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Journal of Hazardous Materials 158 (2008) 568–576
Journal of Hazardous Materials
www.elsevier.com/locate/jhazmat

Removal of Cr(VI) and Ni(II) from aqueous solution by fused yeast: Study of cations release and biosorption mechanism

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Received 4 April 2007; received in revised form 25 October 2007; accepted 31 January 2008
Available online 13 February 2008

Abstract

Biosorption of Cr(VI) and Ni(II) by a fused yeast from *Candida tropicalis* and *Candida lipolytica* under varying range of pH, initial metal concentration and reaction time was investigated. Net cation release and Cr removal reached 2.000 mmol/l and 81.37% when treating 20 mg/l Cr(VI) at pH 2 with 25 mg/l biomass for 30 min, while for Ni were 0.351 mmol/l and 64.60%, respectively. Trace metal elements such as Co, Cu, Mn, Mo, Se and Zn played active role in biosorption as important ingredients of functional enzymes. Cr(VI) was reduced to less toxic Cr(III) and chelated with extracellular secretions, and further accumulated inside the cells. For Ni biosorption, however, largely a passive uptake process influenced by ion gradient led to lower adsorption capacity and cations release. Fourier transform infrared (FTIR) spectrum analysis indicated that amide and pyridine on cells were involved in binding with Cr, but for Ni, bound-OH and nitro-compounds were the main related functional groups. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) analysis confirmed that considerable amounts of metals precipitated on cell surface when dealing with high concentration metals.

Keywords: Fused yeast; Heavy metal; Ion transport; Biosorption mechanism

1. Introduction

Wastewaters from electric plating, mining, refining, printing and dyeing have been a serious menace to our ecological security because of various toxic and non-biodegradable heavy metals [1,2]. Conventional approaches to these heavy metal-containing wastewaters mainly include precipitation, oxidation–reduction, evaporation, ionic exchange, electrochemical treatment, membrane separation technique, etc. The main drawbacks of these methods lie with relatively low-treatment efficiency, complicated operation, high cost and possible secondary pollution [3]. Compared with these techniques, biosorption has emerged as an attractive alternative to combat heavy metal contamination because of its good selectivity, high efficiency, low cost, broad applicability, and strong ability of precious metal ion recovery [4]. It is very important to understand in depth the biosorption mechanism for optimizing biosorption condition and rebuilding high quality biosorbents.

Over the past decades, scientists have put forward several theories on biosorption mechanism: in accordance with locating of removed metal ions on cell, biosorption is classified as extracellular accumulation or precipitation, cell surface uptake or precipitation, and intracellular accumulation. Based on adsorptive dynamics it is divided into active uptake and passive uptake. According to metabolic process it is sorted into metabolism-dependent and metabolism-independent. Ion metabolism process mainly includes simple diffusion, carrier-mediated transport across membrane, ionic pump transport, ion pathway, etc. [5,6].

The mechanisms involved in metal biosorption vary, depending on metal species and types of biosorbents. In the present study we investigated the adsorption behaviors of Cr(VI) and Ni(II) and concomitant cation release, based on the ion metabolism in the process of biosorption. The effects of parameters such as initial pH, heavy metal concentrations and reaction time were examined. Biosorption sites and cell surface morphology were analyzed by means of Fourier transform infrared (FTIR) spectrum, scanning electron microscopy (SEM) and atomic force microscopy (AFM) analysis, and possible mechanisms of Cr(VI) and Ni(II) adsorption were explored.

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doi:10.1016/j.jhazmat.2008.01.113

2. Materials and methods

2.1. Materials

Fused yeast was obtained from cell fusion of *Candida tropicalis* and *Candida lipolytica*.

The biomass was grown in liquid medium (glucose 20 g/l, malt extract 2 g/l, peptone 2 g/l, and $MgSO_4$ 0.05 g/l, pH 6.0) for 30 h at 30 °C under rotary shaking at 220 rpm, and then was harvested as adsorbent by centrifugation at 4000 rpm for 5 min. The absorbent was 7 g (wet weight)/l medium in strain yield and 85.71% in moisture content which was detected through drying to constant weight at 105 °C.

The stock solution of heavy metals was prepared by dissolving, respectively $K_2Cr_2O_7$ and $NiCl_2{\cdot}6H_2O$ in de-ionized water as the source of Cr(VI) and Ni(II) ions.

2.2. Cations transport test procedures

Adsorbent (25 g/l dosage) was individually added to de-ionized water and 20 mg/l Cr(VI) solution at pH range 1.0–9.0, agitated at 220 rpm and 30 °C for 4 h followed by centrifugation to separate biomass from solution. Cations (K, Na, Mg, and Ca) release amounts and residual Cr(VI) content in the supernate were measured using inductively coupled plasma-atomic emission spectrometry (ICP-AES). The most favorable pH value (pH 2) for yeast biomass to adsorb Cr, which was determined later in the experiment, was then applied in the following experiments to investigate the effects of varying interaction time (5, 10, 20. . .240 min) and feed metal concentration (5, 20, 50. . .250 mg/l) on Cr removal efficiency. Net cation release amount and Cr removal ratio were calculated from Eqs. (1) and (2), respectively.

Similarly, 25 g/l adsorbent was individually added to de-ionized water and 20 mg/l Ni(II) solution. Cation release amounts and removal ratio were characterized under different pH values. The variations of the two with time were measured at pH 5.

$$Q_t = Q_c - Q_e \tag{1}$$

where Q_t is net cation release amount (mmol/l), Q_c and Q_e are cation release amount (mmol/l) in heavy metal solution and de-ionized water, individually.

$$q = (C_0 - C_e) \times \frac{100}{C_0} \tag{2}$$

where q represents heavy metal removal ratio (%), C_0 and C_e are initial and final heavy metal concentration, individually.

