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Cystine-modified biomass for Cd(II) and Pb(II) biosorption

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Abstract

The surface of dried biomass of baker's yeast was modified by crosslinking cystine with glutaraldehyde. X-ray photoelectron spectroscopy and microscope were used to characterize the modified biomass. The adsorption capacity of the modified biomass for Cd^{2+} and Pb^{2+} showed an increase compared with the pristine biomass due to the presence of cystine on the biomass surface. Experimental data showed that the adsorption of the two metal ions increased with time until equilibrium was achieved. The adsorption capacities for Cd^{2+} and Pb^{2+} were 11.63 and 45.87 mg g^{-1}, respectively, which were determined from the Langmuir isotherm. The loaded biosorbent was regenerated using HCl solution and could be used repeatedly at six times with little loss of uptake capacity. FTIR spectroscopy revealed that carboxyl, amide, and hydroxyl groups on the biomass surface were involved in the adsorption of Cd^{2+} and Pb^{2+}.

Keywords: Baker's yeast; Cystine; Glutaraldehyde; Crosslinking; Adsorption

1. Introduction

Heavy metals in wastewater generated from various industries are hazardous to human and other living organisms when discharged into the environment [1,2]. This concern has led to the development of various methods for the removal of metals from wastewater such as biological treatment, ion exchange, chelation, reverse osmosis, coagulation–precipitation, electrochemical operation, filtration, and adsorption [3,4]. Biosorption has been recognized as a promising technology that shows potential as an alternative to conventional processes for the treatment of water with trace levels of metal contaminant [5–9]. Microorganisms have rich contents of polysaccharides and several important functional groups, such as carboxyl, hydroxyl and amino in the cell wall, which are mainly responsible for higher metal biosorption. Ion exchange, surface complex formation and microprecipitation are used to explain the biosorption mechanisms. Microorganisms including bacteria, fungi and algae have been investigated in metal adsorption studies [10–12]. Among the microorganisms used for biosorption, baker's yeast is an inexpensive, readily available source of biomass for heavy metal removal from wastewater. Native baker's yeast biomass is unsatisfactory due to their poor mechanical strength and low adsorption capacity [13]. To increase the adsorption capacity of biomass for metal ions, some workers investigated the surface modification of the biomass to increase the amount of functional groups such as carboxylate, hydroxyl, sulfate, phosphate, amide, and amino groups. Matis et al. reported that pretreatment of *Pencicillium chrysogenum* biomass with surfactants and cationic polyelectrolyte was found to improve the adsorption efficiency for As(V) anions [14]. Deng et al. noted that modified biomass of *P. chrysogenum* with polyethylenimine (PEI) significantly improved the adsorption capacity for copper, lead and nickel [15]. Klimmek demonstrated that the maximum adsorption capacities of the alga *Lyngbya taylorii* could be increased significantly after phosphorylation [16]. Other common chemical modifications were alkaline, acid, ethanol and acetone treatments of the biomass [17–20].

Cystine is a good absorbent for metal ions due to the presence of two carboxyl groups, two amido groups and two sulfur atoms in a molecule. It was often used to modify adsorbent surface to increase the adsorption capacity. However, the use of cystine to modify biomass has not been reported in the literatures.

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In this paper, the biomass of baker's yeast was modified by crosslinking cystine on its surface and its adsorption capacity for the common toxic metal ions, Cd^{2+} and Pb^{2+}, were studied. The adsorption kinetics and equilibriums were investigated, and pseudo second-order equation, Langmuir, and Freundlich adsorption models were used to fit the experimental data. The adsorption mechanisms of the modified biomass for Cd^{2+} and Pb^{2+} were investigated using FTIR analysis.

2. Materials and methods

2.1. Materials

Baker's yeast was purchased from China General Microbiological Culture Center (Beijing, China). It was dried in an oven at 60 °C for 24 h before use. Other chemicals were of reagent grade.

2.2. Surface modification

The treatment of the biomass was carried out on a rotary shaker operating at 150 rpm and room temperature. Sample of 1.5 g of the biomass was suspended in 100 mL of glutaraldehyde solution (0.3 wt% in water) for 0.5 h, and then different amount of cystine water solution was added to the suspension and continued shaking for another 12 h. After the reaction, the biomass was thoroughly rinsed with distilled water to remove residual glutaraldehyde and cystine, and then dried at 60 °C overnight in an oven before use.

2.3. Morphology observation

The surface morphologies of the biomass before and after modification were examined with a microscope (Olympus BX51, Japan). After the reaction, 20 μL of the original samples were taken out and placed on glass-slides for observation directly.

2.4. XPS analysis

XPS (VGMultilab 2000) was used in the surface analysis of the dried biomass before and after modification. The analysis was made with an Mg X-ray source to determine the O and S atoms present. The pressure in the analysis chamber was maintained at less than 10^{-8} Torr during measurement. All binding energies were referenced to the neutral C (1s) peak at 284.6 eV to compensate for the surface charging effects. The software package of advantae 3.22 was used to fit the XPS spectra peaks.

