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Theoretical and experimental study of Au(III)-containing wastewater treatment using magnetotactic bacteria

Song Huiping[a,b], Li Xingang[b], Cheng Huaigang[a,c,*], Cheng Fangqin[a,*]

[a]*Institute of Resources and Environment Engineering, State Environment Protection Key Laboratory of Efficient Utilization of Coal Waste Resources, Shanxi University, Taiyuan 030006, China*
Tel./Fax: +86 351 7016893; emails: huaigangcheng@yahoo.com.cn; cfangqin@sxu.edu.cn
[b]*School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China*
[c]*Taiyuan National High-tech Industrial Development Zone, Taiyuan 030006, China*

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ABSTRACT

A magnetotactic bacterial isolate was found a good biosorbent for removing Au(III) from wastewater in our preliminary studies. In this study, the process and the mechanism of biosorption were investigated from several aspects, including surface complexation, ion exchange, electrostatic attraction, and oxidation–reduction reaction. According to the water treatment experiments, these bacteria were confirmed to quickly purify the wastewater-containing Au(III). The results showed that the role of ion exchange was a secondary mechanism in the biosorption process. The molecular dynamics simulation revealed that electrostatic attraction and thermal motion had effects on the motion of Au(III), and the electrostatics of different functional groups was dissimilar. Using chemical modified and unmodified biomass as absorbents, it was found that the functional groups (including carboxylate, hydroxyl, and phosphoryl groups present on cell wall) were the main reason for the adsorption. The experimental data could be well fitted with the surface complexation model. The analyses from X-ray photoelectron spectroscopy indicated that the reduction of Au(III) to Au(I) and Au(0) on the biomass surface occurred. Comprehensive analysis of the above, a two-stage process model was built: (1) in the electric field of charged cells, metal ions were attracted. This process was the physical adsorption of multimolecular layer; (2) the metal ions arrived the cell surface were chelated or complexed with functional groups, accompanied by ion exchange and reduction reactions.

Keywords: Magnetotactic bacteria; Gold; Biosorption; Molecular dynamics simulation; Surface complexation model; Redox

1. Introduction

Nowadays, gold is in extensive use for electric and electronic devices due to its high chemical stability as well as high conductivity. Growing demand for gold and decreasing natural resources make it crucial to recover the gold from the inevitably increasing waste products for recycling and reuse purposes [1,2]. In recent years, biosorption has been reported to be one of the effective and economical processes for the removal and recovery of metals [3]. The biggest prob-

*Corresponding author.

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lem for its application is that free microbial biomass cannot be used directly in the standard biosorption process due to its small particle size and low strength and density [4]. Immobilization of the biomass within a suitable matrix can overcome this problem by offering ideal size, mechanical strength, rigidity and porous characteristics to the biological materials [5]. However, biosorption efficiency of the immobilized cells might be significantly reduced due to the mass transfer problems in the matrix [6,7].

Magnetotactic bacteria (MTB), which were first isolated in 1975 [8], have the ability to "manufacture" magnetic nanoparticles by consuming iron salts. Previous research has shown that the MTB were capable of removing Au(III) from the contaminated water with a high biosorption capacity [9,10], and Au (III)-loaded MTB biomass could be successfully removed from wastewater by harnessing their magnetic properties in a process termed orientation magnetic separation [11,12].

The mechanism by which a sorbent binds metal ions has recently received increased attention as the advantages of understanding such mechanisms become more apparent. Broadly, sorption can be divided into chemical and physical sorption mechanisms. Chemical mechanisms include chelation, microprecipitation, and microreduction, while physical mechanisms generally involve electrostatic forces or ion exchange. The mechanism of metal biosorption is a complicated process. And the process of biosorption is generally based on physicochemical interactions between metal ions and the functional groups present on the cell surface, such as electrostatic interactions, ion exchange, and metal ion chelation or complexation [13,14]. Functional groups most commonly implicated in such interactions include carboxylate, hydroxyl, amine, and phosphoryl groups present within cell wall components such as polysaccharides, lipids, and proteins [15,16].

