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Adsorption of thorium(IV) ions from aqueous solution by citric acid modified *Lemna minor*

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ABSTRACT

The adsportion of thorium(IV) by the citric acid modified *Lemna minor* was study. The adsorption was found to be at a maximum with 97.49% of removal efficiency and 162.5 mg g^{-1} of adsorption capacity, thorium(IV) concentration 100 mg L^{-1}, contact time 60 min, pH 5.0, with 0.03 g dry *Lemna minor* biomass by citric acid treated. The results shows that pseudo-second-order kinetic model was fit the data very well. The adsorption equilibrium was well described by Langmuir isotherm model. In addition, FTIR analysis indicates that hydroxyl, carbonyl and amino groups act as the important roles in the adsorption process.

Keywords: Adsorption; Thorium; Citric acid; Chemical treatment; *Lemna minor*; Isotherm

1. Introduction

The presence of thorium(IV) in the environment not only originates from the nuclear industry but also from other anthropogenic activities, like ore processing, lignite burning in power stations and the use of fertilizers [1,2]. The thorium(IV) ions is very toxic, even at trace levels, so that toxic nature of this radionuclide has become to be a public health problem for many years. When thorium(IV) ions enter into the living organisms, they will be accumulated in spleen, liver, lung, marrow, and cause severe damage to human beings [3]. Environmental disposal of the industrial effluents containing thorium(IV) ions has become a serious cause of concern. A number of methods including chemical precipitation, reverse osmosis, ion exchange, electro floatation and adsorption have been developed to recover thorium(IV) from aqueous solutions [4–10]. However, most of these methods suffer from some disadvantages such as high capital and operational cost, limited tolerance to pH change, incomplete metal removal and high cost of reagent and energy requirements [11–14]. Therefore, the above methods have been restricted in application.

Biosorption is a process that utilizes inexpensive non-living biomass to sequester heavy metals through physicochemical adsorption. Compared with conventional physicochemical technologies, biosorption has attracted considerable interest over the last decades for its high adsorption efficiency, low cost and effectiveness for low-concentration metal ions [15,16]. Recently, the removal of heavy metals from wastewaters by biosorption on aquatic organisms has attracted a lot of attention because of their abundance, adsorption capacity and economic viability. The aquatic organisms can be used in the natural form or modified by some chemical treatment [17].

For *Lemna minor L*, the initial work showed that it had the ability of absorption uranium(VI) and thorium(IV). In order to further improve the adsorption capacity, the modification of biomass materials to increase their adsorption capacity has been extensively investigated [18]. The objective of this study was to investigate the removal of thorium(IV) from aqueous solution by citric acid modified *Lemna minor*. A combination of chemical modifications, metal-binding

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experiments, and infrared spectroscopy were performed to gain insight into the role played by functional groups in thorium(IV) binding.

2. Materials and methods

2.1. Materials

The stock solution (1 g L^{-1}) of thorium(IV) was prepared by dissolving 2.3795 g reagent grade $Th(NO_3)_4{\cdot}4H_2O$ (Jing-Chun reagent co., LTD, Shanghai, CHINA) in 20 mL of 7 mol L^{-1} HCl (Guo-Yao reagent co., LTD, Shanghai, CHINA) and diluting with distilled water to 1 L. Experiment solutions of metal having known initial concentrations were prepared by appropriately diluting the stock solution. The arsenazo-III (Guang-Fu fine chemical industry research institute, Tianjin, CHINA) solution was obtained by dissolving 0.1250 g arsenazo-III in 5 mL nitric acid (Guo-Yao reagent co., LTD, Shanghai, CHINA) with pH 3.0, then diluting it to 250 mL with distilled water. The pH of the experimental solutions was adjusted by adding different concentrations of (0.001, 0.01, 0.1, 1.0 and 2.0 mol L^{-1}) HCl or NaOH (Guo-Yao reagent co., LTD, Shanghai, CHINA) solutions. All chemicals used in this study were of analytical grade.

2.2. Preparation of the biosorption materials

Lemna minor was obtained from an ecological farm in Huaihua city, China, and sampled in the polyethylene bags back to the laboratory immediately. Using tap water elutriation three times, then in the Hoagland medium cultivation of the temperature of 25 ± 2°C box (in light: dark = 1:1) culture keep 10 d. Hoagland solution was prepared according to the method of literature [19]. After *Lemna minor* washed with distilled water to removal soil and dust, and then dried in an oven at 70°C until constant weight, ground into fine powder, and sieved through 100 mesh.