2.5. Batch adsorption experiments

Batch adsorption experiments were conducted to study the adsorption kinetics and equilibriums. The adsorption experiments were performed at room temperature and 150 rpm on a rotary shaker with 0.0500 g of the biomass in a 100 mL conical flask containing 50.00 mL of cadmium or lead nitrate solution. In the adsorption kinetics and isotherms experiments, 0.0500 g biomass in 50.00 mL of metal solution at various concentrations was conducted. After adsorption, the biomass was separated from the solution, and then dried for the FTIR analysis, while the metal concentration in the filtrate was analyzed using atomic adsorption spectrophotometer (AA6300, Shimadzu, Japan). All the experiments were conducted in duplicate, and the mean values were reported.

2.6. FTIR spectroscopy

The samples of the biomass before and after chemical modification and biomass after metal adsorption were analyzed with a FTIR (Nicolet NEXUS-470) spectrometer under ambient conditions.

2.7. Desorption experiments

In the desorption experiments, the biomass with Cd^{2+} adsorption was regenerated with 20 mL of 0.1 mol L^{-1} HCl solution on a rotary shaker operating at 150 rpm for 1 h and then washed with distilled water until a neutral pH was obtained. The regenerated biomass was reused in the next cycle of adsorption experiments.

3. Results and discussion

3.1. Preparation and characterization of biomass adsorbent

Due to the poor mechanical strength, directly using native baker's yeast biomass would lead to organic leaching during adsorption or desorption process. Organic leaching would affect the adsorption capacity. Many literatures had reported that chemical modification of biomass with glutaraldehyde could prevent organic leaching [13,21], but often it could not improve its adsorption capacity. Cystine is a good absorbent for metal ions due to the presence of two carboxyl groups, two amido groups and two sulfur atoms in a molecule. The basic object of our approach was that through modification of biomass with cystine using glutaraldehyde, it was possible to improve the mechanical strength and adsorption capacity of the biomass at the same time. Firstly, glutaraldehyde reacted with cystine and formed a long chain compound through the following Schiff-base reaction:

$$\mathrm{CHO(CH_2)_3CHO + NH_2CH(COOH)CH_2S\text{–}SCH_2CH(COOH)NH_2} \rightarrow \mathrm{CHO(CH_2)_3\text{–}[\text{–}C{=}NCH(COOH)CH_2S\text{–}SCH_2CH(COOH)N{=}C\text{–}]\text{–}}n\mathrm{(CH_2)_3CHO} \quad (1)$$

Secondly, glutaraldehyde fixed the long chain compound on the surface of the biomass through the reaction with hydroxyl or amide groups [13] and obtained biomass with good mechanical strength and higher adsorption capacity.

Fig. 1 showed the micrographs (×1000) of baker's yeast before and after surface modification. Little interaction with

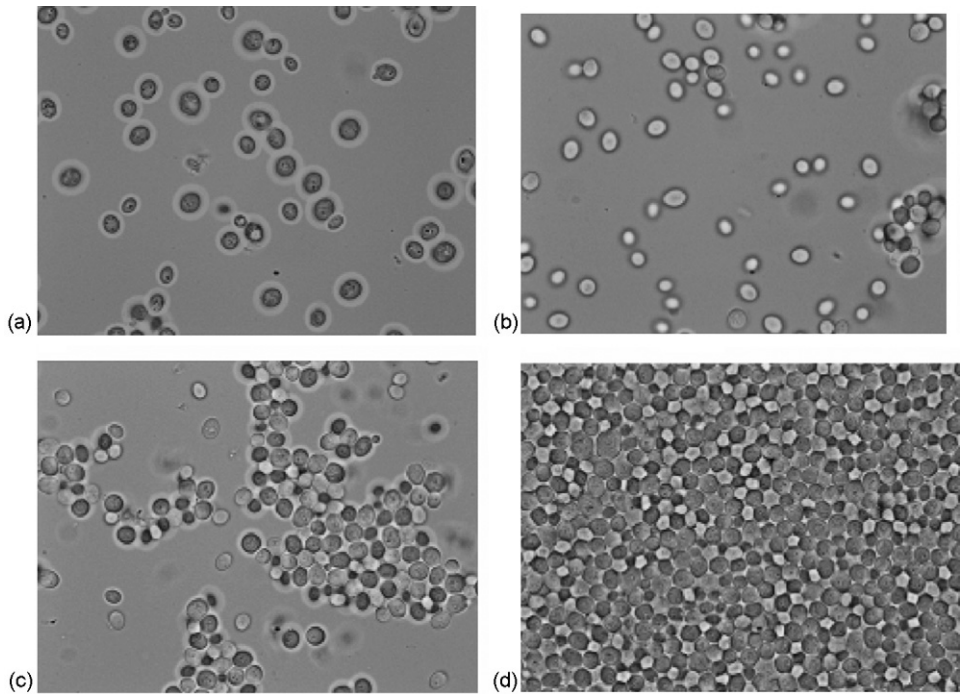


Fig. 1. Micrographs of baker's yeast before and after the surface modification: (a) the pristine biomass, (b) glutaraldehyde treated biomass, (c) modified biomass with 0.03 g mL^{-1} cystine and (d) modified biomass with 0.05 g mL^{-1} cystine.

other cells was observed in the pristine and glutaraldehyde treated biomass. After the modification, the cells tended to aggregate and become more compact. More serious aggregation between the cells was found with increasing amount of cystine. These results indicated that crosslinking reaction occurred on the surface of adjacent cells.