2.3. Reduction capacity of extracellular secretions for Cr(VI) ions

The fermented liquid after harvesting yeast biomass was collected and Cr(VI) was added in it to terminal concentration 20 mg/l. After 4 h of agitation at 220 rpm and 30 °C, the residual concentration of Cr(VI) in the liquid was measured using a spectrophotometer and then reduction ratio of Cr(VI) was obtained according to Eq. (3):

$$q_t = (C_a - C_b) \times \frac{100}{C_a} \tag{3}$$

where q_t stands for reduction ratio (%), C_a and C_b are initial and final Cr(VI) concentration, respectively.

2.4. Trace metal elements analysis in the process of biosorption

The yeast was inoculated in liquid medium for 30 h at 220 rpm and 30 °C, and then the supernate was collected by centrifugation at 4000 rpm for 5 min. ICP-AES was used to determine ion concentrations of Co, Cu, Mn, Mo, Se and Zn in the supernate and original liquid medium in order to figure out the content of those trace metals in cells.

Similar to the cation transport experiment method described earlier, trace metal elements (Co, Cu, Mn, Mo, Se, and Zn) released in the adsorptive process was determined.

2.5. Analytical techniques for cell microstructure observation and functional group determination

Cells untreated and treated by 250 mg/l Cr were suspended in sterilized water, fixed on cover-glass. Microstructure of cells was observed using AFM.

The same cells as above were rinsed, fixed, dried in vacuum and then observed by SEM.

The functional groups present in the biomass, before and after interaction with Cr(VI) (20 mg/l and 200 mg/l) and Ni(II) (20 mg/l and 200 mg/l) were detected using a Fourier transform infrared (FTIR) spectrometer. The spectrum was recorded in the range of 4000–450 cm^{-1}.

3. Results and discussion

3.1. Effect of initial pH on cations transport and heavy metal removal

Previous studies on biosorption of heavy metals have shown that pH was one of the most important parameters affecting the adsorption process [7]. To find the optimum pH for the cation release and heavy metal removal, our experiments were performed at varying range of initial pH (1.0–9.0). As seen in Fig. 1a, in acidic de-ionized water a large number of cations (K, Na, Ca, and Mg) was released from cells and total release amounts achieved 1.807 mmol/l at pH 2. It was noticed that the cation release from cells was in the descending order of K > Ca > Na > Mg, which did not fit well with the order of cation content inside the cells (K > Mg > Na > Ca). This is probably related to the different functions cations posed in the physiological–biochemical process and microstructure. Among these macro elements, potassium is known to be abundantly present in ionic form and is also an active agent of many enzymes that are involved in substance transport and

