

Biosorption Equilibrium and Kinetics of Au(III) and Cu(II) on Magnetotactic Bacteria*

SONG Huiping(宋慧平)^a, LI Xingang(李鑫钢)^a, SUN Jinsheng(孙津生)^{a,**}, YIN Xiaohong(尹晓红)^b, WANG Yanhong(王艳红)^a and WU Zhenhua(武振华)^a

^a National Engineering Research Center of Distillation Technology, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China

^b School of Chemistry and Chemical Engineering, Tianjin University of Technology, Tianjin 300191, China

Abstract Magnetotactic bacteria (MTB) as biosorbents for the adsorption of Au(III) and Cu(II) ions from aqueous solution have been investigated. The optimum adsorption conditions for both metal ions were the initial pH scope of 1—5.5 for Au(III) and 2.0—4.5 for Cu(II), room temperature, biomass concentration of 10.0g·L⁻¹ and sorption duration more than 10 min. When the initial metal concentration were within 500mg·L⁻¹, the maximum biosorption capacity of 1.0g of MTB (dry mass basis) for Au(III) and Cu(II) were calculated as 505.2mg of Au(III) and 493.1mg of Cu(II) by Langmuir model in single system, respectively. The isotherm equilibrium of Au(III) and Cu(II) ions in the Au-Cu binary system reflected a unique phenomenon that the adsorption of Au(III) was reinforced and that of Cu(II) prohibited, compared respectively with their performances in the single metal system. When the concentration of Au(III) and Cu(II) were below 80mg·L⁻¹, the wastewater after MTB treating was below 1.0mg·L⁻¹, which is in conformity with Environmental Performance Standards (EPS) of Canada. Besides, all the kinetic data were fitted well to the pseudo second-order kinetic model with a high correlation coefficient ($R^2 > 0.999$).

Keywords magnetotactic bacteria, selective adsorption, adsorption equilibrium, adsorption kinetics, Au(III)

1 INTRODUCTION

Toxicity reduction and the recovery of valuable metals are two important motives for the removal of metals from aqueous solution. Many conventional methods such as chemical precipitation, membrane separation, ion exchange and evaporation have been employed to remove metals in industrial wastewater, but they have several disadvantages, including high energy requirements, generation of mixed wastes and ineffective at metal concentrations below 100mg·L⁻¹ [1—3]. In the last two decades, more interest has been focused on using different biosorbents to remove metal ions. Many algae, yeasts, bacteria and fungi are capable of concentrating metal species from dilute aqueous solutions and accumulating them within their cell structures[4]. However, the main obstacle of biosorption was how to remove the metal ions-loaded microorganisms from aqueous solution[5]. Generally, Millipore filtration and evaporation method were used, but the high cost of membrane and high energy consumption made them limited in application.

Magnetotactic bacteria (MTB), discovered by Blakemore[6], might be one of the most promising options for solving this problem, because these bacteria can move along the local magnetic field lines because of the magnetosomes (MS) within their intracellular and can be easily separated from the solutions. Most previous studies about MTB focused specifically on two aspects: the isolation and cultivation condition of MTB and MS[7—9] and the magnetic movement of MTB in different separators[10,11]. Some publications are available with respect to the biosorption of single metal ions on MTB[12—14], whereas only few

are available on the selective or competitive biosorption of multi-metal ions, which was of great guidance for wastewater treatment technology.

Au(III) ion often coexists with other metals such as Cu(II) ion in actual wastewaters[15]. In this study, competitive biosorption of Au(III) and Cu(II) ions by MTB from binary solute system was studied. The biosorption selectivity of MTB for Au(III) ions was investigated using Freundlich isotherms model and the pseudo second-order kinetic model. And, the mechanism for biosorption preference was analyzed in respect of the physical-chemical properties of the metal ions.