To obtain further insights into the changes on the surface of biomass after modification, XPS analysis were conducted. Fig. 2 showed the O (1s) and S (2p) spectra of the biomass before and after modification. As shown in Fig. 2a, two peaks at 537.0 and 528.0 eV could be fitted to the O (1s) spectrum of the pristine biomass, which were attributed to the oxygen in O–C and O=C–N, respectively. This result verified that a higher concentration of hydroxyl groups and a lower concentration of carboxyl groups were present on the pristine surface. After modification, a new peak at 531.0 eV, which was ascribed to the oxygen in

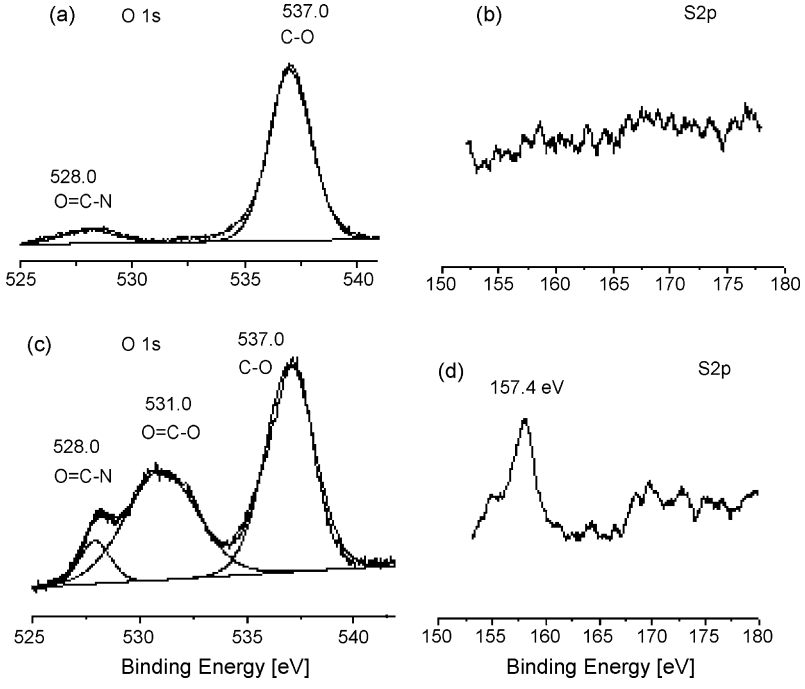


Fig. 2. O (1s) and S (2p) XPS spectra of the pristine biomass (a and b) and modified biomass (c and d).

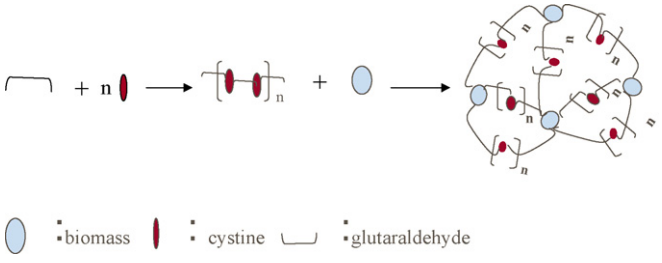
Table 1
Area ratios of O (1s) spectra for the pristine and modified biomass

Biomass	Peak area ratio (100%)		
	537.0 eV (O–C)	531.0 eV (O=C–O)	528.0eV (O=C–NH_2)
Pristine biomass	92.6	0	7.4
Modified biomass	52.6	40.5	6.9

O=C–O, was observed (see Fig. 2c). Additionally, the area ratios for different oxygen peaks of the pristine and modified biomass were listed in Table 1. As shown in Table 1, the area ratio for the peak at 531.0 eV attributed to carboxyl groups (from cystine) increased from 0% to 40.5% after the modification, indicating that cystine had modified on the biomass surface. It could also be seen that the area ratio decreased from 92.6% to 52.6% for O–C, which might be attributed to the crosslinking reaction with glutaraldehyde. Fig. 2b and d presented the S (2p) XPS spectra of the pristine biomass and modified biomass. No peak was observed in Fig. 2b, indicating that almost no sulfur atom was present in the pristine biomass. However, the binding energy at 157.4 eV, which could be ascribed to S atom (coming from cystine), was found in the modified biomass (Fig. 2d). From the results above, it was clear that by the present method, cystine had modified on the biomass surface through the crosslinking reaction.