The *Lemna minor* was chemically modified with citric acid (Guo-Yao reagent co., LTD, Shanghai, CHINA) solution using the method described by Bo Zhu and Tongxiang Fan [20]. The preparation process for the product CA-*Lemna minor* (citric acid treated *Lemna minor*): at first, 20 g of sieved leaves powder was placed in 0.4 L of NaOH (0.1 mol L^{-1}) and the slurry was stirred at 300 rpm for an hour at 25°C. Next, the base-washed powders were rinsed two more times with distilled water to ensure the removal of the excess base, and dried overnight at 50°C. Then 3 g of base-washed powders were treated with 100 mL citric acid of 0.6 mol L^{-1}, and the mixed solution containing the *Lemna minor* was stirred at 300 rpm for 30 min at 25°C, dried overnight at 50°C. Subsequently, the thermochemical reaction between acid and powders proceeded by raising the oven temperature to 120°C for 90 min. After cooling down, the reacted product was washed several times with distilled water until the pH of the distilled water ceased to change while washing. Finally, it was dried in an oven at 50°C until constant weight. The mechanism of citric acid modified *Lemna minor* is schematically expressed in Fig. 1.

2.3. Biosorption experiments

Batch experiments are carried out at room temperature using 250 mL Stoppard glass bottles. A concussion agitation speed of 150 rpm was adopted for all experiments. Batch experiments were conducted to characterize the kinetics, equilibrium and mechanisms of the biosorption process. The thorium(IV) concentration in the solution was determined by UV visible spectrophotometer at 660 nm by the thorium(IV) arsenazo(III) complex method [21]. All experiments were run in triplicate. The biosorption efficiency (R) and biosorption quantity (q_e) were calculated using Eqs. (1) and (2):

$$R(\%) = \frac{C_0 - C_e}{C_0} \times 100 \tag{1}$$

$$q_e(mgg^{-1}) = \frac{(C_0 - C_e)V}{m} \tag{2}$$

where q is (mg) metal ions per (g) dry biosorbent; V is the reaction volume (mL); C_0 and C_e are the initial and the equilibrium metal concentrations (mg L^{-1}); m is the amount of dry biosorbent (g), respectively.

2.4. FTIR spectroscopy analysis

The functional groups present in the adsorbent were characterized by a Fourier transform infrared (FTIR) spec-

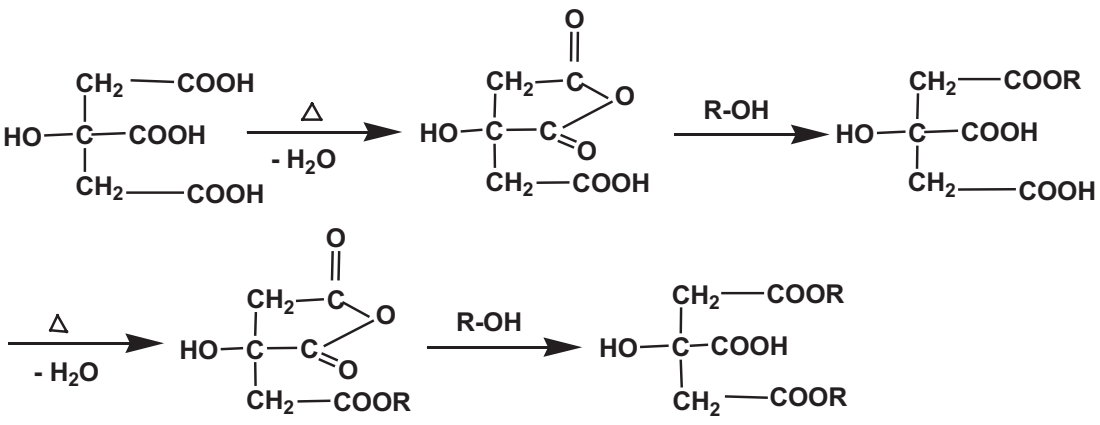


Fig. 1. Thermochemical reaction of *Lemna minor* and citric acid.

trophotometer, using KBr (Guo-Yao reagent co., LTD, Shanghai, CHINA) discs to prepare the sorbent CA-*Lemna minor* samples. Data analysis was focused on the 400~4000 cm^{-1} region [22].