2 MATERIALS AND METHODS

2.1 Preparation of the microorganisms

Wastewater and sediment samples were taken from the lagoon of a wastewater treating plant, Jizhuangzi, Tianjin. One-thousand-milliliter bottles were filled to approximately two-thirds of their volume with a 2 : 1 ratio of sediment and culture medium (pH 6.7—6.8)[16]. The loosely covered bottles were left undisturbed in dim light at room temperature (22°C). After one month's incubation, microorganisms in the medium were observed using a phase-contrast microscope (Nikon Eclipse TS100). To provide a magnetic field for microscope slide preparations, a rectangular samarium-cobalt magnet of size 200mm×15mm×15mm was placed on the stage of a microscope. When the trajectories of bacteria became U-shaped through switching the direction of the magnetic field by hand, microorganisms were harvested using the "special-made

Received 2007-01-08, accepted 2007-07-23.

* Supported by the National Natural Science Foundation of China (No.20206024) and the Natural Science Foundation of Tianjin (No.07JCYBJC06800).

** To whom correspondence should be addressed. E-mail: jssun2006@vip.163.com

collecting apparatus" as described by Matsunaga *et al.*[17], and was washed twice with deionized water to remove any trace of medium constituents. These bacteria collected were magnetotactic, because nearly no bacteria were observed in contrast experiment without magnetic field through biological microscope (B1-223A Motic, Shanghai Cany Precision Instrument Co., China). The biomass was then concentrated by centrifugation at $4000\text{r}\cdot\text{min}^{-1}$ and used for the following biosorption studies. To avoid the aggregation of the dry biomass and maintain the structure of the cells, the wet biomass stored at 4°C was used and dispersed evenly in solution before biosorption experiments. However, the biosorption capacity was still expressed in dry mass in order to make a comparison with previous studies. The ratio of wet biomass to dry biomass was determined by placing measured wet biomass in the oven at 60°C to constant values, and its ratio in the present study was 13.4.

2.2 Preparation of metal ions solution for biosorption

The stock solutions of Au(III) and Cu(II) ($500\text{mg}\cdot\text{L}^{-1}$) were prepared by dissolving a specific amount of analytical grade chloroauric acid ($\text{HAuCl}_4\cdot 4\text{H}_2\text{O}$, analytical reagent, Guangfu Reagent, China) and copper sulfate pentahydrate ($\text{CuSO}_4\cdot 5\text{H}_2\text{O}$, analytical reagent, Guangfu Reagent, China) in deionized double-distilled sterilized water, respectively. Biosorption with and without cells were conducted in order to investigate the real sorbents in the sorption process.

2.3 Optimum adsorption conditions experiments

In this section, adsorption conditions including pH values, temperature, initial metal-ion concentration and biomass concentration were investigated.

Experiments were carried out in 250-ml conical flasks containing 100ml of $80\text{mg}\cdot\text{L}^{-1}$ Au(III) or Cu(II) solution. Bottles were agitated on a shaker at $130\text{r}\cdot\text{min}^{-1}$ for 1h, allowing sufficient time for adsorption equilibrium. To study the effects of pH, temperature and biomass concentration on metal biosorption on MTB, series of experiments were conducted at pH 1–13 (by adding $0.1\text{mol}\cdot\text{L}^{-1}$ HCl and NaOH solution), $10\text{--}35^\circ\text{C}$, $2.0\text{--}12.0\text{g}\cdot\text{L}^{-1}$ (wet mass basis), respectively.

After reaching equilibrium, 5ml sample was taken from each flask and filtered with millipore filters of $0.22\mu\text{m}$ pore size. The filtrate was collected for metal-ions analysis.

2.4 Adsorption isotherms experiments

In order to determine the characteristics of MTB for biosorption of Au(III) ions, three groups of experiments were designed according to the coexisting Cu(II) concentrations (0, 80, $320\text{mg}\cdot\text{L}^{-1}$) in solution. In each group, initial Au(III) solution was diluted to five typical concentrations of 80, 200, 320, 400, $500\text{mg}\cdot\text{L}^{-1}$, respectively. Similar methods were used to investigate the characteristics of MTB for biosorption of Cu(II) ions.