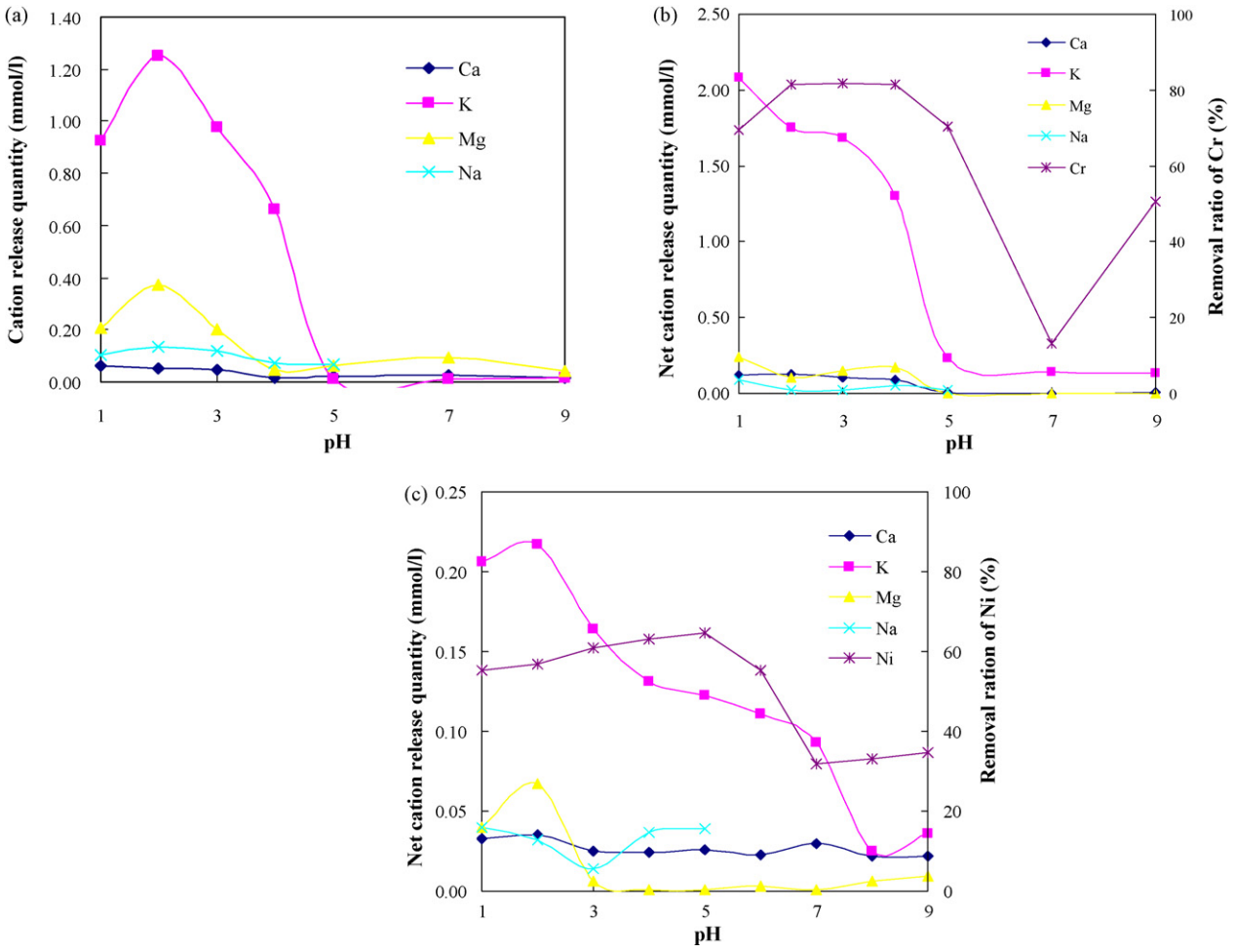

Fig. 1. Effect of pH on cation release and heavy metal removal: (a) in de-ionized water; (b) in 20 mg/l Cr(VI); (c) in 20 mg/l Ni(II).

energy metabolism. Sodium exists as a widely distributed element and plays crucial role in keeping appropriate osmotic pressure, water activity and acid–base balance inside the cell by rapid ion exchange. Magnesium is very important in catalytic process, and calcium is an essential element of cell structure and also a cofactor for a number of extracellular enzymatic reactions [8]. Fig. 1b showed that cations release increased significantly in 20 mg/l Cr-containing solution compared with that in de-ionized water. At pH 2, Cr removal efficiency achieved maximum value of 81.37% and net cations release reached 2.000 mmol/l. When pH > 5 Cr removal efficiency decreased until lowest point at pH 7 with increasing feed pH, and then backed up at pH 9 because of Cr deposition under alkaline condition. It was worth mentioning that participating of a large number of protons in Cr reduction (reduction equation: $Cr_2O_7^{2-} + 6e + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O$) [9] led to the rise of final pH. Transportation of heavy metal ions and H^+ in aqueous phase was coupled with the release of intracellular K^+, Mg^{2+}, Na^+ and Ca^{2+} in adsorptive process and Na and K pumps were formed as carriers. As main proton power source of the microbe, H^+ can react with adenosine diphosphate (ADP) to generate adenosine triphosphate (ATP) in cells for satisfying energy demand of substance metabolism and ion transport [10]. Meanwhile, many organic molecules such as saccharide, lipid and protein are secreted onto the cell surface as reducing and binding substances for Cr(VI). In order to determine the effect of these secretions on Cr(VI) removal, we applied extracellular secretion containing fermented liquid to Cr(VI) solution, and the result demonstrated that 60.55% of Cr(VI) reduction to Cr(III) was attributed to the secretions when treating 20 mg/l Cr(VI) solution. Because of lower toxicity and better bioavailability, Cr(III) is easily bonded with organic biomolecule, which reduces its charge density and enhances its lipotropism, making it more easily penetrate the cell membrane to be saved in cells [11].

For the biosorption of Ni the variation trend of cations release with pH appeared very similar to that of Cr and both maximum cation release and Ni removal occurred in acidic condition (Fig. 1c). However, the release amount and removal efficiency were only 0.351 mmol/l and 64.60%, apparently lower than that of Cr. The results indicate that in Cr-containing solution cation metabolism capacity of cell is far higher than that in Ni solution, which owes to the improved permeability of cell membrane induced by the redox reaction of Cr on cell surface. The biosorp-