3. Results and discussion

3.1. FTIR spectra characterization of biomass

The vibrations of the main functional groups on CA-*Lemna minor* biosorbent surface that bind metals were investigated using infrared spectroscopy. The FTIR spectra of the virgin and thorium(IV)-loaded biosorbents of CA-*Lemna minor* powders are respectively shown in Figs. 2a and b. As seen in Fig. 2a, the peaks observed at 2923.9 cm^{-1} and 2854.5 cm^{-1} can be assigned to the C–H group, and the peaks around 1031.8 cm^{-1} are characteristics of C–O group of primary hydroxyl stretching that may be attributed to cellulose structure of the *Lemna minor*. The broad and strong band ranging from 3200 to 3600 cm^{-1} might be due to –OH groups or $–NH_2$ groups, and the strong peak at 1625.9 cm^{-1} was produced by –C=O stretching vibration. Comparison of the IR spectra of samples of the virgin CA-*Lemna minor*, FTIR spectrum of thorium(IV)-loaded CA-*Lemna minor* in Fig. 2(b) displayed significant shift in some peaks. It could be seen that the shift of the peak from 1625.9 to 1647.1 cm^{-1} reflected the changes in the stretching frequency of carboxylate upon binding of thorium(IV). The FTIR spectroscopic analysis of thorium(IV)-loaded biosorbents indicated intensity shifted strong asymmetrical stretching bands at 3381.0 cm cm^{-1} (indicative of –OH and –NH groups) when compared with that of unloaded biomass which showed the same absorption at 3355.9 cm^{-1}. These observations indicated the involvement of these functional groups (–OH, –NH, and –C=O) in the biosorption process, and they acted as the important roles in the biosorption. So, it can be concluded that CA-*Lemna minor* presents an adequate chemical characteristics to adsorb metal ions.

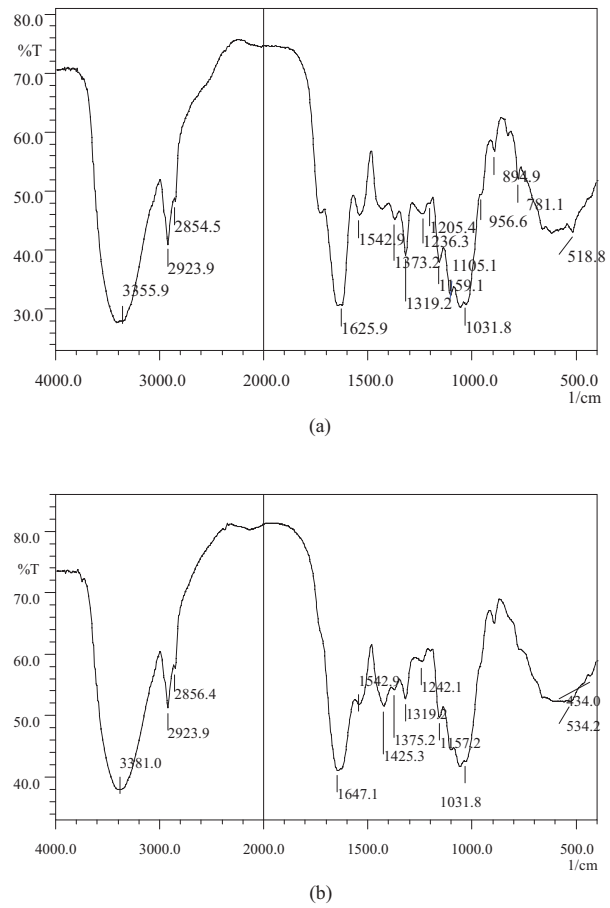


Fig. 2. Infrared (FTIR) spectra for CA-*Lemna minor* before (a) and after (b) loaded with thorium(IV).

3.2. Effect of solution pH on the sorption efficiency

The interaction between the metal ions and the functional groups of the biomass depends on the pH of the solution that considerably influences the metal speciation, sequestration, and/or mobility [23]. To examine this effect, a series of experiments were carried out with varying pH from 3 to 7. The influence of the initial pH on thorium(IV) adsorption is given in Fig. 3. The results showed thorium(IV) uptake was significantly affected by pH, and the maximum biosorption efficiency was observed at pH 5.0 (CA modified), which is obviously higher than the pH 5.5 of thorium(IV) maximum biosorption efficiency for the natural. This could be explained as below: it is generally known that at low pH values, concentrations of H^+ ions far