2.5 Adsorption kinetic experiments

The initial Au(III) and Cu(II) ions concentrations were $80\text{mg}\cdot\text{L}^{-1}$, and samples (5ml) were taken before mixing MTB solution and metal-bearing solution at predetermined time intervals (0.5, 1, 3, 5, 10, 30, 60min) for determining the residual metal-ion concentration in the solution.

2.6 Measurement of metal ions

The concentration of unadsorbed Au(III) and Cu(II) ions in solution was determined by Atomic Absorption Spectrophotometer (HITACHI 180-80, Beijing Ruili Analytical Instrument Company, China). The uptake of metal ion q_{eq} ($\text{mg}\cdot\text{g}^{-1}$) and the adsorption yield Y (%) was selected as the test criteria, which can be calculated from Eqs. (1) and (2), respectively:

$$q_{\text{eq}} = \frac{C_0 - C_{\text{eq}}}{m} \quad (1)$$

$$Y = \frac{C_0 - C_{\text{eq}}}{C_0} \times 100\% \quad (2)$$

where C_{eq} was the free metal-ion concentration in solution at equilibrium ($\text{mg}\cdot\text{L}^{-1}$), C_0 was the initial metal-ion concentration ($\text{mg}\cdot\text{L}^{-1}$), and m was the biomass concentration (wet mass basis, $\text{g}\cdot\text{L}^{-1}$).

Each aforementioned experiment was repeated three times and the following data were given as average.

3 RESULTS AND DISCUSSION

3.1 The optimum adsorption conditions

3.1.1 Effect of initial pH

The pH value was the most important environmental factor in the biosorption process, because not only the site dissociation but also the solution chemistry of the heavy metals, that is, hydrolysis, complexation by organic and/or inorganic ligands, redox reactions, precipitation were all strongly influenced by pH. Fig.1 illustrates that the removal of Au(III) or Cu(II) ions were efficient with decreasing pH values. With the same sorption conditions of $80\text{mg}\cdot\text{L}^{-1}$ initial metal-ions concentration, 25°C and biomass concentration of $10.0\text{g}\cdot\text{L}^{-1}$ (wet mass basis), the adsorption

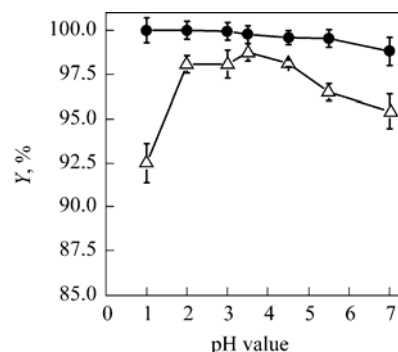


Figure 1 Effect of pH value on adsorption yield of Au(III) or Cu(II) ions on MTB
[$T=25^\circ\text{C}$, MTB $10.0\text{g}\cdot\text{L}^{-1}$ (wet mass), $C_0=80\text{mg}\cdot\text{L}^{-1}$, $130\text{r}\cdot\text{min}^{-1}$, 10min]
● Au(III); △ Cu(II)

yield of Au(III) ions on MTB was obtained 99.53%—100% in the long range of pH 1.0—5.5, and that of Cu(II) ions was 98.07%—98.75% in the range of pH 2.0—4.5, and the corresponding uptake of Au(III) and Cu(II) ions were nearly 8.0 and 7.9mg·g⁻¹, respectively.

Cell walls had binding sites that were considered as being part of ionizable groups such as carboxyl, hydroxyl, amino and imino. At highly acidic pH values, cell wall ligands would be closely associated with H₃O⁺ which restricts metal ions access to ligands as a result of repulsive forces. It was to be expected that as pH values increased, more ligands with a negative charge would be exposed with subsequent increase in attraction for positively charged metal ions[18]. However, high efficiency in the adsorption process of Au(III) or Cu(II) ions had been obtained at highly acid solution. Similar pH effect on the adsorption trend had also been obtained by Nasernejad *et al.*[19] and Gamez *et al.*[20]. Taking into account that the industry effluents and leaching liquid were strong acid, the working adsorption pH was chosen as 2.0 in the following experiments.