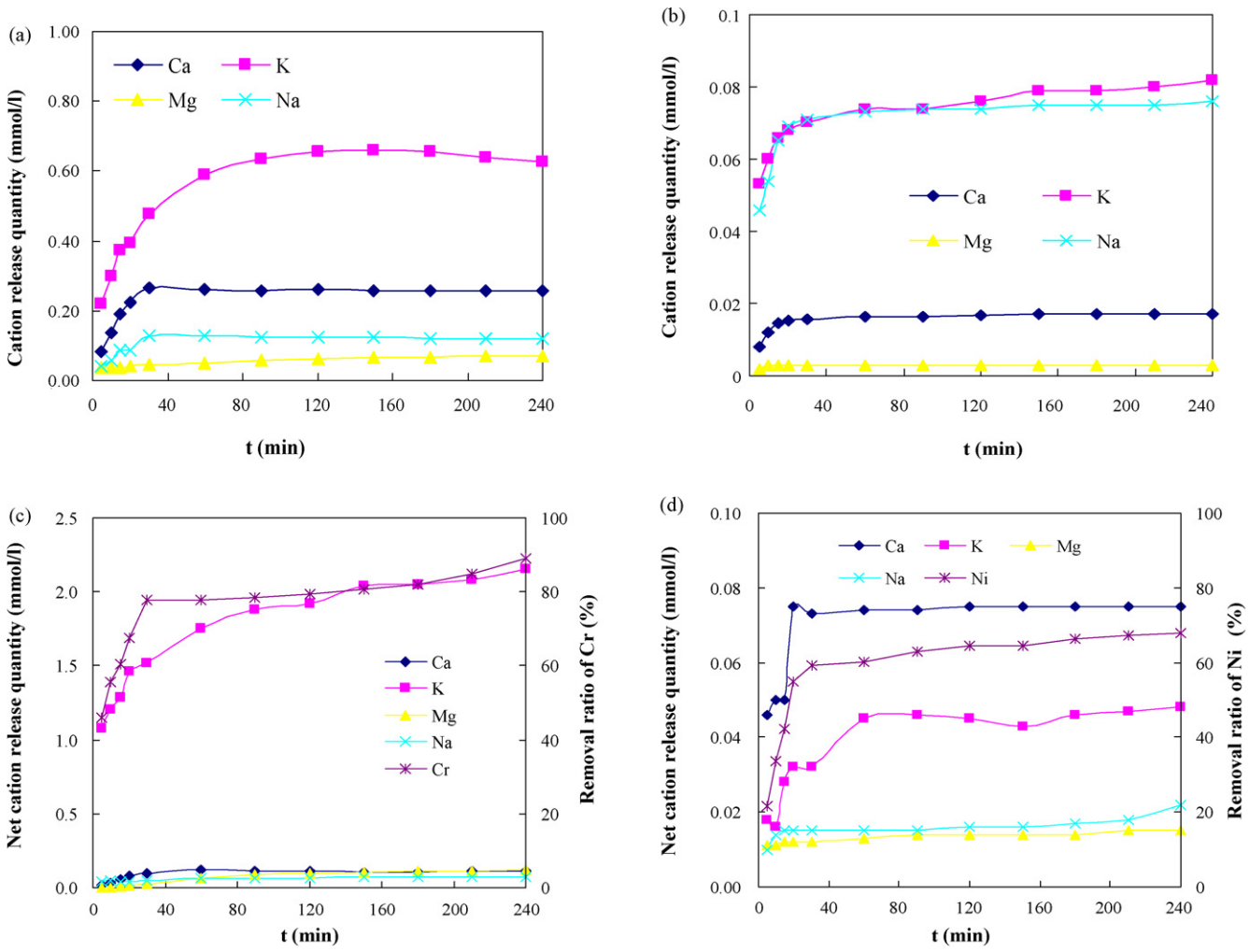

Fig. 2. Effect of reaction time on cation release and heavy metal removal: (a) in de-ionized water (pH 2); (b) in de-ionized water (pH 5); (c) in 20 mg/l Cr(VI) solution; (d) in 20 mg/l Ni(II) solution.

tion of Ni mainly depends on passive uptake and main dynamic force for ion transport is ion gradient between aqueous and solid phase. Ion gradient formation is also an energy-dependent process and the required energy is supplied by ADP and inorganic phosphate [12]. Yet the difference is that Cr can be accumulated continuously in cell by active transport and thus the biosorption capacity for Cr is obviously larger than that for Ni, exhibiting the yeast's particular biosorption affinity for Cr. From Fig. 1a–c it is evident that net cation release amounts are not equal to heavy metal biosorption amounts for both Cr and Ni, attesting to the hypothesis that heavy metal biosorption is critically linked to ion exchange, but it is not determinant and still needs some driving force and energy.

3.2. Effect of reaction time on cation transport and heavy metal removal

The net cation release in de-ionized water at pH 2 and 5 was studied as a function of time and the results are shown in Fig. 2a and b. At early stage of the interaction ionic strength and osmotic pressure in cells were stronger than those in de-ionized water and hence caused the diffusion of K^+, Na^+, Ca^{2+} and Mg^{2+} from across the cells to water until dynamic equilibrium was achieved. However, differences still existed at pH 2 and 5: high cation release amount and ion transfer equilibrium reached in 120 min when pH was at 2; whilst at pH 5 cation release decreased significantly with very short equilibrium time of 20 min. It is noteworthy that in very acid condition the existence of mass amounts of H^+ accelerated ATP formation, which guaranteed the good activity and strong ion metabolism capacity of yeast cells in sterile de-ionized water.

The net cation release and heavy metal removal were next investigated and the results are depicted in Fig. 2c and d. It was evident that heavy metal adsorption and cation release were rapidly achieved within the first 30 min interaction time. The equilibrium time for Cr biosorption process was longer than that for Ni, which proved that Cr biosorption was a slow, complex bioaccumulation process and required more substances participation, and yet Ni biosorption depended to a great extent on passive transport along electrochemical gradient, and the driving force were chemical potential, potential difference, friction force, etc. [13].

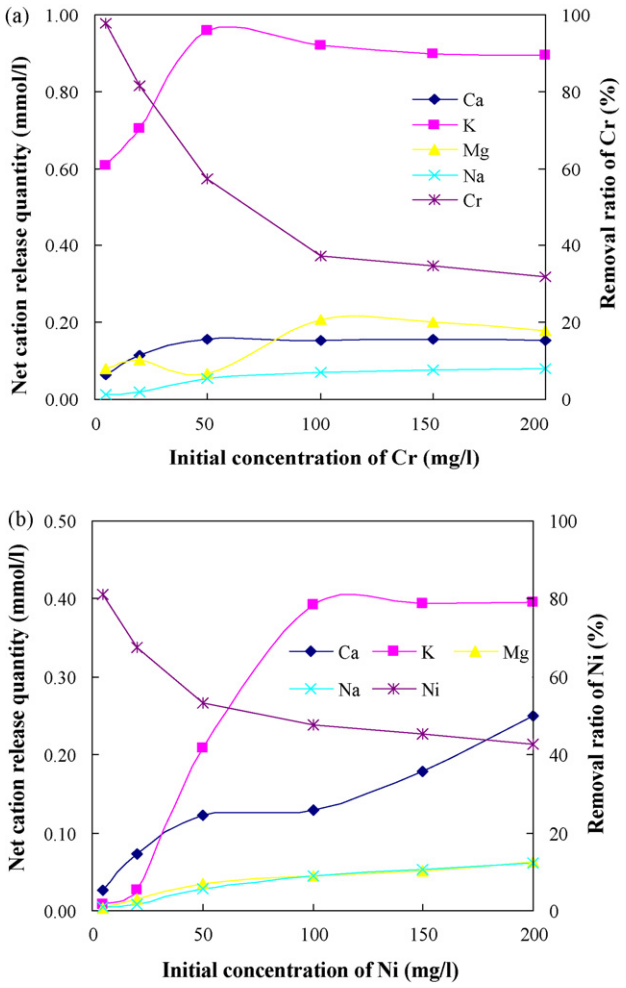

Fig. 3. Effect of initial heavy metal concentration on cation release and heavy metal removal: (a) in Cr-containing solution and (b) in Ni-containing solution.