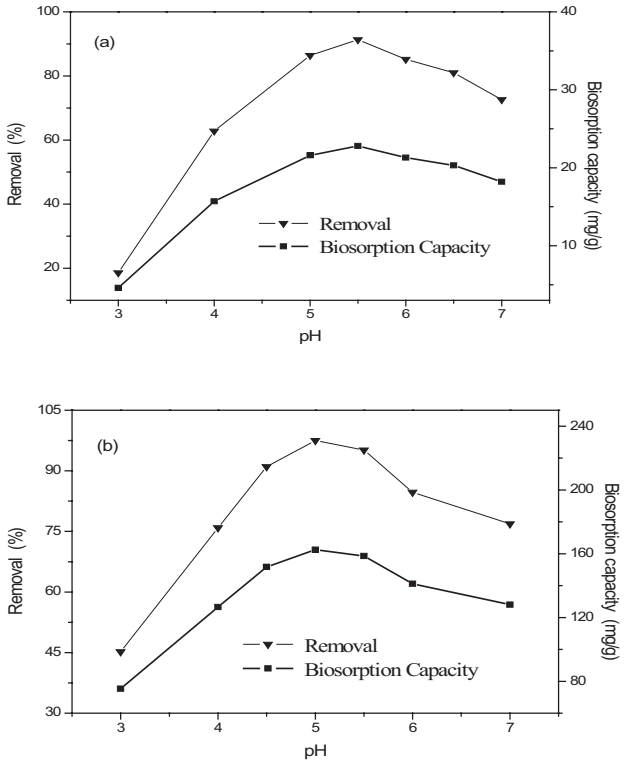


Fig. 3. Effect of pH on thorium(IV) biosorption by nature (a) and citric acid modified (b) *Lemna minor* V = 50 mL, m(a) = 0.1 g, m(b) = 0.03 g, contact time = 60 min, C_0(a) = 50 mg L^{-1}, C_0(b) = 100 mg L^{-1}.

exceeds that of the metal thorium(IV) ions and hence H^+ ions compete with thorium(IV) ions for the surface of the adsorbent which would hinder the thorium(IV) ions from reaching the binding sites of the adsorbent resulting in a low adsorption amount of thorium(IV). When solution pH is in the range of 3.0~5.0, the competing effect of hydrogen ions decreases, instead, thorium(IV) ions biosorption increases. At pH 5.0, maximum adsorption of 97.5% (162.5 mg g^{-1}) was observed for CA modified *Lemna minor*, which was obviously higher than maximum adsorption of 91.3% (22.8 mg g^{-1}) was observed for nature biomass at pH 5.5. The adsorption will decreased with further increase in pH, which might be attributed to the coordination of OH^- with the metal ion. When pH varied from 5.0 to 7.0, thorium(IV) was presented in the form of $Th(OH)^{3+}$, $Th(OH)_2^{2+}$, $Th_2(OH)_2^{6+}$ and $Th_6(OH)_{15}^{9+}$, and this resulted in the decline of thorium(IV) percentage removal and biosorption efficiency [24,25].

3.3. Effect of the biosorbent dose on the sorption efficiency

Biosorbent dose was also an important parameter affecting biosorption capacity as well as removal efficiency. The effect of adsorbent dose on the removal of thorium(IV) is shown in Fig. 4. The removal ratio increased gradually as the biosorbent mass increased from 0.01 to 0.03 g, simultaneously the biosorption capacity fell inversely. When using CA modified *Lemna minor*, maximum adsorption of 97.5% (162.5 mg g^{-1}) was observed at 0.03 g, which was obviously higher than maximum adsorption of 91.3% (22.8 mg g^{-1}) was observed for nature dry biomass at a dosage of 0.1 g. This implies that carboxyl groups in citric acid are introduced into the surface of *Lemna minor* by the esterification reaction. It's obvious that with the increase of biosorbents, more binding sites were available and thus the removal efficiency went up. However, under specific initial concentration, redundant biosorbents were not necessary for an efficient biosorption process, as the biosorption efficiency began to reduce with the decrease of metal ions.

3.4. Effect of contact time on the sorption efficiency

In order to determine the equilibrium time for maximum uptake, a contact time study was performed, and the results are presented in Fig. 5, from which the least time required for biosorption equilibrium could be concluded. It was clear that all sorbent sites were unoccupied and the metal concentration gradient was high at the beginning of the biosorption. After equilibrium time, the change of sorption efficiency for thorium(IV) didn't show notable effects. In the case of naturally dried biomass, the time required for equilibrium was 30 min, after that the q (mg g^{-1}) value was nearly constant. However, the appropriate equilibrium reached at 20 min for CA modified *Lemna minor*.