3.1.2 Effect of temperature

Figure 2 shows that an increase of temperature in the interval of 15—20°C dealt with an increase in the adsorption yield, and began to decrease slowly with increasing temperature from 25 to 35°C. As a whole, both metal ions were effectively adsorbed by MTB in the range of 10—35°C. Namely, temperature was not a significant effect on the adsorption yield of MTB for Au(III) or Cu(II) in the designed temperature interval. A reasonable explanation might be that the actual attachment of the metal ions on the cellular surface was mainly chemisorption and ion exchange, but not physical adsorption and enzymatic reaction, for the latter could be affected easily by thermal movement of the ions with high temperature. Now that the temperature of biosorption process was not significant on the uptake and the adsorption yield for the biosorption of Au(III) or Cu(II) ions, room temperature, 25°C, was selected in the following experiments.

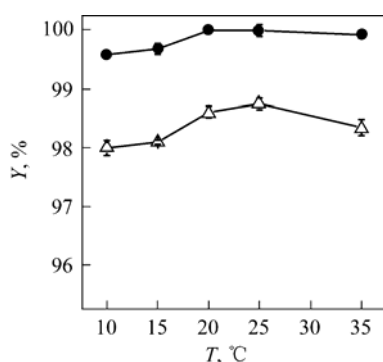


Figure 2 Effect of temperature on adsorption yield of Au(III) or Cu(II) ions on MTB [pH 2.0, MTB 10.0g·L⁻¹(wet mass), C₀=80mg·L⁻¹, 130r·min⁻¹, 10min] ●Au(III); △Cu(II)

3.1.3 Effect of the biomass concentration

The biosorption capacity of Au(III) or Cu(II) ions

decreased with an increase of biomass concentration (2.0—12.0g·L⁻¹, wet-mass basis) when initial metal concentration was 80mg·L⁻¹ as shown in Fig.3. For both Au(III) and Cu(II), the maximum adsorption yield was achieved at biomass concentrations (wet mass basis) of more than 10.0g·L⁻¹. Therefore, 10.0mg·g⁻¹ was as the optimum biomass concentration in the following experiments.

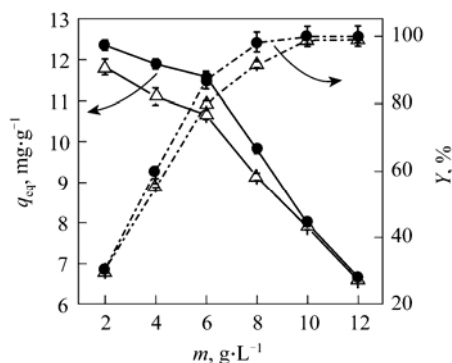


Figure 3 Effect of the biomass concentration on adsorption yield of Au(III) or Cu(II) ions on MTB (T=25°C, pH 2.0, 130r·min⁻¹, C₀=80mg·L⁻¹, 10min) ●Au(III); △Cu(II)

3.2 Adsorption isotherms of Au(III) and Cu(II) ions with MTB

Sorption equilibrium provides a fundamental physicochemical data for evaluating the applicability of sorption process as a unit operation. In order to model the biosorption behavior and to calculate the biosorption capacity of MTB, adsorption isotherms were studied. Fig.4 illustrates the equilibrium isotherms for the biosorption of Au(III) and Cu(II) ions on MTB. Although the uptakes of Cu(II) and Au(III) ions were almost equal in single component solution, the uptake of Au(III) ion was significantly increased, whereas that of Cu(II) was sharply decreased in the binary system, which indicates that the MTB cell walls have high selectivity towards Au(III) ions in binary-solute biosorption process. And when the