Based on the results above, we proposed a possible mechanism to explain the whole modification process (see Scheme 1). Cystine reacted with glutaraldehyde through Schiff-base reaction and formed a long chain compound (see reaction (1)). As glutaraldehyde was in excess, the end of the long chain will be predominantly aldehyde groups. On one hand, these aldehyde groups crosslinked with hydroxyl or amido groups on two cells and cause the biomass to aggregate. With the increase of the cystine concentration, more long chain compounds were formed, promoting the crosslinking reaction among the cells, and highly aggregated biomass was obtained. On the other hand, this crosslinking reaction could occur on the surface of one cell, which can improve its mechanical strength. When there was no cystine, the crosslinking reaction between the biomass and glutaraldehyde tend to occur on one cell due to steric hindrance. And interaction with other cells was rarely observed as shown in Fig. 1b.

In order to determine the optimal reaction conditions, the modified biomass obtained at different cystine concentration



Scheme 1. Schematic illustration of the possible modification process.

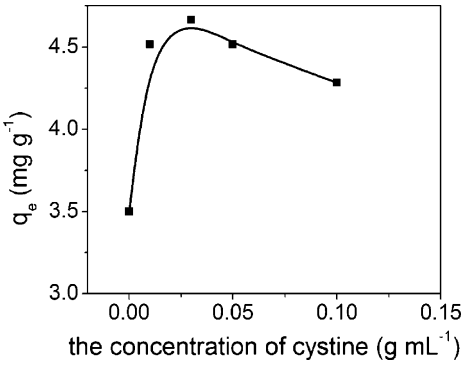


Fig. 3. Effect of the amount of cystine on the adsorption capacity of the modified biomass for Cd^{2+}.

was prepared and investigated in the adsorption of Cd^{2+} from aqueous solution. In the adsorption experiments, 0.0500 g of the modified and pristine biomass was added to 50.00 mL of 5 mg L^{-1} Cd^{2+} solution. Fig. 3 showed the effect of cystine concentration on the adsorption capacity. It could be seen that the adsorption capacity firstly increased and then decreased with increasing cystine concentration and the optimal concentration of cystine was 0.03 (g mL^{-1}). The decrease in the adsorption capacity was due to more extensive crosslinking, which induced the aggregation of the biomass and decreased the surface area and adsorption sites.

3.2. Adsorption kinetics study

Fig. 4a and b showed the adsorption kinetics of Cd^{2+} and Pb^{2+} using the modified biomass at different initial metal ions concentration. The adsorption process was found to be extremely rapid: the systems both attained the final equilibrium plateau within 20 min. Rapid interaction of the metal ions to be separated with the adsorbent was desirable and beneficial for practical adsorption applications. In order to obtain further insight into the mechanism of the adsorption of Cd^{2+} and Pb^{2+} on the biomass, a pseudo-second-order mechanism was investigated. The pseudo-second-order equation was given by [22,23]:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (2)$$

where k_2 (g mg^{-1} min^{-1}) is the rate constant for the pseudo-second-order adsorption; q_e (mg g^{-1}) is the adsorption capacity at equilibrium; q_t (mg g^{-1}) is the adsorption capacity at time t (min). Separating the variables in Eq. (2) and integrating gives:

$$\frac{t}{q_t} = \frac{1}{k_2\, q_e^2} + \frac{t}{q_e} = \frac{1}{v_0} + \frac{t}{q_e} \quad (3)$$

where v_0 represents the initial adsorption rate (mg g^{-1} min^{-1}). The equilibrium adsorption capacity q_e and the pseudo second-order rate constant k_2 can be experimentally determined from the slope and the intercept of the plot t/q_t against t. Results using the pseudo-second order equation for Cd^{2+} and Pb^{2+} adsorption kinetics were conducted and the corresponding parameters and regression coefficients for the plots were given in Table 2,

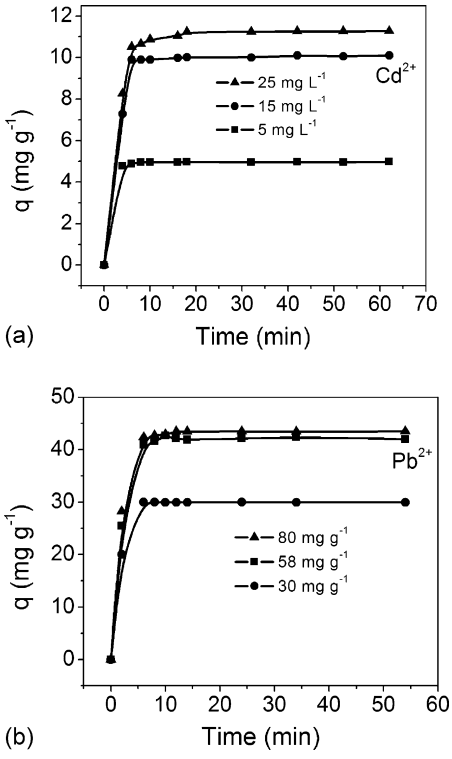


Fig. 4. Adsorption kinetics of Cd^{2+} (a) and Pb^{2+}(b) on the modified biomass.