3.3. Effect of initial heavy metal concentration on ion transport and heavy metal removal

The initial concentration provides an important driving force to overcome mass transfer resistance of metal ions between aqueous and solid phases. Hence a high initial heavy metal concentration will create high biosorption capacity and cation release. Such an effect is clearly demonstrated in Figs. 3 and 4. Metal removal efficiency dropped and adsorptive capability of cell went upward oppositely as increasing feed heavy metal (Cr and Ni) concentration. At low initial Cr concentration (<50 mg/l) cation release increased continuously with increasing Cr concentration and then reached a plateau at Cr 50 mg/l, showing the saturation of binding sites and equilibrium of ionic transportation at elevated concentration level. For the Ni adsorptive process the equilibrium point was achieved at 100 mg/l. It can be explained that the transport of Cr is an active process depending on transport carrier and substance metabolism, whereas for Ni it is a passive process with membrane balance electric potential as its driving force which is determined by ion gradient. The process followed Nernst equation, $V = (RT/ZF)\ln(c^{out}/c^{in})$ [14], where electric potential V, gas factor R, absolute temperature T, ionic charge Z, Faraday constant F, extracellular ion concentration c^{out}, intracellular ion concentration c^{in}. The greater is the concentration gradient, the faster is the ion transport. However, it is not an unrestricted process. If intracellular heavy metal concentration overloads, the instinctive detoxicating action of biomass, such as metal ion/H^+ antiport, surface chelation and ion entrapment in spaces of the cell structural network, will be started to avoid the toxicity of heavy metal [6]. The surface morphology of biomass before and after biosorption under AFM is shown in Fig. 4. As seen in Fig. 4a, native cell surface appeared very smooth and full and covered with 0.2 um thick secretions that mostly were extracellular secretions such as polysaccharide, protein, amide, etc. [15]. After Cr (250 mg/l) adsorption (Fig. 4b) these substances interconnected, with Cr as their chelating centre, forming granular organic crystals. These particle-shaped crystals were attached to cell surface and aggre-

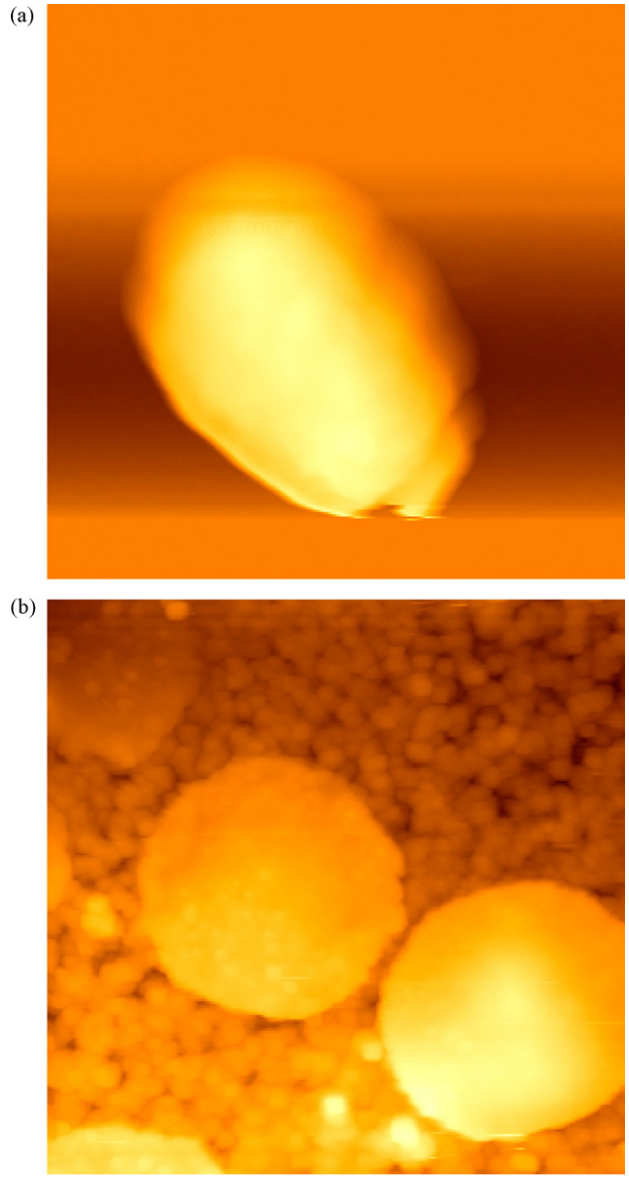

Fig. 4. AFM photographs of cell before (a) and after (b) biosorption: (a) native cell (8 um) and (b) cell saturated with Cr (8 um).

Table 1
Bio-functions of trace metals

Metal element	Functions
Se	Existence in many kinds of enzymes
Mo	Nitrogen fixation, oxidase
Mn	Photosynthesis, oxidase, structure
Co	Oxidase, hydrocarbon transfer
Ni	Hydrogenase, hydrolase
Cu	Oxidase, electron transfer
Zn	Structure, hydrolase

gated each other, which led to rough surface morphology of cells. This behavior was also supported by the experiment on Cr(VI) reduction by extracellular secretions described earlier. As the crystals congregated part of the heavy metals were removed from solution and toxicity pressure into the cells was relieved.