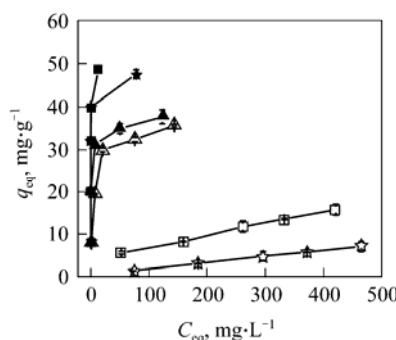


Figure 4 The comparison of adsorption isotherms of Au(III) and Cu(II) ions on MTB [T=25°C, pH 2.0, MTB 10.0g·L⁻¹(wet mass), 130r·min⁻¹, 10min] ▲ Au(III) (C_{0,Cu}=0); △ Cu(II) (C_{0,Au}=0); ■ Au(III) (C_{0,Cu}=80mg·L⁻¹); ★ Au(III) (C_{0,Cu}=320mg·L⁻¹); □ Cu(II) (C_{0,Au}=80mg·L⁻¹); ☆ Cu(II) (C_{0,Au}=320mg·L⁻¹)

Table 1 The Freundlich parameters and the correlation coefficients

$C_{0, \text{other metal}}$ $\text{mg}\cdot\text{L}^{-1}$	Au(III) ions			Cu(II) ions		
	K_F	n	R^2	K_F	n	R^2
0	27.56	15.6985	0.9901	16.09	11.0254	0.9428
80	44.33	22.8833	0.9265	1.27	5.1125	0.9693
320	38.64	10.2669	0.9214	0.04	1.4656	0.9857

Note: $C_{0, \text{other metal}}$ represents the other metal concentration in solution. When $C_{0, \text{other metal}}=0$, it is single ion solution; when not, it is binary system.

Table 2 The Langmuir parameters and the correlation coefficients

$C_{0, \text{other metal}}$ $\text{mg}\cdot\text{L}^{-1}$	Au(III) ions			Cu(II) ions		
	$Q^0, \text{mg}\cdot\text{g}^{-1}$	$b, \text{L}\cdot\text{mg}^{-1}$	R^2	$Q^0, \text{mg}\cdot\text{g}^{-1}$	$b, \text{L}\cdot\text{mg}^{-1}$	R^2
0	37.7	0.9780	0.9939	36.8	0.1605	0.9985
80	48.8	4.1000	1.0000	22.4	0.0046	0.9260
320	47.6	5.2500	1.0000	27.7	0.0007	0.9026

Note: The meaning of $C_{0, \text{other metal}}$ is the same as Table 1.

concentration of Au(III) and Cu(II) were within $80\text{mg}\cdot\text{L}^{-1}$, the wastewater after MTB treatment was below $1.0\text{mg}\cdot\text{L}^{-1}$, which is in conformity with Environmental Performance Standards (EPS) of Canada[21].

Analysis of the experimental results by equilibrium sorption equation often provides some insights into the sorption mechanism and the properties of the adsorbent. Several isotherm models describe the equilibrium between adsorbed metal ions on the cell (q_{eq}) and unadsorbed component remaining in solution (C_{eq}) at certain temperature. The well-known Freundlich model was based on the sorption on a heterogeneous surface, suggesting that binding sites are not equivalent and/or independent, as described by the following equation:

$$\lg q_{\text{eq}} = \lg K_F + \frac{1}{n} \lg C_{\text{eq}} \quad (3)$$

where K_F was an indicator of the adsorption capacity of the adsorbent, and $1/n$ was the adsorption intensity. One way to test the Freundlich model was by plotting $\lg q_{\text{eq}}$ against $\lg C_{\text{eq}}$.

The Langmuir model suggests, as a hypothesis, that uptake occurs on a homogeneous surface by monolayer sorption without interaction between adsorbed molecules, and its linear form is expressed as in the following equation:

$$\frac{C_{\text{eq}}}{q_{\text{eq}}} = \frac{1}{Q^0 b} + \frac{C_{\text{eq}}}{Q^0} \quad (4)$$

where Q^0 ($\text{mg}\cdot\text{g}^{-1}$) represents the maximum sorption capacity, and b ($\text{L}\cdot\text{mg}^{-1}$) is the sorption constant related to the affinity of the binding sites. Q^0 and b can be determined from the plot of $C_{\text{eq}}/q_{\text{eq}}$ versus C_{eq} .