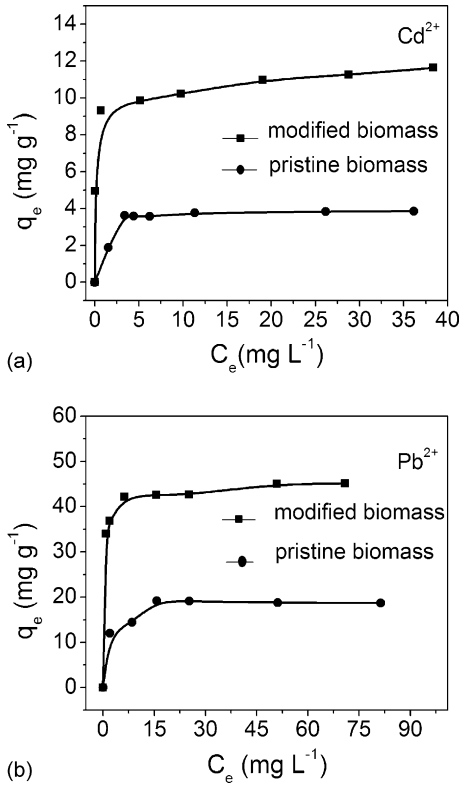


Fig. 5. (a) Adsorption isotherms of Cd^{2+} on the pristine and modified biomass and (b) adsorption isotherms of Pb^{2+} on the pristine and modified biomass.

As shown in Table 2, the values of the calculated q_e were in agreement with those found experimentally, and good fits were obtained for both the metals. These results indicated that the adsorption of Cd^{2+} and Pb^{2+} followed the pseudo second-order kinetics. It could also be seen that the equilibrium adsorption capacity, q_e, increased with an increase in the initial concentration; however, the percentage of metal removed and the rate constant decreased. These results demonstrated that Pb^{2+} and Cd^{2+} adsorption by baker's yeast were a chemically equilibrated and saturable mechanism. Because the completion of the adsorption process needed only 20 min, the adsorption time was fixed at 30 min in subsequent adsorption experiments.

3.3. Adsorption isotherms

Langmuir and Freundlich isotherms had been used to model many adsorption processes. The Langmuir isotherm assumes monolayer coverage of adsorbate over a homogeneous adsorbent surface, and the adsorption of each molecule onto the surface has equal adsorption activation energy. While the Freundlich isotherm assumes a heterogeneous surface with a nonuniform distribution of heat of adsorption over the surface and a multilayer adsorption can be formed. The Langmuir and Freundlich isotherms may be expressed as Eqs. (4) and (5), respectively:

$$q_e = \frac{q_m C_e}{1/b + C_e} \quad \text{or} \quad \frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \tag{4}$$

$$q_e = aC_e^{1/n} \quad \text{or} \quad \log q_e = \log a + \frac{1}{n}\log C_e \tag{5}$$

where q_m is the maximum amount of adsorption (mg g^{-1}), b is the adsorption equilibrium constant (L mg^{-1}), C_e is the equilibrium concentration of substrates in the solution (mg L^{-1}), a is the constant representing the adsorption capacity, and n is the constant depicting the adsorption intensity.

Fig. 5a and b showed the adsorption isotherms of Cd^{2+} and Pb^{2+} on the pristine and modified biomass. The adsorption capacities for both metal ions increased with an increase in the equilibriums metal concentration. Langmuir and Freundlich adsorption constants evaluated from the isotherms with the correlation coefficients were listed in Table 3. As it could be seen that the Langmuir isotherm gave better fit than the Freundlich isotherm for Cd^{2+} and Pb^{2+} adsorption, which demonstrated that the adsorption on the biomass surface was a monolayer, not a multilayer adsorption. According to the Langmuir equation, the maximum uptake capacities (q_m) for Cd^{2+} and Pb^{2+} were 11.63 and 45.87 mg g^{-1}, respectively, which were higher than that of pristine biomass (3.90 and 19.01 mg g^{-1}, respectively). The

Table 2
Kinetic parameters of the pseudo-second-order equation for Cd^{2+} and Pb^{2+} adsorption (q_{ee}: the experimental q_e value and q_{ec}: calculated q_e value)

Initial concentration (mg L^{-1})	Cd^{2+}			Pb^{2+}		
	5	15	25	30	58	80
V_0 (g mg^{-1} min^{-1})	51.47	19.52	16.71	126.58	121.95	123.46
q_{ec} (mg g^{-1})	4.99	10.12	11.43	30.21	42.55	43.86
q_{ee} (mg g^{-1})	4.98	10.10	11.26	29.95	42.01	43.48
R^2	0.998	0.997	0.999	0.999	0.998	0.999

Table 3
Langmuir and Freundlich isotherm constants for Cd^{2+} and Pb^{2+} adsorption on the pristine and modified biomass