3.4. Analysis of trace metal element related to bio-enzyme

Besides those major metal elements, several trace elements are also required by microorganism to promote its growth and adjust intracellular physiological–biochemical reactions (Table 1) [16–18]. Table 2 illustrated that metal elements (Co, Cu, Mn, Mo, Se, and Zn) were utilized in the growth period of biomass with metal content in mature cells Zn > Se > Mo > Mn = Cu > Co. There was no cation release from cells in de-ionized water, whereas Co, Mn and Zn were released from cells in the case of treating 20 mg/l chromium, and Mn and Zn were released in the case of treating 20 mg/l nickel with Zn release reaching the maximum of 0.339 mg/l and 0.094 mg/l in both cases. This was due to the functions Zn posed in constitutive enzyme and hydrolase. The result implied that the related transport enzymes were involved in the heavy metal adsorption process. Combined with these transport enzymes, chromium and nickel ions, instead of trace metal ions, were transported and saved inside the cells by means of relevant ion channel. This also resulted in the alteration of the cell membrane structure and permeability, accelerating the intracellular accumulation of heavy metals. On the other hand, however, the inappropriate combining of these heavy metal ions with metal enzymes also led to the alteration of the conformation of the bio-macromolecular active sites, causing deactivation of the functional enzymes and inhibition of normal physiological–biochemical reactions [19]. In addition, mass release of cations from cell also damaged its microstructure and resulted in the cell retraction, cavity and fission. As seen in Fig. 5, before biosorption cells were characterized as oval shape, smooth surface and inner fullness, whereas after biosorption cavity and granular substances attached to

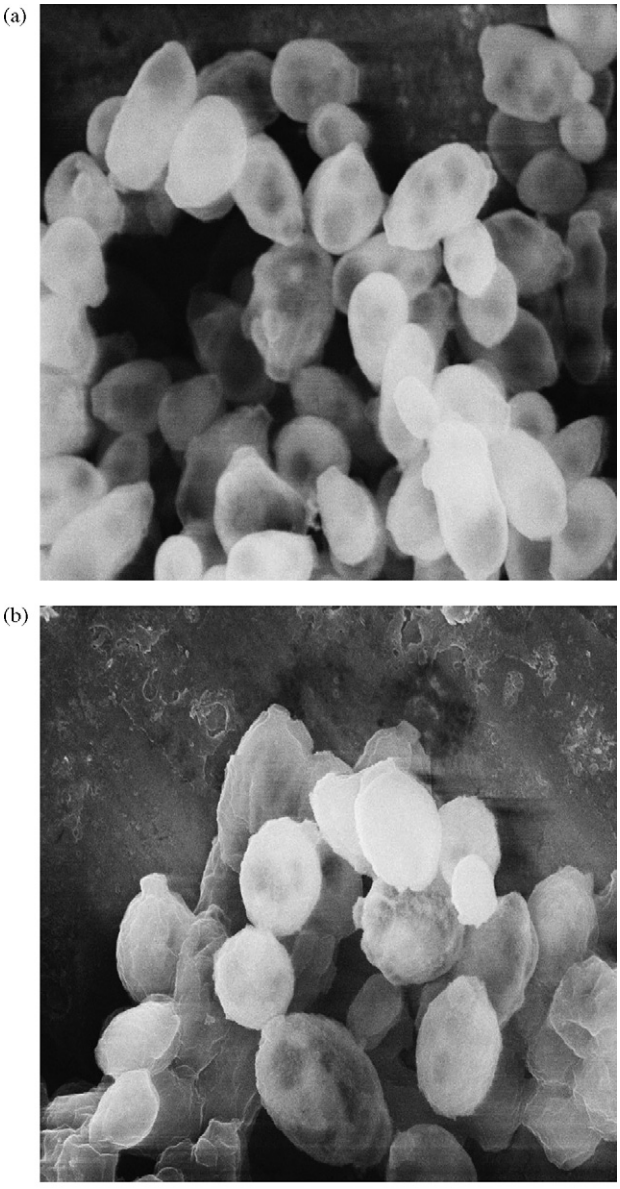

Fig. 5. SEM photographs of cell before (a) and after (b) biosorption: (a) native cell (22 um) and (b) cell saturated with Cr (22 um).

Table 2
Trace metals content and release from cells

Sample	Co	Cu	Mn	Mo	Se	Zn
Content in culture media (mg/l)	0.004	0.015	0.008	0.007	0.162	0.312
Content in zygotic fluid (mg/l)	0.003	0.012	0.005	0.004	0.075	0.029
Content in cells (mg/g)	0.000	0.000	0.000	0.034	0.034	0.040
Release in de-ionized water (pH 2) (mg/l)	0.000	0.000	0.000	0.000	0.000	0.000
Release in 20 mg/l Cr-containing solution (mg/l)	0.001	0.000	0.006	0.000	0.000	0.339
Net release for biosorption of Cr (mg/l)	0.001	0.000	0.006	0.000	0.000	0.339
Release in de-ionized water (pH 5) (mg/l)	0.000	0.000	0.000	0.000	0.000	0.000
Release in 20 mg/l Ni-containing solution (mg/l)	0.000	0.000	0.003	0.000	0.000	0.094
Net release for biosorption of Ni (mg/l)	0.000	0.000	0.003	0.000	0.000	0.094

Table 3
FTIR spectra analysis of adsorbents before and after treatment with heavy metals