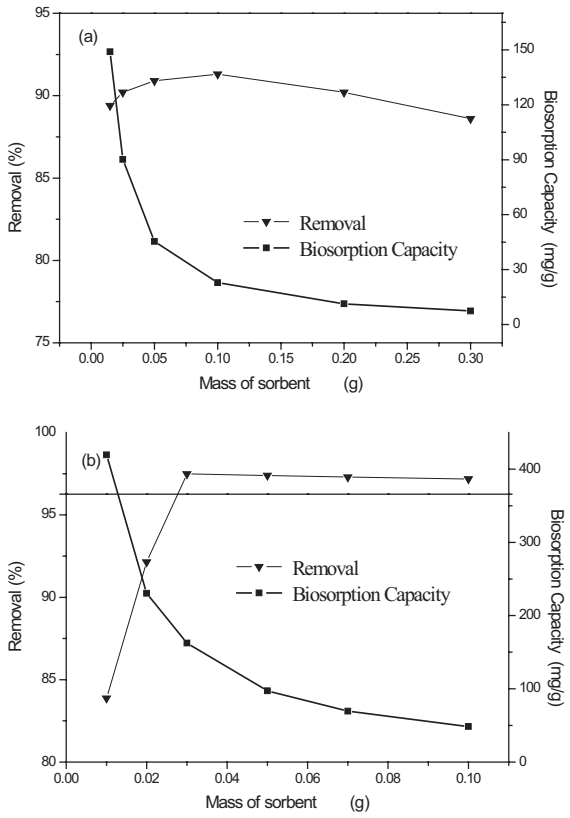


Fig. 4. Effect of biomass on thorium(IV) biosorption by nature (a) and citric acid modified (b) *Lemna minor* V = 50 mL, pH(a) = 5.5, pH(b) = 5.0, contact time = 60 min, C_0(a) = 50 mg L^{-1}, C_0(b) = 100 mg L^{-1}.

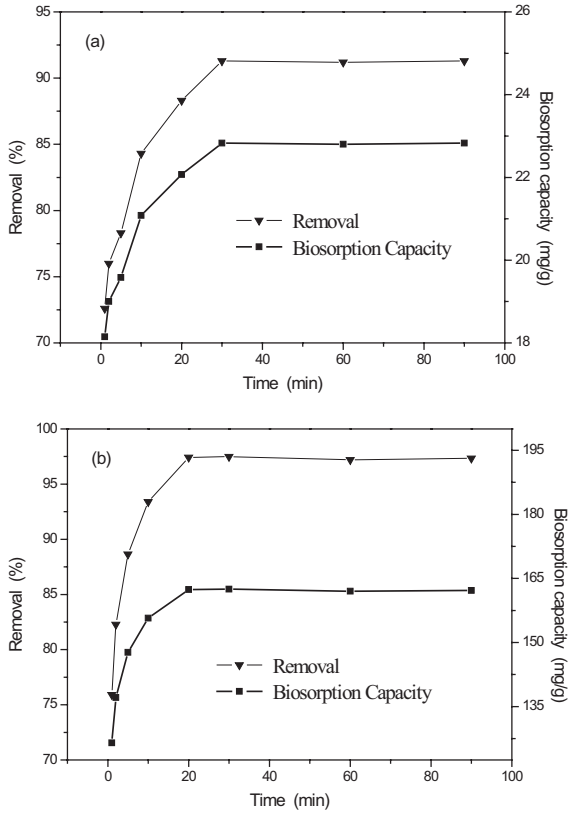


Fig. 5. Effect of contact time on thorium(IV) biosorption by nature (a) and citric acid modified (b) *Lemna minor* V = 50 mL, m(a) = 0.1 g, m(b) = 0.03 g, pH(a) = 5.5, pH(b) = 5.0, C_0(a) = 50 mg L^{-1}, C_0(b) = 100 mg L^{-1}.

3.5. Effect of initial thorium(IV) concentration on the sorption efficiency

Several experiments were undertaken to study the effect of initial thorium(IV) concentration on the thorium(IV) removal from the solution. The results obtained are shown in Fig. 6, and the maximum biosorption efficiency was observed at 100 mg L^{-1} (CA modified), which is obviously higher than 50 mg L^{-1} of thorium(IV) maximum biosorption efficiency for the natural. It was clear that the removal efficiency increased when initial concentration varied from 20 to 50 mg L^{-1}, and the removal efficiency decreased when the initial thorium(IV) concentration was over 100 mg L^{-1}. The change might be due to the available free sites (metal binding sites) approach saturation at higher thorium(IV) concentration. As a result, the *Lemna minor* adsorbent is more efficient for the wastewaters of low ion concentrations, and the purification yield can be increased by diluting the wastewaters containing high metal ion concentrations.

3.6. Adsorption kinetics

Kinetic study can provide valuable information for the mechanism of adsorption and the optimum operating conditions of industrial-scale batch process. With respect to the kinetics modeling of thorium(IV) biosorption, the pseudo-first-order, pseudo-second-order and Elovich kinetic models are used to interpret the experimental kinetic data [26], and their rate equations are represented as follows:

$$\text{Pseudo-first-order: } In(q_e - q_t) = Inq_e - k_1 t \tag{3}$$

$$\text{Pseudo-second-order: } \frac{t}{q_t} = \frac{1}{k_2 (q_e)^2} + \frac{t}{q_e} \tag{4}$$

$$\text{Elovich equation: } q_t = \frac{In(\alpha\beta)}{\beta} + \frac{Int}{\beta} \tag{5}$$

where q_t (mg g^{-1}) and q_e (mg g^{-1}) is sorption capacity at time t (min) and at equilibrium, 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; α is the initial sorption rate (mg g^{-1} min^{-1}), and β is on behalf of the activation energy for chemisorption (g mg^{-1}).

