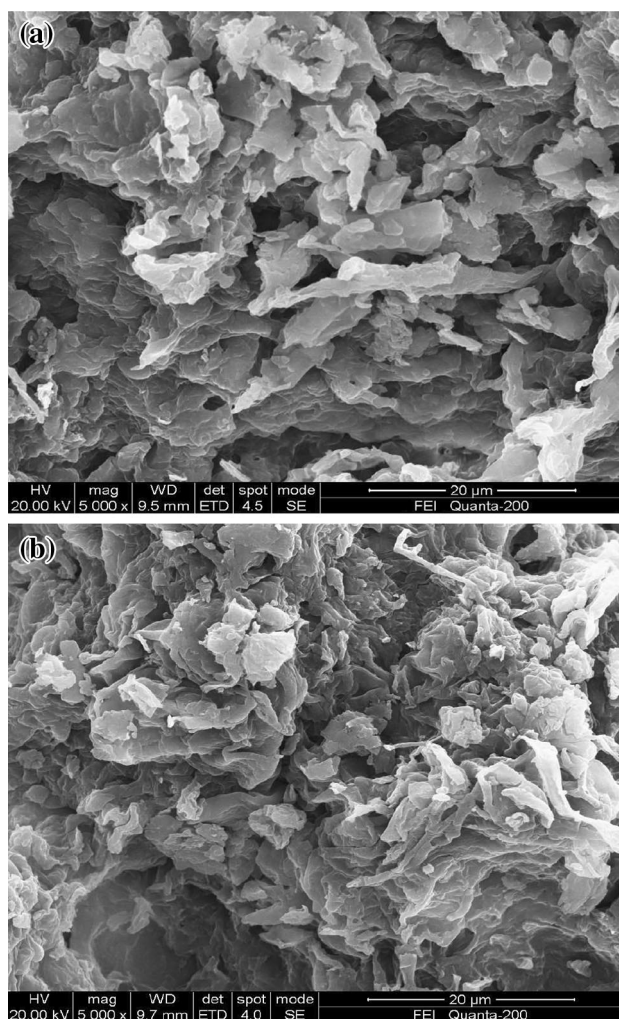

Fig. 2 Scanning electron micrographs for fungus *Fusarium sp.* #ZZF51 biomass before (**a**) and after (**b**) loaded with thorium(IV)

biomass can provide ready access and rich surface area for thorium(IV) ions onto the binding sites.

Effect of pH on biosorption

It has been shown that the affinity of cationic species towards the functional groups present in the surface is strongly dependent on the pH value in solution [12]. Figure 3 describes the relation of pH values and the adsorption of thorium(IV) ions by living mycelium. The batch biosorption experiments results show thorium(IV) uptake is significantly affected by pH, and the optimal biosorption efficiency is observed at pH 5.0, which is obviously higher than the pH 3.0 of thorium(IV) maximum biosorption efficiency for the non-living biomass of fungus *Fusarium sp.* #ZZF51 [15]. This can be explained as the result of living mycelium fond of the mildly acidic environment for thorium(IV) adsorption. When pH is between 4.0 and 5.0, thorium(IV) ions biosorption increases with the decrease of hydrogen ions competing effect. At pH value 5.0, the biosorption efficiency attains maximum. With further increase in pH values, thorium(IV) hydroxides such as $Th(OH)^{3+}$, $Th(OH_2^{2+})$, $Th_2(OH_2^{6+})$, $Th_6(OH_{15}^{9+})$ and so on start forming, which leads to the decline of thorium(IV) percentage removal and biosorption efficiency [22].

Effect of contact time on biosorption

In general, the adsorbed metal ions tend to desorb and go back into the aqueous solution in the late of adsorption process. Figure 4 illustrates the effect of time on thorium(IV) biosorption. It was clear that large amount of sorbent sites are vacant and the thorium(IV) concentration gradient is high at the beginning of biosorption. After 8 h, the change of sorption efficiency for thorium(IV) does not
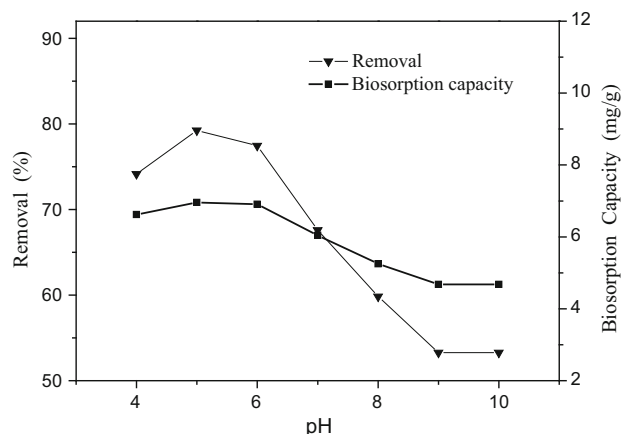