Cells adsorptive capability mmol/g	Wavenumber (cm^{-1})			
	Treating Cr (20 mg/l): 2.02 mmol/g	Treating Cr (200 mg/l): 2.26 mmol/g	Treating Ni (20 mg/l): 1.53 mmol/g	Treating Ni (200 mg/l): 1.62 mmol/g
Hydroxyl groups bound to alcohol				
Before biosorption	3415	3415	3415	3415
After biosorption	3415	3415	3414	3425
Variation	0	0	−1	10
CH_2 ν_{as}(C–H)				
Before biosorption	2927	2927	2927	2927
After biosorption	2928	2925	2926	2928
Variation	1	−2	−1	1
Amide(I) ν(C═O)				
Before biosorption	1648	1648	1648	1648
After biosorption	1637	1649	1648	1646
Variation	−11	1	0	−2
Amide(II) β(N–H) + ν(C–N)				
Before biosorption	1552	1552	1552	1552
After biosorption	–	1542	1552	–
Variation	–	−10	0	–
Amide(III) ν(C–N)				
Before biosorption	1407	1407	1407	1407
After biosorption	1407	1403	1405	1409
Variation	0	−4	−2	2
Secondary amide ν(C–N) + γ(N–H)				
Before biosorption	1243	1243	1243	1243
After biosorption	1237	1243	1243	1242
Variation	−6	0	0	−1
Pyridine β(C–H)				
Before biosorption	1078	1078	1078	1078
After biosorption	1079	1078	1077	1077
Variation	1	0	−1	−1
Pyridine β(C–H)				
Before biosorption	1039	1039	1039	1039
After biosorption	1042	1032	1041	–
Variation	3	−7	2	–

rough cell surface were observed. This result was also in agreement with AFM (Fig. 4b) features that cells were enwrapped in thick layer of particle-shaped crystals. Under adverse condition rupture and distortion even occurred on some cells.

3.5. FTIR spectrum analysis of adsorptive functional groups

The FTIR spectra of biomass before and after interaction with heavy metals (Cr and Ni) are shown in Figs. 6–8. As demonstrated in Fig. 6, several intense characteristic bands related with functional groups present in proteins and polysaccharides were observed. The sharp peak at 3415 cm^{-1} was characteristic of hydroxyl groups bound to alcohol, and strong CH_2 stretching frequency gave rise to peak at 2927 cm^{-1}. The strong peaks at 1648, 1552 and 1407 cm^{-1} were assigned to amide(I), amide(II) and amide(III) groups, respectively. The bands indicating the existence of pyridine appeared at 1078 and 1039 cm^{-1}. Some bands in fingerprint region could be attributed to the phosphate and nitrate groups [20,21]. Figs. 7 and 8 and Table 3 showed

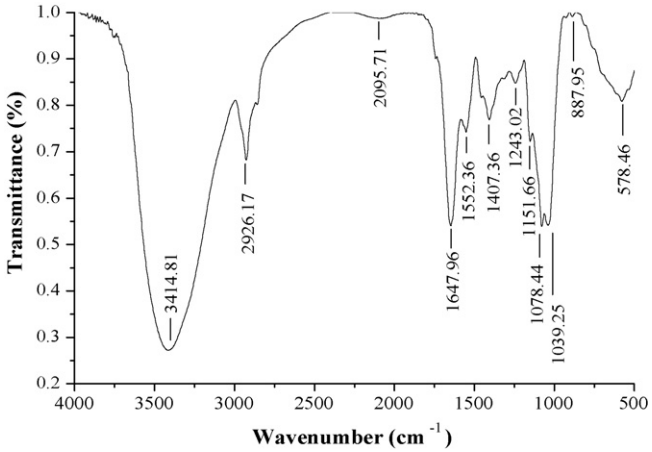

Fig. 6. FTIR spectrum of native biomass.

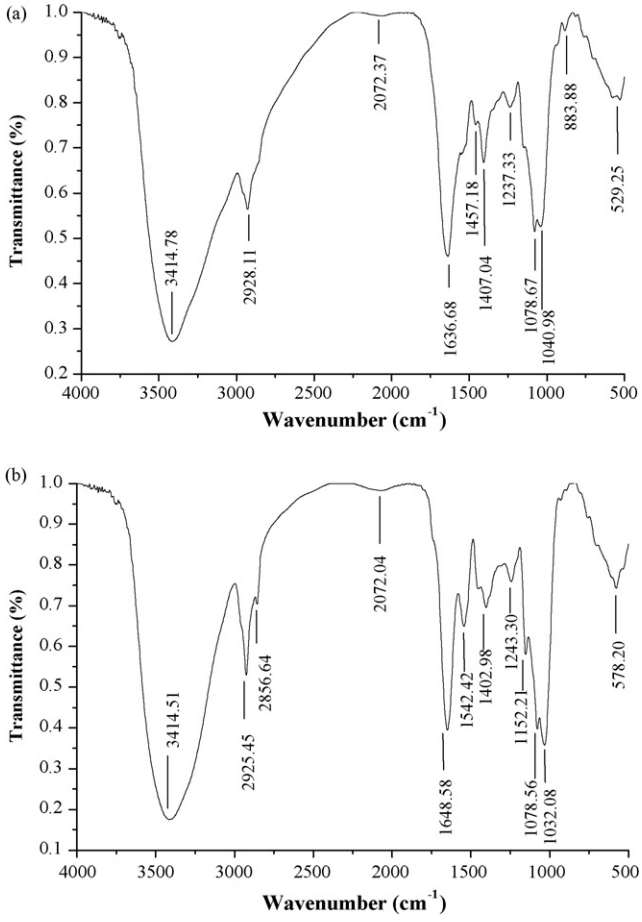

Fig. 7. FTIR spectra of adsorbents after treatment with Cr: (a) biomass after treatment with 20 mg/l Cr and (b) biomass after treatment with 200 mg/l Cr.