	Metal ions	Langmuir constants			Thermodynamic constants	Freundlich constants		
		b (L mg^{-1})	q_m (mg g^{-1})	R^2	ΔG° (kJ mol^{-1})	a (mg$^{1-1/n}$ g^{-1} L$^{1/n}$)	n	R^2
Pristine	Pb^{2+}	1.06	19.01	0.999	−0.15	11.56	7.67	0.777
Biomass	Cd^{2+}	1.32	3.90	0.999	−0.70	2.42	6.16	0.507
Modified	Pb^{2+}	1.25	45.87	0.998	−0.56	35.35	16.00	0.915
Biomass	Cd^{2+}	1.52	11.63	0.996	−1.05	7.65	8.64	0.884

higher metal ions uptake values obtained by modified biomass may be explained by the introduction of cystine on the surface of the biomass through the crosslinking reaction. Moreover, the Gibbs free energy (ΔG°) can also be calculated from the Langmuir isotherm (see Eq. (6)) [24]:

$$\Delta G^\circ = -RT \ln K \quad (6)$$

where K corresponds to b in the Langmuir isotherm [24]. Using the constant b in the Langmuir isotherm, the Gibbs free energies of adsorption for metal ions were calculated and listed in Table 3, the negative values of ΔG° indicated that the adsorption of Cd^{2+} and Pb^{2+} on the biomass were spontaneous under our experimental conditions.

Many biomass were used to remove Cd^{2+} and Pb^{2+} from aqueous solution. It had been reported that the maximum adsorption capacity of ethanol treated waste baker's yeast biomass for Pb^{2+} was 15.63 mg g^{-1} [25]. Pardo et al. had reported that the maximum adsorption capacity of Pb^{2+} by inactive biomass of *Pseudomonas putida* was 2.6 mg g^{-1} at pH 4.5 [26]. For the biomass of *Aspergillus niger*, the maximum biosorption capacities of Pb^{2+} was obtained as 32.6 mg g^{-1} at pH 4.0 [27]. Although literatures had reported that other biosorbent had higher adsorption capacity for the two metal ions [5,8], the modified biomass in this work had comparatively better adsorption.

3.4. Effect of pH on metal sorption

pH is an important parameter that affects metal ions adsorption; it not only influences the properties of sorbent surface but also affects metal speciation in solution. In our experiments, the initial solution pH was adjusted to less than 6.0 to prevent metal ions precipitation [28,29], and the concentrations used were 8 and 50 mg L^{-1} for Cd^{2+} and Pb^{2+}, respectively. Fig. 6 showed the adsorption of Cd^{2+} and Pb^{2+} on the modified biomass as a function of the solution pH. In both instances, the adsorption capacity increased with increasing solution pH and a rapid increase in uptake was observed at pHs ranging from 3.0 to 4.5. According to Low et al., the adsorption below pH 2 was little due to the competition of hydrogen ions for the active sites [30]. That is to say, at higher H^+ concentration, the adsorbent surface became more positively charged thus reducing the attraction between the biomass and the metal ions. In contrast, as the pH increased, more negatively charged surface became available thus facilitating greater metal uptake.

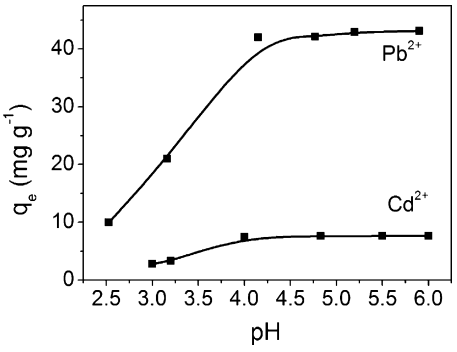


Fig. 6. Effect of pH on adsorption of Cd^{2+} and Pb^{2+} on the modified biomass.

3.5. FTIR analysis

Fig. 7 showed FTIR spectra of the modified biomass before and after metal ions adsorption. The spectrum of modified biomass was complex due to the numerous functional groups on the surface of the biomass. The peaks at 3381, 2924, 1652, 1541, 1240 and 1071 cm^{-1} were observed. The broad and strong band ranging from 3100 to 3700 cm^{-1} was due to the overlapping of O–H and N–H stretching vibration, which were consistent with the peaks at 1071 and 1240 cm^{-1} assigned to alcoholic C–O and C–N stretching vibration, thus, showing the presence of hydroxyl and amine groups on the biomass surface. The peaks at 1652 and 1541 cm^{-1} were attributed to C=O and N–H stretching vibration, respectively. Another peak at 2928.7 cm^{-1} was due to CH stretching vibrations of CH, CH_2, and CH_3 groups. After Cd^{2+} and Pb^{2+} adsorption, N–H stretching vibration were shifted to 1530 and 1529 cm^{-1}, respectively. The significant shifts of these specific peaks to the lower wavenumber after the metal ions adsorption suggested that chemical interactions

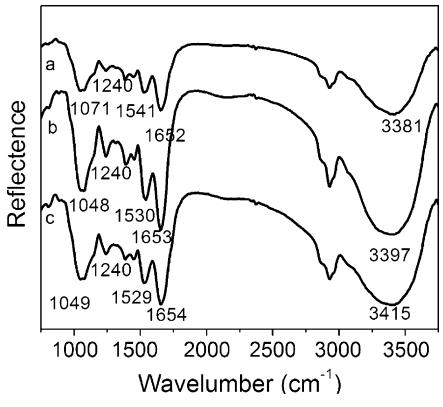


Fig. 7. FTIR spectra of: (a) modified biomass, (b) modified biomass with Cd^{2+} adsorption and (c) modified biomass with Pb^{2+} adsorption.