The Freundlich and Langmuir constants evaluated from linear regression analysis are listed in Tables 1 and 2, respectively. Within the metal concentration range of $80\text{--}500\text{mg}\cdot\text{L}^{-1}$, both models were suitable for describing the adsorption isotherms of Au(III)

or Cu(II) ions; that of Au(III) was more fitted by Langmuir model and that of Cu(II) by Freundlich in binary system. The magnitude of Freundlich constants, n , were greater than unity and this indicated that the adsorption was favorable[22]. The values of K_F of Au(III) in binary system were nearly doubled as in the single system, whereas those of Cu(II) were sharply dropped. When the coexisting ion concentrations were 80 and $320\text{mg}\cdot\text{L}^{-1}$, the K_F of Au(III) were 44.33 and 38.64, whereas those of Cu(II) were only 1.27 and 0.04, respectively. The larger values of K_F and n of Au(III) indicate that MTB has higher adsorption capacity and intensity of Au(III) over Cu(II).

The adsorption capacities (Q^0) and affinity (b) of MTB for Au(III) or Cu(II) were obtained by Langmuir equation and is given in Table 2. The large value of b implied strong bonding. The larger the value of b , the greater the fractional surface coverage at a fixed temperature and at a fixed value of C_{eq} . The highest adsorption capacity of MTB (dry mass basis) were calculated according to the dry-wet ratio (13.4) and the Langmuir constant Q^0 , and they were higher than other bacteria and fungal adsorbents, but lower than that of chitosan listed in Table 3. Therefore, MTB was a potential biosorbent for precious metals. Differences

Table 3 Maximum adsorption capacity of biosorbents for Au(III) or Cu(II)

Types of biosorbents	Au(III) _f $\text{mg}\cdot\text{g}^{-1}$	Cu(II) _f $\text{mg}\cdot\text{g}^{-1}$
MTB	505.2	493.1
<i>Alfalfa</i> biomass[20]	36.0	3.4
<i>Cetraria islandica</i> [23]	7.4	19.2
<i>Cladosporium cladosporioides</i> [24]	81.0—101.0	—
<i>Aspergillus niger</i> (fungus)[25]	170.0	7.2
<i>Sargassum natans</i> [26]	420.0	—
chitosan[27]	565.5—624.0	—

of metal uptake are a result of the properties of each adsorbent such as structure, functional groups and surface area. The major advantage of MTB for precious metal sorption may be, like chitosan, that the amino sites of them were easily protonated in acid media, accentuating the electrostatic forces often implicated in the initial stages of sorption.

3.3 Adsorption kinetics of Au(III) and Cu(II) ions on MTB

Microorganism was known to accumulate metals by two distinct stages containing passive physical adsorption and active uptake. Initially, metal ions diffused to the surface of the cell walls where they bind to the active sites on the cell surface formed by the presence of various chemical groups such as the carboxylate, hydroxyl, amino and phosphate which exhibit affinity for the metal ions. Generally, such adsorption was very fast, reversible, and not a limiting factor in biosorption kinetics when dealing with dispersed cells. Biosorption was often followed by slower binding process in which additional component was bound, often irreversibly[28].

Similar results had been obtained in the time-dependence experiments, and Fig.5 shows that the adsorption yield of Au(III) on MTB in single system increased rapidly up to 99.96% within 1min, and for Cu(II) ions 96.13% was obtained within the initial 5min. After this equilibrium time of 5min, the amount of adsorbed metals ions did not significantly change with time, 100% and 98.0% were achieved at the final biosorption equilibrium time, respectively. In the binary system, the equilibrium of Au(III) biosorption

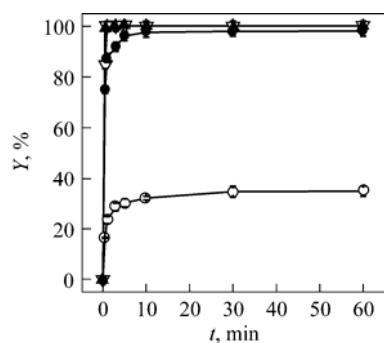


Figure 5 Effect of adsorption time on adsorption yield of Au(III) and Cu(II) ions by MTB

[$T=25^{\circ}\text{C}$, $\text{pH } 2.0$, $\text{MTB } 10.0\text{g}\cdot\text{L}^{-1}$ (wet mass), $C_0=80\text{mg}\cdot\text{L}^{-1}$, $130\text{r}\cdot\text{min}^{-1}$]

▲ Au(III); ● Cu(II); ▽ Au(III) (Au+Cu); ○ Cu(II) (Au+Cu)

was still achieved within 5min and the adsorption yield reached 100%, whereas that of Cu(II) was only 66.61% after 30min.