Some of the potential mechanisms of gold and other precious metal uptake processes discussed by different workers have been reported here. Chitosan used for precious metal sorption is because that the amino sites of chitosan are easily protonated in acid media, accentuating the electrostatic forces often implicated in the initial stages of sorption [17]. Tannins are also potent precious metal sorbents but are more commonly used for their redox capabilities than for functional group composition [18,19]. Au(III) bioreduction with biomass have been reported [20–22]. Gold was formed on the surface of biomass by reduction of Au(III) to Au(0). Some functional groups present in the algal polysaccharides were found to be involved in the gold bioreduction. In this study, the mechanisms, including ion exchange, surface complexation, redox, and the electrostatic attraction, of gold biosorption by MTB were discussed.

2. Materials and methods

2.1. Determination of ions concentration

In order to explore the adsorption efficiency of MTB for Au(III) ($HAuCl_4{\cdot}4H_2O$) and the proportion of ion-exchange reaction in the adsorption process, biosorption experiments were investigated. The MTB stain used in this study was same as the previous research [11]. The residual Au(III), K(I), Na(I), Mg(II), and Ca(II) concentration in solution were determined by atomic absorption spectroscopy (TAS-990, Pgeneral, China) and their detection wavelengths were 242.8, 766.5, 589.0, 202.6, and 422.7 nm, respectively.

2.2. Potentiometric titration

The bacterial surface groups were determined by acid-base titration measurements [23,24]. About 10 mL biomass (2.5 g/L in bacteria concentration) and 90 mL deionized water were added into a conical beaker, adjusting pH at 2 with drops of HNO_3 solutions. After the continuous stirring with a magnetic stirrer at the temperature of 25°C for 1 h, the titration using a standard solution of NaOH (0.1 mol/L) was performed in the N_2 atmosphere. During the titration process, a digital pH meter (PHS-3C, China) was used to monitor and record the solutions' pH value.

2.3. X-ray photoelectron spectroscopy analysis

X-ray photoelectron spectroscopy (XPS) (PHI-1600, PE, US) was performed to examine the synthesized gold nanoparticles. The powders of dried samples were spread on adhesive tape, while it is pressed into a sheet for XPS analyses.

3. Results and discussion

3.1. Ion-exchange interaction

Small amounts of K(I), Ca(II), Na(I), Mg(II), and other ions existed in the bacterial cells. These ions were binding with the intracellular organic anion-based group by the form of the covalent bonds. When they encountered heavy metal ions, some of the heavy metal ions would produce stable complexation reaction with the organic-based group, and K(I), Ca (II), Na(I), Mg(II), etc. will be disconnected and

Table 1
Change of concentration of metal ions before and after biosorption (mg/L, $C_{0,Au} = 80$ mg/L)

Au(III)	−79.6
K(I)	+0.7
Na(I)	+6.4
Mg(II)	+0.9
Ca(II)	+0.4

Note: + represents increase, and − represents decrease.

released into the solution. The ratio of displacement reaction by Au(III) in the adsorption process was studied, and the results were listed in Table 1. There were more or less increases in the concentration of K (I), Ca(II), Na(I), Mg(II), but the increase gross was quite different from the decrease in Au(III) concentration. This implied that ion-exchange interaction was not the main mechanism of biosorption of Au(III) on MTB.

3.2. Surface complexation

3.2.1. The species and concentrations of functional groups on the surface of MTB biomass

To better understand the surface complexation in the process of biosorption of gold ions on MTB, the following will use the surface complexation theory model to analyze the process. The fitting analysis of acid-base titration curve using the surface complexation model was done to obtain the dissociation constant K_a of group. Generally, each K_a corresponded to a specific group, and thus, the types of functional groups on MTB could be determined on the basis of dissociation constants in literatures.

The K_a values were got by potentiometric titration that was originally developed by Fourest and Volesky [23] metal biosorption. If n acidic sites on the biomass were thought to be involved in protons uptake, the following chemical models could be defined:

$$B_iH = B_i^- + H^+, K_{ai} = \frac{[B_i^-][H^+]}{B_iH} \quad (1)$$

where $[B_i]_{Tot}$ is the total concentrations of the weakly acidic site i in the form of dissociated (B_i^-) and associated (B_iH); K_{ai} is the dissociation constant.