The parameters of pseudo-first order, pseudo-second order and Elovich rate kinetics are presented in Table 1. The theoretical q_e values from the first-order kinetic give significantly different values compared with the experimental values, and the correlation coefficients are also found to be slightly lower. The correlation coefficients for the second-order kinetic model and the theoretical values of q_e, they agree well with the experimental values. This indicated that the adsorption process included the both courses of chemical sorption and rate-limiting step.

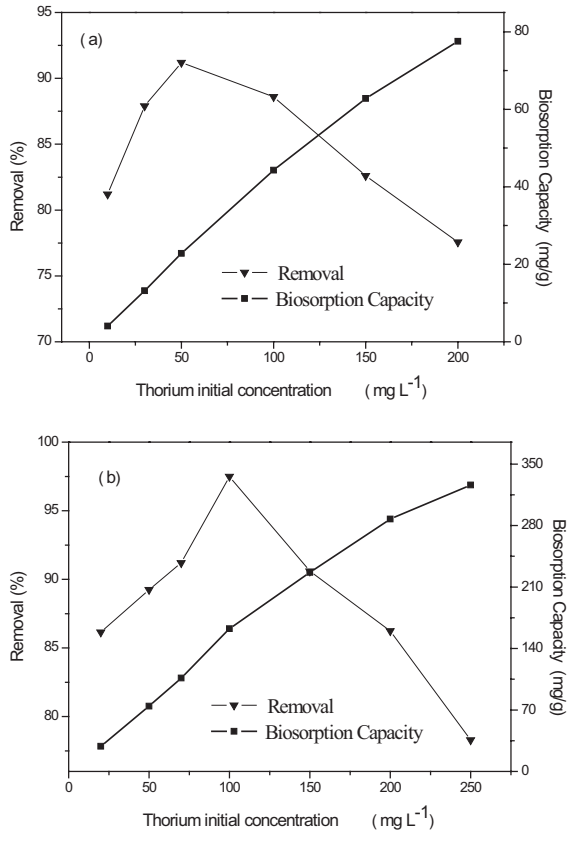


Fig. 6. Effect of initial thorium concentration on biosorption by nature (a) and citric acid modified (b) *Lemna minor V* = 50 mL, *m*(a) = 0.1 g, *m*(b) = 0.03 g, contact time = 60 min, *pH*(a) = 5.5, *pH*(b) = 5.0.

3.7. Biosorption isotherm

There are many theoretical models to describe the adsorption process of heavy metal ions by active and inactive adsorbent. Among these models, the Langmuir, Freundlich and Temkin equilibrium models have been applied in this study [27,28]. The Langmuir isotherm equation is valid for monolayer sorption onto surface containing finite number of identical sorption sites. The Freundlich equation is purely and empirically based on sorption of heterogeneous surface. The three isotherms may be expressed respectively as:

$$\text{Langmuir adsorption isotherm: } \frac{1}{q_e} = \frac{1}{Q} + \frac{1}{bQC_e} \tag{6}$$

$$\text{Freundlich adsorption isotherm: } Inq_e = Ink + \frac{InC_e}{n} \tag{7}$$

$$\text{Temkin adsorption isotherm: } q_e = BInA + BInC_e \ldots B = (RT)/b \tag{8}$$

where Q (mg g^{-1}) represents the amount of adsorption and b (L mg^{-1}) denotes the sorption equilibrium constant, respectively; k is the constant of sorption capacity, and $1/n$ represents the constant of sorption intensity; 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.