In order to investigate the mechanism of biosorption and potential rate controlling step such as mass transport and chemical reaction process, kinetic models have been used to test experimental data. Numerous studies reported that the pseudo first-order Lagergren kinetics and the pseudo second-order kinetics were available for the sorption of metals[29,30]. The Lagergren rate equation was widely used for the sorption of liquid-solid system on the basis of solid capacity, and expressed as

$$q_t = q_{\text{eq}(\text{theo})} \left(1 - e^{-k_1 t}\right) \quad (5)$$

where $k_1(\text{min}^{-1})$ was the rate constant of the second-order adsorption for each component, q_t and $q_{\text{eq}(\text{theo})}(\text{mg}\cdot\text{g}^{-1})$ were the adsorption capacities measured at time $t(\text{min})$ and calculated at equilibrium, respectively. $q_{\text{eq}(\text{theo})}$ and k_1 could be estimated by nonlinear regression technique using the Sigmaplot 9.0 software.

However, in most cases the first-order equation of Lagergren does not fit well for the whole range of contact time and was generally applicable over the initial time of the sorption process[31]. The pseudo second-order equation can be used in this case assuming that the measured concentrations are equal to cell surface concentrations, and it is more likely to predict behavior over the whole range of adsorption and is in agreement with an adsorption mechanism being the rate controlling step. The linear form of the pseudo second-order adsorption kinetic rate equation for each component in single and binary system was expressed as in Eq.(6):

$$\frac{t}{q_t} = \frac{1}{k_2 q_{\text{eq}(\text{theo})}^2} + \frac{1}{q_{\text{eq}(\text{theo})}} t \quad (6)$$

where k_2 was the rate constant of each component for the second-order biosorption ($\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$). The plot of t/q_t against t should give a linear relationship, from which q_{eq} and k_2 could be determined from the slope and intercept of the plot and there it was not necessary to know any parameter beforehand.

The experimental equilibrium specific uptake of Au(III) and Cu(II) q_{eq} was compared with the $q_{\text{eq}(\text{theo})}$ obtained using Lagergren first-order and second-order equation and are given in Table 4. A high degree of correlation coefficients (almost 1.0) were obtained for the second-order kinetic model for sorption of both

Table 4 Comparison of pseudo first- and second-order kinetic model constants

		The pseudo first-order kinetic model			The pseudo second-order kinetic model			$q_{\text{eq}}, \text{mg}\cdot\text{g}^{-1}$
		k_1, min^{-1}	$q_{\text{eq}(\text{theo})}, \text{mg}\cdot\text{g}^{-1}$	R^2	$k_2, \text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$	$q_{\text{eq}(\text{theo})}, \text{mg}\cdot\text{g}^{-1}$	R^2	
single metal system	Au(III)	8.58	8.0	1.0000	78.13	8.0	1.0000	8.0
	Cu(II)	2.91	7.7	0.9950	0.96	7.9	1.0000	7.8
binary metal system	Au(III)	3.85	8.0	0.9996	6.00	8.0	1.0000	8.0
	Cu(II)	1.97	4.7	0.9049	0.19	5.4	0.9991	5.3

components. And the large deviation between q_{eq} and $q_{eq(theo)}$ also showed that the first-order kinetic model did not represent the sorption of both metals adequately. The results suggested that the biosorption system followed the second-order kinetics and indicated that the rate-limiting step may be chemical sorption involving valency forces through sharing or exchange of electrons between sorbents and sorbate.