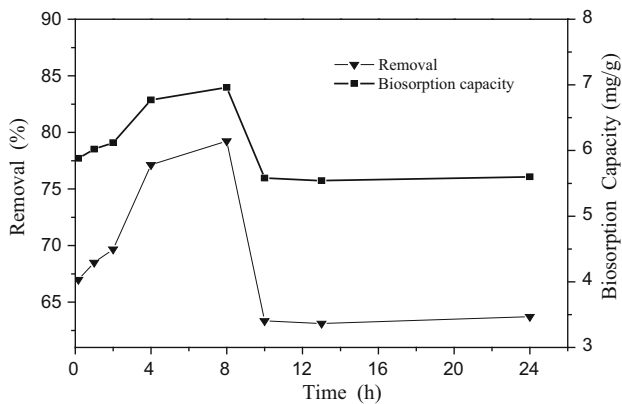**Fig. 3** Effect of different pH on thorium(IV) biosorption

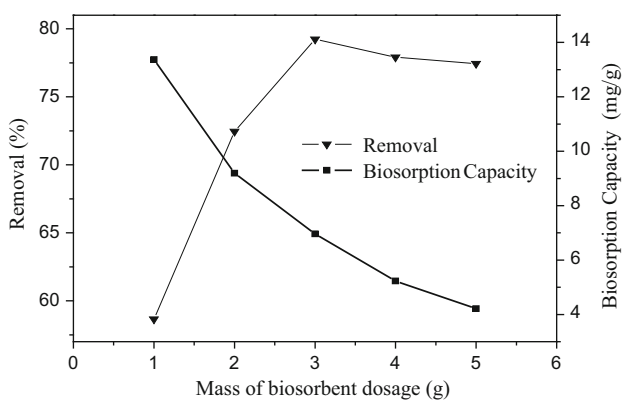**Fig. 4** Effect of different contact time on thorium(IV) biosorption

Fig. 5 Effect of biosorbent dosage on thorium(IV) biosorption

show notable effects, and this may be because of the metal binding sites saturation. Therefore, it can be concluded that the equilibrium reachs at 8 h, which is much longer than the thorium(IV) removal time 20 min for the non-living mycelium of fungus *Fusarium sp.* #ZZF51 [15]. The data obtained from the experiments are successfully evaluated by the following kinetics models.

Effect of biosorbent dosage on biosorption

Biosorbent dose also is an important parameter, which can influence the biosorption capacity and efficiency. The effect of adsorbent dosage on thorium(IV) removal is shown in Fig. 5. When biomass dose increases from 1.0 g to 3.0 g, thorium(IV) sorption efficiency increases significantly, which mainly owes to the increase of active sites in biomass, so the metal ions can easily go onto the adsorption sites. When the adsorbent dosage exceeds 3.0 g, the percentage removal of thorium(IV) ions decreases, and it can be explained that high dosage material produces a 'screen effect' on the cell wall, which protects the binding sites [23].
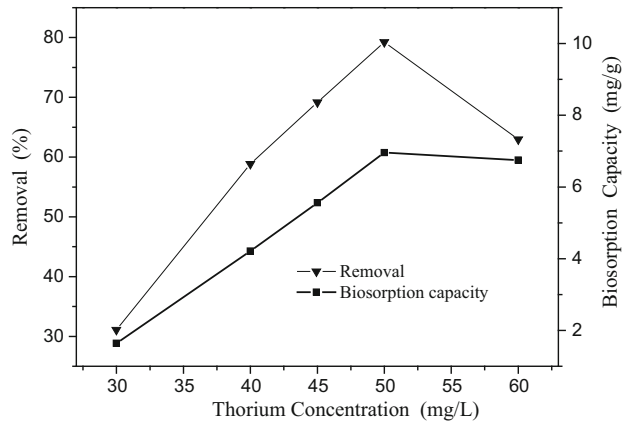

Fig. 6 Effect of different initial thorium(IV) concentration on biosorption

Effect of initial thorium(IV) concentration on biosorption

The other parameters such as pH value, solution volume and contact time are kept the above optimal values, and the effect of initial thorium(IV) concentration varying from 20 to 60 mg L^{-1} on biosorption by the tested living mycelium is shown in Fig. 6. It is clear that the sorption capacity increases when the initial thorium(IV) concentration increases from 30 to 50 mg L^{-1}, and the sorption capacity slightly decreases when the initial concentration is over 50 mg L^{-1}. The maximum biosorption capacity for the living biomass is 6.96 mg g^{-1}, which is less than that (11.35 mg g^{-1}) for the non-living mycelium [15]. The maximum biosorption capacity should come at the moment of available free sites (metal binding sites) approaching saturation at higher thorium(IV) concentration. From the sorption characteristic, it can be perceived that the surface saturation of sorbents is dependent on the concentration of initial thorium(IV) solution, and the binding sites of the sorbents are regarded as constant [24].