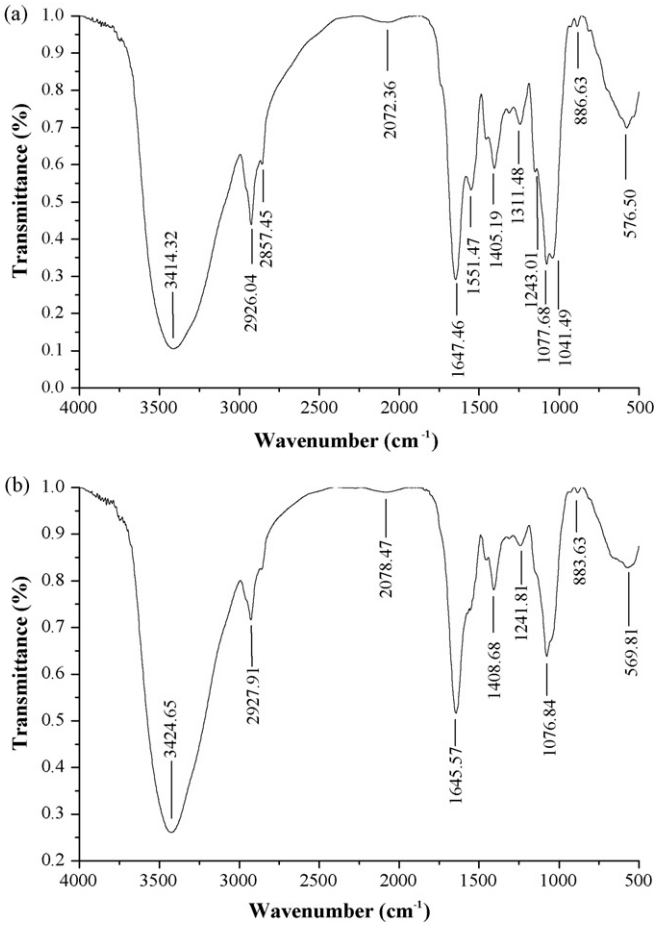

Fig. 8. FTIR spectra of adsorbents after treatment with Ni: (a) biomass after treatment with 20 mg/l Ni and (b) biomass after treatment with 200 mg/l Ni.

that after treatment with 20 mg/l Cr the red-shift of amide(I) and secondary amide band position occurred and amide(III) band nearly disappeared, while after interaction with 200 mg/l Cr adsorption bands of amide(II) and amide(III), and pyridine shifted to lower wavenumber. This suggested that amide and pyridine combine with Cr intensively [22]. But for the case of Ni different phenomena appeared. The bands of amide and other groups were almost invariant after treatment with 20 mg/l Ni, while the obvious blue-shift of the bound-OH band and the red-shift of the nitro-compound band were observed when dealing with 200 mg/l Ni. It indicates that groups binding with Cr and Ni are different. For the Cr biosorption the position and intensity of amide peak that is characteristic of protein have changed apparently, implying that protein plays important roles as carrier of Cr transport and chelating substances. In addition, the appearance of pyridine bands proves that nucleic acid is the main organics related to biosorption, which also attests to the hypothesis that the Cr biosorption is coupled with cellular metabolism and active transport. However, Ni is apt to bind with some active groups on cell surface. Besides, group changes under different concentrations validate that the uptake behaviors of cells for the metals of different concentrations are also different. High concentration metal ion poses strong toxicity pressure to the cell and induces cell to start its detoxicating paths. For the case of Cr the extracellular secretions are used to immobilize heavy metal, and the precipitation of Ni on cell surface is accomplished by the surface-active group uptake.

4. Conclusions

The following conclusions can be drawn from present study:

- Biosorption of heavy metals (Cr and Ni) in solution by the yeast was effective and accompanied with large quantity of cations (K, Ca, Na, and Mg) release. The net cation release amount and Cr removal ratio reached 2.000 mmol/l and 81.37% when treating 20 mg/l Cr(VI) at pH 2 with 25 g/l biomass, while for Ni were 0.351 mmol/l and 64.60%, respectively.
- Acidic condition favored heavy metal biosorption, especially for Cr, due to the intracellular mass formation of ATP to satisfy the required energy for normal physiological–biochemical metabolism in cells. In the first 30 min reaction time the biosorption of chromium and nickel was both near saturation and high initial heavy metal concentration caused the increase of biosorption capability and decrease of removal efficiency.
- Some trace metal elements such as Co, Cu, Mn, Mo, Se and Zn were utilized by biomass in its growth and biosorption

process. But Cr and Ni inappropriately binding with active sites of functional enzymes resulted in the variation of biomacromolecule conformation, damage of microstructure and prohibition of physiological metabolism for cells.

- The yeast showed different biosorption characteristics for the uptake of Cr and Ni. Cr(VI) could be reduced to Cr(III) by extracellular secretions and further saved inside the cells by active transport. Passive uptake was identified as the dominant mechanism of adsorbing nickel and the adsorptive process was easily affected by ion gradient.
- FTIR spectrum analysis of functional groups suggested that organic molecules such as protein and pyridine be main carriers of active transport. Bound-OH and nitro-compound on cell surface could combine with Ni intensively. High concentration of metal ions posed strong toxicity pressure to cell and induced its detoxification action. The functional groups on cell surface or in extracellular secretions were employed as bonders and carriers to reduce the toxicity.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (nos. 50278040 and 50778081).

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