Table 1
Kinetic parameters of thorium (IV) adsorption for CA-*Lemna minor*

Duckweed	Psendo-first-order			Pseudo-second-order			Elovich equation		
	K_1 (1 min^{-1})	q_e (mg g^{-1})	R^2	K_2 (mg mol^{-1} min^{-1})	q_e (mg g^{-1})	R^2	α (mg g^{-1} min^{-1})	β (g mg^{-1})	R^2
Nature	0.0947	4.90	0.9920	0.0739	22.99	0.9999	6.63×10^5	0.73	0.9745
Modified	0.3015	61.40	0.9583	0.0186	163.93	0.9999	1.51×10^6	0.09	0.9781
Q_e (exp)	Nature (dry powder)			22.8 (exp)					
(mg g^{-1})	CA modified			162.5 (exp)					

Table 2
Isotherm model constant parameters of thorium (IV) adsorption for CA-*Lemna minor*

Duckweed	Freundlich isothem			Langmuir isothem			Temmlin isothem		
	K_F (mg g^{-1})/ (mg L^{-1})$^{1/n}$	n	R^2	q_{max} (mg g^{-1})	b (L g^{-1})	R^2	A_T (L g^{-1})	B_T	R^2
Nature	4.02	1.16	0.8879	56.18	–0.04	0.9049	0.5863	23.8	0.9945
Modified	19.08	1.26	0.8886	94.34	–0.08	0.9985	0.4513	108.2	0.9758

The calculated values of the Langmuir, Freundlich and Temkin parameters are listed in Table 2. As shown in Table 2, the equilibrium data fitted both the Langmuir and Temkin expressions with a satisfactory correlation coefficient values higher than 0.9. Moreover, the correlation coefficients of Langmuir isotherm were higher than that of Temkin model for CA modified *Lemna minor* biomass. But for the raw biomass, Temkin mode looked more appropriate. The better agreement of the experimental data with the Langmuir model implies that monolayer adsorption dominates the sorption process of CA modified *Lemna minor* biomass.

4. Conclusion

Batch adsorption experiments show that CA-*Lemna minor* has good thorium(IV) biosorption ability. Thorium(IV) biosorption experiments by CA-*Lemna minor* powders is optimized at pH 5.0, equilibrium time 30 min, initial thorium(IV) concentration 100 mg L^{-1} and adsorbent dose 0.6 g L^{-1} with 97.49% of removal efficiency and 162.5 mg g^{-1} of adsorption capacity, which is obviously greater than that (22.8 mg g^{-1}) of the untreated *Lemna minor* powders for thorium(IV) biosorption under the optimized condition, and this is the result that carboxyl groups in citric acid are introduced into the surface of *Lemna minor* powders by the esterification reaction. The pseudo-second order model (R^2 = 0.9999) best describe the kinetics and the Langmuir model (R^2 = 0.9985) best-fit equilibrium data for the biosorption of CA-*Lemna minor* powders. By comparing the FTIR spectra for the CA-*Lemna minor* powders before and after thorium(IV) adsorption, carbonyl and hydroxyl groups had an important contribution in the adsorption process.

References

[1] K.C. Bhainsa, F.D. Stanislaus, Thorium biosorption by *Aspergillus fumigatus*, a filamentous fungal biomass, J. Hazard. Mater., 165 (2015) 670–676.

[2] I. Shtangeeva, Uptake of uranium and thorium by native and cultivated plants, J. Environ. Radioact., 101 (2010) 458–463.

[3] J.D. Van Horn, H. Huang, Uranium(VI) bio-coordination chemistry from biochemical, solution and protein structural data, Coord. Chem. Rev., 250 (2006) 765–775.

[4] H.F. Li, Y.B. Lin, W.M. Guan, J.L. Chang, L. Xu, J.K. Guo, G.H. Wei, Biosorption of Zn(II) by live and dead cells of Streptomyces ciscaucasicus strain CCNWHX 72-14, J. Hazard. Mater., 179 (2010) 151–159.

[5] M.A. Zazouli, D. Belarak, F. Karimnezhad, F. Khosravi, Removal of fluoride from aqueous solution by using of adsorption onto modified lemna minor: Adsorption isotherm and kinetics study, JMUMS, 24 (2014) 195–204.

[6] R. Diyanati, J. Yazdani, D. Belarak, Effect of sorbitol on phenol removal rate by lemna minor, JMUMS, 23 (2013) 58–65.

[7] R.-A. Dyanati-Tilaki, Z. Yousefi, J. Yazdani-Cherati, The ability of azollaand lemna minor biomass for adsorption of phenol from aqueous solutions, JMUMS, 23 (2013) 140–146.

[8] D. Balarak, Kinetics, isotherm and thermodynamics studies on bisphenol a adsorption using barley husk, Int. J. Chem. Tech. Res., 9 (2016) 681–690.

[9] R.A. Dyanati, Z.A. Yousefi, J.Y. Cherati, Investigating phenol absorption from aqueous solution by dried azolla, JMUMS, 22 (2013) 13–20.

[10] D. Balarak, A. Joghataei, Biosorption of phenol using dried rice husk biomass: kinetic and equilibrium studies, Der Pharma Chemica., 8 (2016) 96–103.