Table 4
The adsorption capacity of the modified biomass in treating wastewater

Wastewater composition	Initial concentration ($mg\,L^{-1}$)	Equilibrium concentration ($mg\,L^{-1}$)	Removal (%)
Cd^{2+}	5	0.70	86.0
Pb^{2+}	20	0.11	99.5

between the metal ions and the amide groups occurred on the biomass surface. The broad peak at 3381 cm^{-1} shifted to 3397 and 3415 cm^{-1}, indicating that hydroxyl, carboxyl and amide groups were involved in the sorption. It could be also seen that the peak at 1071 cm^{-1} shifted to the lower wavenumber of 1048 cm^{-1}, which also demonstrated that hydroxyl groups were involved in the metal ions adsorption. These results indicated that the carboxyl, hydroxyl and amide groups on the modified biomass surface were all involved in the adsorption of Cd^{2+} and Pb^{2+}.

3.6. Adsorption ability of the modified biomass in treating simulated wastewater

The adsorption behavior of the modified biomass in treating wastewater was studied. The wastewater came from the Nanhu Lake (Wuhan, China). Because of the concentrations of Cd^{2+} and Pb^{2+} were too low, amounts of cadmium or lead nitrate were added and the obtained concentration of Cd^{2+} and Pb^{2+} were 5 and 20 $mg\,L^{-1}$. The simulated wastewater was pretreated by adjusting pH value to 5.5, and filtered. 0.0500 g modified biomass was added into 50.00 mL of the obtained wastewater. After adsorption, the concentration of the two metals was analyzed and the results were listed in Table 4. From Table 4, it can be seen that the removal of Cd^{2+} and Pb^{2+} reached 86.0% and 99.5%. Using 0.1 $mol\,L^{-1}$ HCl solution as desorption agent, it was found that the 95% heavy metal ions could be desorbed from the adsorbent surface, and then the adsorbent could be reused.

3.7. Desorption study

After adsorption of the metal ions, the sorbent was regenerated using hydrochloric acid (0.1 $mol\,L^{-1}$), then rinsed with deionized water and used in subsequent experiments. Fig. 8 showed that biomass could be regenerated and used six times with little loss of uptake capacity.

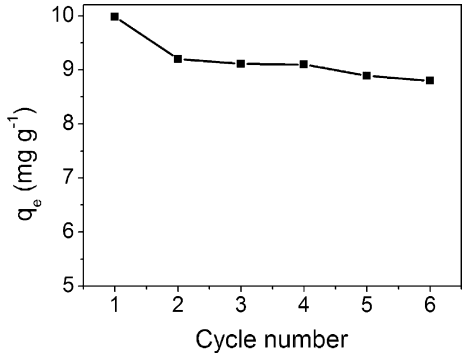


Fig. 8. Comparative adsorption capacities of the modified biomass for Cd^{2+} in six adsorption–regeneration cycles.

4. Conclusion

Cystine was introduced onto the baker's yeast biomass through a simple crosslinking reaction. XPS analysis confirmed that the biomass surface was modified with cystine. The adsorption capacity of the modified biomass was higher than that of the pristine biomass. Moreover, the adsorption isotherm obeyed the Langmuir isotherm. FTIR results indicate that carboxyl, hydroxyl and amide groups on the modified biomass surface were involved in the adsorption of the metal ions.