The acidic sites mass balance and electric charge balance in solution could be expressed in Eqs. (2) and (3), respectively.

$$[B_i]_{Tot} = [B_iH] + [B_i^-] \quad (2)$$

$$[Na^+] + [H^+] = \sum_{i=1}^{n}[B_i^-] + [OH^-] \quad (3)$$

Combining Eqs. (1)–(3), Eq. (4) could be determined as follows: Where K_w is the ion product of water ($K_w = 1.0 \times 10^{-14}$ at 25°C),

$$[Na^+] = \sum_{i=1}^{n}\frac{K_{ai} \times [B_i]_{Tot}}{[H^+] + K_{ai}} + \frac{K_w}{[H^+]} - [H^+] \quad (4)$$

Since NaOH added in the solution was the only source of Na^+ ion in solution, assuming the change of Na^+ and $[Bi]_{Tot}$ followed the volume change, Eqs. (5) and (6) could be deduced:

$$[Na^+] = \frac{V_{NaOH} \times C_{0,NaOH}}{V_0 + V_{NaOH}} \quad (5)$$

$$[B_i]_{Tot} = \frac{N_i \times C_{0,B} \times V_0}{V_0 + V_{NaOH}} \quad (6)$$

where V_{NaOH}, V_0, $C_{0,NaOH}$, C_{0B}, and N_i represent the added volume of NaOH, initial suspension volume, initial concentration of NaOH, initial biomass concentration, and total concentration of acidic site i on biomass, respectively.

Combining Eqs. (4)–(6), parameters K_{ai} (dissociation constant) and N_i (total concentration of acidic site i on biomass) in the model were estimated by nonlinear regression method.

According to the fitting of acid-base titration curve, a three acidic sites model ($n = 3$) representing three main functional groups on biomass was chosen.

The three pK_{ai}, logarithm form of the dissociation constant K_{ai}, were determined as 3.5, 6.2, and 9.6. Based on the literatures, these pK_a values should represent −COOH, $-PO_3H$, and −OH groups at the values of 1.7–4.7 [25,26], 6.1–6.8 [24,27], and 9.5–13 [28], respectively. The titration data were also used to calculate the concentrations of these groups [29], 0.3 mmol/g for −COOH, 0.5 mmol/g for $-PO_3H$, and 0.6 mmol/g for −OH, respectively. The result that −COOH, $-PO_3H$, and −OH were the main groups on MTB was in agreement with the literatures [30,31].

3.2.2. Surface complexation model

On the basis of biosorption mechanism mentioned previousl, the three-site surface complexation model was proposed. The binding reactions for Au(III) in the present study could be defined as follows:

$$B_i^- + Au(III) \Leftrightarrow B_iAu(II) \quad (7)$$

$$K_i = \frac{[B_i Au(II)]}{[B_i^-][Au(III)]} \quad (8)$$

where K_i represent the binding constant between functional group i and Au(III). Mass balance of the binding site i was:

$$[B_i]_{Tot} = [B_i Au(II)] + [B_i^-] \quad (9)$$

Combining Eqs. (8)–(9), total Au(III) uptake by all functional groups, i.e. the total of $[B_i Au(II)]$, could be calculated according to:

$$q = \sum_{i=1}^{3} q_i = \sum_{i=1}^{3} [B_i Au(II)] = \sum_{i=1}^{3} \frac{K_i \times [Au(III)] \times [B_i]_{Tot}}{1 + K_i \times [Au(III)]} \quad (10)$$

Markai [32] had mentioned that not all functional groups on the biomass surface participated in the complexation reaction. Thus, a parameter of a_i, the ratio of functional group i participating in the complexation reaction, was introduced to Eq. (10). And Eq. (10) could be deduced:

$$q = \sum_{i=1}^{3} \frac{K_i \times [Au(III)] \times a_i \times [B_i]_{Tot}}{1 + K_i \times [Au(III)]} \quad (11)$$

Experimental data of the relationship between biosorption capacity and the equilibrium pH were used to fit Eq. (11), and the predicted curve based on Eq. (11) were also illustrated in Fig. 1. The parameters K_i and a_i were obtained by nonlinear regression method and listed in Table 2. The binding constant of phosphonate group was significantly higher than that of the other functional groups, indicating that phosphonate group had a stronger affinity to Au(III), and was the main complex ligand. As shown in Fig. 1, the predicted curve could well describe the relationship between equilibrium pH and sorption capacity. This close fit confirmed that surface complexation was one of the main mechanisms involved in biosorption of Au(III) on biomass. The values of a_i were less than 1, implying that only part of the functional groups took part in the complexation reaction. The rest of functional groups on biomass surface would make contributions to other adsorption mechanisms such as redox and ion exchange.