Adsorption kinetics

Kinetic study can provide valuable information for the mechanism of adsorption and the optimum operating conditions of industrial-scale batch process. In the study, the pseudo-first-order, pseudo-second-order and Elovich kinetic models are used to interpret the experimental kinetic data [25], and their rate equations are represented as follows:

$$\text{Pseudo} - \text{first} - \text{order}: \text{In}(q_e - q_t) = Inq_e - k_1 t$$

$$\text{Pseudo} - \text{first} - \text{order}: \frac{t}{q_t} + \frac{t}{q_e}$$

where q_e (mg g^{-1}) and q_t (mg g^{-1}) are the amounts of

Table 1 Kinetic parameters for thorium(IV) adsorption by living biomass

Kinetic model pseudo-first-order	Value	Kinetic model pseudo-second-order	Value	Kinetic model Elovich equation	Value
K_1 (1 min^{-1})	0.4337	K_2 (mg mol^{-1} min^{-1})	1.0242	α (mg g^{-1} min^{-1})	1.08×10^9
q_e (mg g^{-1})	1.3199	q_e (mg g^{-1})	7.04	β (g mg^{-1})	3.545
R^2	0.8684	R^2	0.9990	R^2	0.7940
		Qe(exp) (mg g^{-1})	6.96		

Table 2 Isotherm model constant parameters of thorium(IV) adsorption by living biomass

Freundlich model		Langmuir model		Temkin model	
Isotherm model	Value	Isotherm model	Value	Isotherm model	Value
K (mg g^{-1})/(mg L^{-1})$^{1/n}$	16.16	Q (mg g^{-1})	4.72	A (L g^{-1})	0.0047
n	−2.79	b (L g^{-1})	−0.294	B	−2.3048
R^2	0.9968	R^2	0.9873	R^2	0.9983

thorium(IV) adsorbed at equilibrium time and t (min), respectively. 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 equation.

Elovich equation: $= \dfrac{In(\alpha\beta)}{\beta} + \dfrac{Int}{\beta}$

where α is the initial sorption rate (mg g^{-1} min^{-1}), and β denotes the activation energy for chemisorption (g mg^{-1}).

The values of q_e, k_1, k_2, α, β are calculated according to the slopes and the intercepts of straight lines, and the relevent experiment data are presented in Table 1. It is obvious that the correlation coefficient ($R^2 = 0.9990$) for the pseudo-second-order model is higher compared with those of the pseudo-first-order adsorption model and Elovich model. So *Lagergren's* pseudo-second-order kinetic model can adequately fit the adsorption data better for the tested sorbent, which indicates that the adsorption process involves the course of chemical sorption in addition to physical rate-limiting step.

Biosorption isotherm

In order to optimize the biosorption process, it is necessary to obtain the appropriate correlation for equilibrium curve. In this study, Langmuir, Freundlich and Temkin adsorption isotherms are used to linear fitting with the experimental data [14]. The Langmuir isotherm equation is valid for monolayer sorption onto surface containing finite number of identical sorption sites, which is described by the following equation:

The Langmuir isotherm: $\dfrac{1}{q_e} = \dfrac{1}{Q} + \dfrac{1}{bQC_e}$

where Q (mg g^{-1}) represents the amount of adsorption and b (L mg^{-1}) denotes the sorption equilibrium constant, respectively.

The Freundlich equation is purely and empirically based on sorption of heterogeneous surface, which is commonly presented as:

The Freundlich adsorption isotherm: $Inq_e = Ink + \dfrac{InC_e}{n}$

where k is the constant of sorption capacity, and $1/n$ represents the constant of sorption intensity.

Temkin adsorption isotherm: $q_e = BInA + BInC_e$ $B = (RT)/b$

where A and B are Temkin isotherm constants, R is the universal gas constant (8.314 J mol^{-1} K^{-1}), T represents absolute temperature, C_e is on behalf of the residual equilibrium concentration (mg L^{-1}), and q_e denotes the amount of adsorbent (mg g^{-1}) at equilibrium. Experimental data are modeled according to Langumir, Freundlich, Temkin isotherms, and the evaluated constants are presented in Table 2. In view of the correlation regression coefficients, the adsorption process can be better described by Temkin model ($R^2 = 0.998$) and Langumir model ($R^2 = 0.997$) than Freundlich model ($R^2 = 0.987$). Consequently, it could be concluded that the biosorption of live biosorbents might follow a special sorption model, and other mechanisms such as intracellular bioaccumulation would contribute to the uptake of thorium(IV) except for surface binding.

Conclusion

Batch adsorption experiments exhibit that the living mycelium of fungus *Fusarium sp.* #ZZF51 has a good ability for thorium(IV) biosorption. The tested sample can provide ready access and rich surface area for thorium(IV) onto the binding sites by SEM analysis. Hydroxyl, amino,

and carbonyl groups have an important contribution to the adsorption process by comparing with Fourier transform infrared spectra for the tested fungus before and after loaded with thorium(IV). Thorium(IV) ions onto the living fungus mycelium was optimized at pH 5.0, equilibrium time 8 h, thorium(IV) initial concentration 50 mg L^{-1} and living biomass dosage 3.0 g in 50 mL solution with 79.24 % of removal efficiency and 6.96 mg g^{-1} of sorption capacity, which is less than that (11.35 mg g^{-1}) of the non-living mycelium for thorium(IV) biosorption under its optimized condition. The experimental data are analyzed by using classical isotherm models and kinetic equations, and it is obtained that the Temkin isotherm model and the pseudo-second-order kinetic model provide better correlation with the experimental data for biosorption of thorium(IV).

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