References

[1] J.G. Arnason, B.A. Fletcher, A 40 year record of Cd, Hg, Pb, and U deposition in sediments of Patroon Reservoir, Albany County, NY, USA, Environ. Pollut. 123 (2003) 383–391.
[2] V.J. Inglezakis, M.D. Loizidou, H.P. Grigoropoulou, Equilibrium and kinetic ion exchange studies of Pb^{2+}, Cr^{3+}, Fe^{3+} and Cu $^{2+}$ on natural clinoptilolite, Water Res. 36 (2002) 2784–2792.
[3] C.C. Liu, M.K. Wang, Y.S. Li, Removal of nickel from aqueous solution using wine processing waste sludge, Ind. Eng. Chem. Res. 44 (2005) 1438–1445.
[4] D.H. Shin, Y.G. Ko1, U.S. Choi1, W.N. Kim, Synthesis and characteristics of novel chelate fiber containing amine and amidine groups, Polym. Adv. Technol. 15 (2004) 446–459.
[5] S.B. Deng, Y.P. Ting, Fungal biomass with grafted poly (acrylic acid) for enhancement of Cu(II) and Cd(II) biosorption, Langmuir 21 (2005) 5940–5948.
[6] K.K. Gaard, M.A. Schembri, P. Klemm, Novel Zn^{2+}-chelating peptides selected from a fimbria-displayed random peptide library, Appl. Environ. Microbiol. 67 (2001) 5467–5473.
[7] W. Bae, C.H. Wu, J. Kostal, A. Mulchandani, W. Chen, Enhanced mercury biosorption by bacterial cells with surface-displayed MerR, Appl. Environ. Microbiol. 69 (2003) 3176–3180.
[8] P. Pokethitiyooka, N. Rangsayatorna, E.S. Upathamb, G.R. Lanza, Cadmium biosorption by cells of *Spirulina platensis* TISTR 8217 immobilized in alginate and silica gel, Environ. Int. 30 (2004) 57–63.
[9] O. Raize, Y. Argaman, S. Yannai, Mechanisms of biosorption of different heavy metals by brown marine macroalgae, Biotechnol. Bioeng. 87 (2004) 451–458.
[10] K. Roberta, H. Shigeaki, Biodegradation of high-molecular-weight polycyclic aromatic hydrocarbons by bacteria, J. Bacteriol. 182 (2000) 2059–2067.
[11] A.L. Juhasz, E. Smith, J. Smith, R. Naidu, Biosorption of organochlorine pesticides using fungal biomass, J. Ind. Microbiol. Biot. 29 (2002) 163–169.
[12] D.H. Cho, E.Y. Kim, Characterization of Pb^{2+} biosorption from aqueous solution by *Rhodotorula glutinis*, Bioproc. Biosyst. Eng. 25 (2003) 271–277.
[13] J.P. Chen, L. Yang, Chemical modification of *Sargassum* sp. for prevention of organic leaching and enhancement of uptake during metal biosorption, Ind. Eng. Chem. Res. 44 (2005) 9931–9942.
[14] M.X. Loukidou, K.A. Matis, A.I. Zouboulis, M. Kyriakidou, Removal of As(V) from wastewaters by chemically modified fungal biomass, Water Res. 37 (2003) 4544–4552.
[15] S.B. Deng, Y.P. Ting, Characterization of PEI-modified biomass and biosorption of Cu(II), Pb(II) and Ni(II), Water Res. 39 (2005) 2167–2177.
[16] R.S. Bai, T.E. Abraham, Studies on enhancement of Cr(VI) biosorption by chemically modified biomass of *Rhizopus nigricans*, Water Res. 36 (2002) 1224–1236.

[17] R. Ashkenazy, L. Gottlieb, S. Yannai, Characterization of acetone-washed yeast biomass functional groups involved in lead biosorption, Biotechnol. Bioeng. 55 (1997) 1–10.
[18] Y. Goksungur, S. Uren, U. Guvenc, Biosorption of cadmium and lead ions by ethanol treated waste baker's yeast biomass, Bioresour. Technol. 96 (2005) 103–109.
[19] J. Rinco'n, F. Gonza'lez, A. Ballester, M.L. Bla'zquez, J.A. Munoz, Biosorption of heavy metals by chemically activated alga *Fucus vesiculosus*, J. Chem. Technol. Biotechnol. 25 (2005) 2568–2575.
[20] P. Lodeiro, B. Cordero, Z. Grille, R. Herrero, M.E. Sastred, Physicochemical studies of cadmium(II) biosorption by the invasive alga in Europe, *Sargassum muticum*, Biotechnol. Bioeng. 88 (2004) 237–247.
[21] R. Jalali-Rad, H. Ghafourian, Y. Asef, S.T. Dalir, M.H. Sahafipour, B.M. Gharanjik, Biosorption of cesium by native and chemically modified biomass of marine algae: introduce the new biosorbents for biotechnology applications, J. Hazard. Mater. 116 (2004) 125–134.
[22] Y.S. Ho, G. McKay, The sorption of lead (II) ions on peat, Water Res. 33 (1999) 578–584.
[23] R. Wang, X.P. Liao, B. Shi, Adsorption behaviors of Pt (II) and Pd (II) on collagen fiber immobilized bayberry tannin, Ind. Eng. Chem. Res. 44 (2005) 4221–4226.
[24] H.G. Fuhrman, J.C. Tjell, D.M. Conchie, Adsorption of arsenic from water using activated neutralized red mud, Environ. Sci. Technol. 38 (2004) 2428–2434.
[25] Y. Goksungur, S. Uren, U. Guvenc, Biosorption of cadmium and lead ions by ethanol treated waste baker's yeast biomass, Bioresour. Technol. 96 (2005) 103–109.
[26] R. Pardo, M. Herguedas, E. Barrado, M. Vega, Biosorption of cadmium, copper, lead, and zinc by inactive biomass of *Pseudomomonas putida*, Anal. Bioanal. Chem. 376 (2003) 26–32.
[27] Y.D. Arzu, A comparative study on determination of the equilibrium, kinetic and thermodynamic parameters of biosorption of copper(II) and lead(II) ions onto pretreated *Aspergillus niger*, Biochem. Eng. J. 28 (2006) 187–195.
[28] N. Akhtar, J. Iqbal, M. Iqbal, Enhancement of lead biosorption by microalgal biomass immobilized onto loofa (Luffa cylindrica) sponge, Eng. Life Sci. 4 (2004) 171–178.
[29] K.S. Low, C.K. Lee, K.P. Lee, Sorption of copper by dye-treated oilpalm fibres, Bioresour. Technol. 44 (1993) 109–112.
[30] J.S. Chang, R. Law, C.C. Chang, Biosorption of lead copper and cadmium by biomass of *Pseudomonas aeruginosa* PU 21, Water Res. 31 (1997) 1651–1658.