3.3. Redox

The XRD analyses confirmed that the reduction of Au(III) to Au(0) by the reductants on the MTB biomass occurred, and the deposition of nano-crystal Au(0) particles, ranging from 24.7 to 31.4 nm, could be estimated on the biomass surface [11]. XPS was further performed to examine the formation of gold nanoparticles. The Au characteristic peak can be seen from the XPS patterns in Fig. 2(A), with binding energy about 100 eV. The XPS analysis of Au 4f, which gave a spectrum (Fig. 2(B)) with peaks of binding energy of 88.42 and 84.67 eV corresponding to Au^+(4f 5/2) and Au^0(4f 7/2), respectively. The results revealed that the reduction process in gold formation was achieved through two stages and Au(I) was an intermediate stage in the reduction from Au(III) to Au (0). In addition, $HAuCl_4{\cdot}4H_2O$ was used as Au(III) donor in adsorption process. Therefore, it was assumed that the reduction process of gold formation could be described as follows:

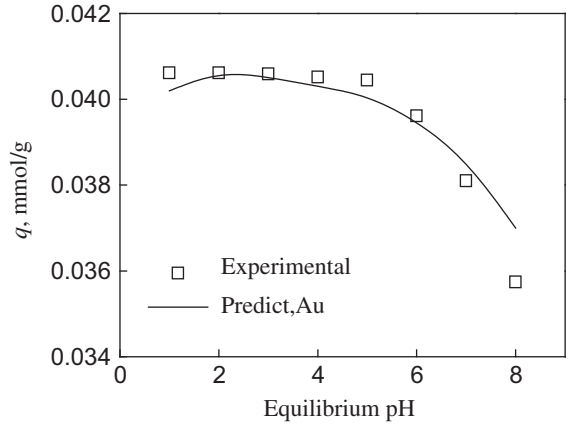

Fig. 1. Biosorption of Au(III) on biomass as a function of equilibrium pH.

$$HAuCl_4 \cdot 4H_2O \rightarrow AuCl \rightarrow Au^0$$

Greene [33] and Hosea [34] had also mentioned that two steps were involved in Au(III) removal by bacterial biomass, namely the redox reaction of Au(III) to Au(I) was the first step and then followed by Au(I) to Au(0) by the reducing sugars on the algal biomass. Similarly, Cai et al. [9] had reported that the Au(III) was converted to Au(I) and Au(0) by the reductants on the MTB biomass.

3.4. Electrostatic interaction

Molecular dynamics simulation was used to analyze the intermolecular attraction between ions and MTB surface groups. Based on the acid-base titration experiments, a bacterium cell model was established

Table 2
Regression results of Au(III) binding constants in pH edge experiment ($R^2 = 0.9066$)

Parameter	R–COO^-		R–PO_4^-		R–O^-	
	K_1	a_1	K_2	a_2	K_3	a_3
Simulation value	2.031×10^{-5}	0.712	3.499×10^{-5}	0.852	2.801×10^{-5}	0.612

Note: K_i represents the binding constant between functional group i and Au(III). a_i is the ratio of functional group i participating in the complexation reaction. R^2 is the regression coefficient of the estimated parameters.