[11] T.S. Anirudhan, S. Rijith, A.R. Tharun, Adsorptive removal of thorium(IV) from aqueous solutions using poly(methacrylic acid)-grafted chitosan/bentonite composite matrix: Process design and equilibrium studies, Colloids Surf. A: Physicochem. Eng. Asp., 368 (2010) 13–22.

[12] H.W. Huang, L.X. Cao, Y.X. Wan, R.D. Zhang, W.F. Wang, Biosorption behavior and mechanism of heavy metals by the fruiting body of jelly fungus (Auricularia polytricha) from aqueous solutions, Appl. Microbiol. Biotechnol., 96 (2012) 829–840.

[13] T.C. Muhammad, Z. Muhammad, R. Naseem, S.T. Subhe, P. Shoukat, Biosorption characteristics of Aspergillus fumigatus for the decolorization of triphenylmethane dye acid violet 49, Appl. Microbiol. Biotechnol., 98 (2014) 3133–3141.

[14] S.H. Kan, B.Y. Sun, F. Xu, Q.X. Song, S.F. Zhang, Biosorption of aquatic copper (II) by mushroom biomass Pleurotus eryngii: kinetic and isotherm studies, Water Sci. Technol., 87 (2014) 107–113.

[15] T. Kikuchi, S. Tanaka, Biological removal and recovery of toxic heavy metals in water environment, Crit. Rev. Env. Sci. Technol., 42 (2012) 1007–1057.

[16] S.J. Kleinübing, E.A. Silva, M.G.C. Silva, E. Guibal, Equilibrium of Cu(II) and Ni(II) biosorption by marine alga Sargassum filipendula in a dynamic system:competitiveness and selectivity, Bioresour. Technol., 102 (2012) 4610–4617.
[17] B. Volesky, Detoxification of metal-bearing effluents: biosorption for the next century, Hydrometallurgy, 59 (2001) 203–216.
[18] W.S. Wan Ngah, M.A.K.M. Hanafiah, Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: a review, Bioresour. Technol., 99 (2008) 3935–3948.
[19] C.Q. He, J.X. Ye, Inhibitory effects of Acorus tatarinowii on algae growth, Acta Ecol. Sin., 19 (1999) 754–758.
[20] B. Zhu, T.X. Fan, D. Zhang, Adsorption of copper ions from aqueous solution by citric acid modified soybean straw, J. Hazard. Mater., 153 (2008) 300–308.
[21] M.A. Bayyari, M.K. Nazal, F.I. Khalili, The effect of ionic strength on the extraction of thorium(IV) from perchlorate solution by didodecylphosphoric acid (HDDPA), Arabian J. Chem., 3 (2010) 115–119.
[22] M.X. Liu, F.Q. Dong, X.Y. Yan, W.M. Zeng, L.Y. Hou, X.F. Pang, Biosorption of uranium by Saccharomyces cerevisiae and surface interactions under culture conditions, Bioresour. Technol., 101 (2010) 8573–8580.
[23] R.A. Anayurt, A. Sari, M. Tuzen, Equilibrium, thermodynamic and kinetic studies on biosorption of Pb(II) and Cd(II) from aqueous solution by macrofungus (Lactarius scrobiculatus) biomass, Chem. Eng. J., 151 (2009) 255–261.
[24] S.K. Yang, N. Tan, X.M. Yan, F. Chen, Y.C. Lin, Adsorption of thorium(IV) from aqueous solution by non-living biomass of mangrove endophytic fungus *Fusarium sp.* #ZZF51, J. Radioanal. Nucl. Chem., 298 (2013) 827–833.
[25] S.K. Yang, N. Tan, X.M. Yan, F. Chen, W. Long, Y.C. Lin, Thorium(IV) removal from aqueous medium by citric acid treated mangrove endophytic fungus Fusarium sp. #ZZF51, Mar. Pollut. Bull., 74 (2013) 213–219.
[26] H.X. Zou, N. Li, L.H. Wang, P. Yu, X.F. Yan, Equilibrium and kinetic studies of Cd^{2+} biosorption by the brown algae sargassum fusiforme, Plos One., 9 (2013) 195–242.
[27] F. Chen, N. Tan, X.M. Yan, S.K. Yang, Z.G. She, Y.C. Lin, Uranium(VI) removal from aqueous solution by poly(amic acid)-modified marine fungus, Sep. Sci. Technol., 49 (2014) 1–8.
[28] X.J. Zuo, R. Balasubramanian, D.F. Fu, H. Li, Biosorption of copper, zinc and cadmium using sodium hydroxide immersed Cymbopogon schoenanthus L, Spreng (lemon grass), Ecol. Eng., 49 (2012) 186–189.