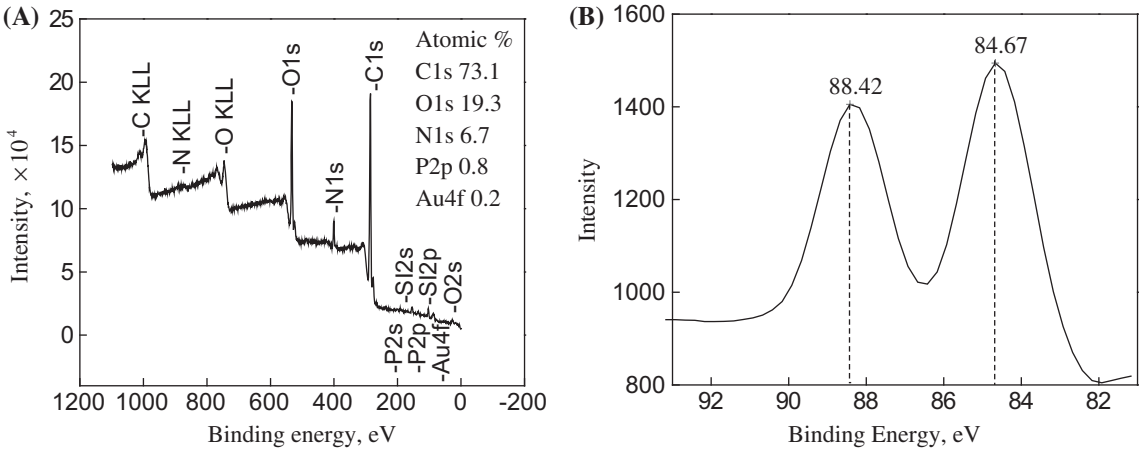

Fig. 2. (A) XPS spectrum of a sample after biosorption. (B) XPS spectrum of Au 4f after biosorption. The vertical lines show the binding energy values for Au.

as a carbochain grafting $-PO_3H$, $-OH$, and –COOH [29]. The contributions of the functional groups to the adsorption of Au(III) were simulated and calculated from the aspects of electrostatic interaction using structured programming method. The simulation spaces of bacterium cell model and Au(III) ions at initial and after adsorption simulation were illustrated in Fig. 3 [12]. The simulation results showed that Au (III) ions after adsorption was moving near the functional groups, suggesting that electrostatic interaction of the functional groups played an important role in the adsorption process.

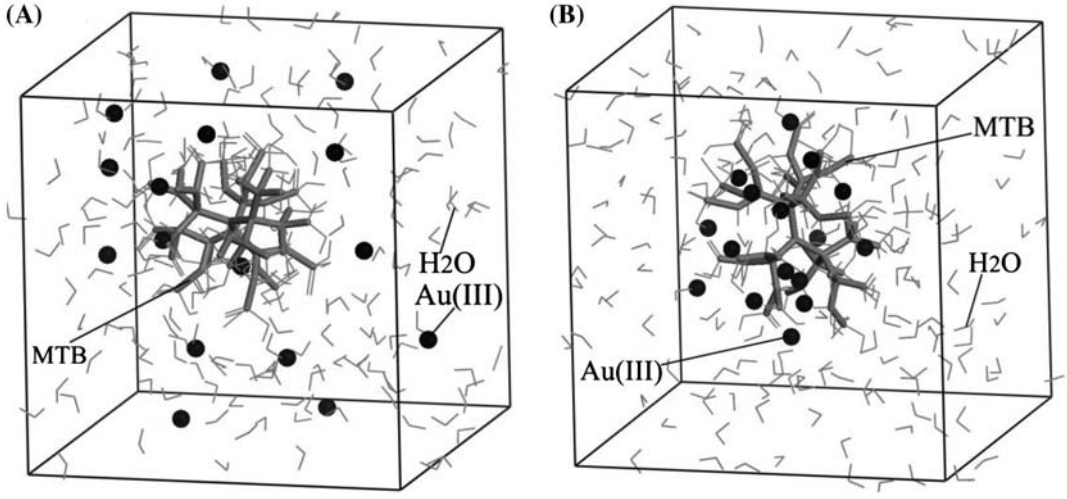

Fig. 3. The states of simulation space before adsorption(A) and after adsorption (B).

3.5. Two-stage adsorption process model

It could be predicted that the biosorption of Au (III) on MTB took place in two stages. In the first stage, metal ions and biomass were attracted in the electric field of charged cells. This process was the physical adsorption of multimolecular layer. In the second stage, chemical reactions took place at the cell surface between Au(III) ions and the functional groups on the biomass cell: (1) the functional groups of carboxylate, hydroxyl, and phosphoryl on the surface of cell wall chelated or complexed with Au(III) ions; (2) small amount of alkali metals binding with another functional groups would take place the ion exchange reaction with gold ions in solution, but this was not the main mechanism; (3) some functional groups such as hydroxyl groups on the surface of cell were involved in the bioreduction of Au(III) to Au(0).

4. Conclusion

This study showed that there was a complicated process of biosorption Au(III) with MTB. the biosorption process was investigated from several aspects, including surface complexation, ion exchange, electrostatic attraction, and oxidation/reduction reaction. The results showed that the role of ion exchange was a secondary mechanism in the biosorption process. Chemical modified experiments data could be well fitted with the simulation results of the surface complexation model, and reflected that carboxylate, hydroxyl, and phosphoryl groups within cell wall components were the main reasons for the adsorption. The analyses from XPS indicated that the reduction of Au(III) to Au(I) and Au(0) by the reductants on the biomass occurred. The molecular dynamics simulation revealed that electrostatic attraction had effects on the motion of Au(III). In summary, biosorption process was a complicated process and had two main steps: (1) metal ions were attracted in the electric field of charged cells; (2) the metal ions arrived on the cell surface were chelated or complexed with functional groups, accompanied by ion exchange and reduction reactions.

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References

[1] S. Syed, Recovery of gold from secondary sources: A review, Hydrometallurgy 115–116 (2012) 30–51.
[2] S. Syed, A green technology for recovery of gold from non-metallic secondary sources, Hydrometallurgy 82 (2006) 48–53.
[3] K. Vijayaraghavan, Y.-S. Yun, Bacterial biosorbents and biosorption, Biotechnol. Adv. 26 (2008) 266–291.
[4] M. Tsezos, Adsorption by microbial biomass as a process for removal of ions from process or waste solutions, In: H. Eccles, S. Hunt (Eds), Immobilization of Ions by Bio-Sorption, Ellis Harwood, Chichester, pp. 201–218, 1986.
[5] N. Akhtar, J. Iqbal, M. Iqbal, Removal and recovery of nickel (II) from aqueous solution by loofa sponge-immobilized biomass of *Chlorella sorokiniana*: Characterization studies, J. Hazard. Mater. 108 (2004) 85–94.
[6] A. Lopez, N. Lazaro, S. Morales, A.M. Marques, Nickel biosorption by free and immobilized cells of *Pseudomonas fluorescens* 4F39: A comparative study, Water Air Soil Pollut. 135 (2002) 157–172.
[7] R.S. Bai, T.E. Abraham, Studies on chromium(VI) adsorption–desorption using immobilized fungal biomass, Bioresour. Technol. 87 (2003) 17–26.
[8] R. Blakemore, Magnetotactic bacteria, Science 190 (1975) 377–379.
[9] F. Cai, J. Li, J.S. Sun, Y.L. Ji, Biosynthesis of gold nanoparticles by biosorption using *Magnetospirillum gryphiswaldense* MSR-1, Chem. Eng. J. 175 (2011) 70–75.
[10] H.P. Song, X.G. Li, J.S. Sun, X.H. Yin, Y.H. Wang, Z.H. Wu, Biosorption equilibrium and kinetics of Au(III) and Cu(II) on magnetotactic bacteria, Chin. J. Chem. Eng. 15 (2007) 847–854.
[11] H.P. Song, X.G. Li, J.S. Sun, S.M. Xu, X. Han, Application of a magnetotactic bacterium, *Stenotrophomonas* sp. to the removal of Au(III) from contaminated wastewater with a magnetic separator, Chemosphere 72 (2008) 616–621.
[12] H.P. Song, Selective biosorption behavior of precious metal ions on magnetotactic bacteria and gold recovery from gold (III) contained solution, PhD Thesis, Tianjin University, 2007. (In Chinese).
[13] C. Mack, B. Wilhelmi, J.R. Duncan, J.E. Burgess, Biosorption of precious metals, Biotechnol. Adv. 25 (2007) 264–271.
[14] A. Özer, D. Özer, H. Ekíz, The equilibrium and kinetic modeling of the biosorption of copper(II) ions on *Cladophora crispata*, Adsorption 10 (2004) 317–326.
[15] D. Nilanjana, Recovery of precious metals through biosorption: A review, Hydrometallurgy 103 (2010) 180–189.
[16] Y.N. Mata, E. Torres, M.L. Blázquez, A. Ballester, F. González, J.A. Munoz, Gold(III) biosorption and bioreduction with the brown alga *Fucus vesiculosus*, J. Hazard. Mater. 166 (2009) 612–618.
[17] E. Guibal, O.N.S. Von, T. Vincent, J.M. Tobin, Sulfur derivatives of chitosan for palladium sorption, React. Funct. Polym. 50 (2002) 149–163.
[18] T. Ogata, Y. Nakano, Mechanisms of gold recovery from aqueous solutions using a novel tannin gel adsorbent synthesized from natural condensed tannin, Water Res. 39 (2005) 4281–4286.
[19] H.W. Ma, X.P. Liao, X. Liu, B. Shi, Recovery of platinum(IV) and palladium(II) by bayberry tannin immobilized collagen fibre membrane from water solution, J. Membr. Sci. 278 (2006) 373–380.
[20] J.L. Gardea-Torresdey, K.J. Tiemann, J.G. Parsonsa, G.I. Gameza, M. Herrera, M. Jose-Yacaman, XAS investigations into the mechanism(s) of Au (III) binding and reduction by alfalfa biomass, Microchem. J. 71 (2002) 193–204.
[21] M.E. Romero-González, C.J. Williams, P.H.E. Gardiner, Pectroscopic studies of the biosorption of gold(III) by dealginated seaweed waste, Environ. Sci. Technol., 37 (2003) 4163–4169.
[22] Z. Lin, J. Wu, R. Xue, Y. Yang, Spectroscopic characterization of Au^{3+} biosorption by waste biomass of *Saccharomyces cerevisiae*, Spectrochim. Acta, Part A 61 (2005) 761–765.
[23] E. Fourest, B. Volesky, Contribution of sulfonate groups and alginate to of *Sargssum fluitans*, Environ. Sci. Technol. 30 (1996) 277–282.

[24] X. Han, S.W. Yuk, F.Y.T. Nora, Surface complexation mechanism and modeling in Cr(III) biosortion by a microalgal isolate, *Chlorella miniata*, J. Colloid. Interface Sci. 303 (2006) 365–371.
[25] B. Volesky, Sorption and Biosorption, BV-Sorbex, St. Lambert, 2003, 41.
[26] N. Yee, L.G. Benning, V.R. Phoenix, Characterization of infrared spectroscopic investigation, Environ. Sci. Technol. 38 (2004) 775–782.
[27] T.J. Beveridge, R.G.E. Murray, Sites of metal deposition in the cell wall of *Bacillus subtilis*, J. Bacteriol. 141 (1980) 876–887.
[28] J.Y. Wang, S.G. Zhu, C.F. Xu, Biological Chemistry, third ed., Higher Education Press, Beijing, 2002, 131.
[29] H.P. Song, H.G. Cheng, F.Q. Cheng, Simulation on biosorption of Ni^{2+} by magnetotactic microorganism in aqueous solution, Ion Exch. Adsorpt. 27 (2011) 392–399, (In Chinese).
[30] H. Seki, A. Suzuki, S.I. Mitsueda, Biosorption of heavy metal ions on *Rhodobacter sphaeroides* and *Alcaligenes eutrphus h6*, J. Colloid. Interface Sci., 197 (1994) 185–190.
[31] Y.S. Yun, B. Volesky, Modeling of lithium interference in cadmium biosorption, Environ. Sci. Technol. 37 (2003) 3601–3608.
[32] S. Markai, Y. Andres, G. Montavon, Study of the interaction between Europium(III) and *Bacillus subtilis*: fixation sites biosorption modeling and reversibility, J. Colloid. Interface Sci. 262 (2003) 351–361.
[33] B. Greene, M. Hosea, R. McPherson, M. Henzl, M.D. Alexander, D.W. Darnall, Interaction of gold(I) and gold(III) complexes with algal biomass, Environ. Sci. Technol. 20 (1986) 627–632.
[34] M. Hosea, B. Greene, R. McPherson, Accumulation of elemental gold on the alga *Chlorella vulgaris*, Inorg. Chim. Acta 123 (1986) 161–165.