Ayla *et al.*[32] have had the results of the biosorption of copper(II) ions on *Cladophora crispate* which showed that the kinetics data were fitted well into the pseudo second-order kinetic model with a high correlation coefficient ($R^2 > 0.99$). Aksu[30] also reported that the biosorption processes of Remazol Black B on dried *R. arrhizus* were strictly followed the pseudo second-order kinetic model.

Compared with single system, the rate constants (k_2) of both ions in binary system dropped markedly, and that of Au(III) dropped from 78.13 to 6.00, and Cu(II) from 0.96 to 0.19, respectively. This may be the result of competitive biosorption of multi-metals. Although the uptake of adsorption of Au(III) and Cu(II) ions in single system were near equal, the coexistence of other metal ions affected the q_{eq} of Cu(II) markedly and had no significant impact on Au(III), which indicated that MTB has the ability of selective sorption of Au(III) from Au-Cu binary system.

3.4 Analysis of adsorption selectivity on MTB for Au(III) ions

The exact mechanisms explaining the biosorption of ions from aqueous solutions are still not fully understood[18]. Factors that affect the biosorption preference of MTB for Au(III) were related to the characteristics of the binding sites, the functions of the solution and the physical and chemical properties of the metal ions. Some physical and chemical properties of Au(III) and Cu(II) ions are listed in Table 5.

Having a higher atomic mass, the movement of Au(III) can generate higher momentum energy, which

may facilitate the biosorption of Au(III) by increasing the probability of effective collision between Au(III) and the cell walls of MTB[33]. For larger electronegativity of Au atom, its ionic form seems to be more easily adsorbed by MTB than Cu(II) ions. The metal ions examined follow a pattern that the higher the ion charge, the higher the affinity for MTB. Au(III) with a higher standard reduction potential tends to exhibit a stronger ionic interaction with electron-rich surface of MTB[34]. All these properties of Au(III) reflect the trend of biosorption preference of Au(III) by MTB.

Another property was the ionic radius. For molecule with smaller ionic radius, more can be adsorbed onto a fixed surface area of biosorbents[35]. This rule was only suitable in single system according to the uptakes (molar value) in Table 6. In binary system, the uptakes of Au(III) increase in a certain way, whereas those of Cu(II) decrease remarkably.

It was difficult to find a common rule from the physical and chemical properties of Au(III) and Cu(II) ions to identify how these ions properties exactly affect their selective sorption by MTB. This was because the observed behavior may have resulted from a combination of many factors except those mentioned earlier. Moreover, the aforementioned rules are deduced primarily on the basis of the properties of metals without consideration of the effects of the characteristics of biosorbents. This inconsistency about ionic radius rule most likely originates from variations in composition and structure of the biosorbent surface caused by changing physicochemical parameters of the solution[18,36].

4 CONCLUSIONS

In this study, MTB had been successfully used as the adsorbent for the adsorption of Au(III) and Cu(II) ions from artificial wastewater. The optimum conditions for both metal ions were the initial pH scope of 1—5.5 for Au(III) and 2.0—4.5 for Cu(II), room temperature, biomass concentration of $10.0\text{g}\cdot\text{L}^{-1}$ and

Table 5 Some physical-chemical properties of Au(III) and Cu(II)

	Atomic mass	Ion charge	Electronegativity	Standard reduction potential, V	Ionic radius, nm
Au(III)	196.97	3	2.40	1.5	0.085
Cu(II)	63.55	2	1.90	0.340	0.072

Table 6 The adsorption uptakes (molar value) of MTB for Au(III) and Cu(II) ions

$C_0, \text{mg}\cdot\text{L}^{-1}$	Adsorption uptake, $\text{mmol}\cdot\text{g}^{-1}$					
	$C_{0, \text{other metal}}=0$		$C_{0, \text{other metal}}=80\text{mg}\cdot\text{L}^{-1}$		$C_{0, \text{other metal}}=320\text{mg}\cdot\text{L}^{-1}$	
	Au(III)	Cu(II)	Au(III)	Cu(II)	Au(III)	Cu(II)
80	0.04	0.12	0.04	0.09	0.04	0.02
200	0.10	0.30	0.10	0.13	0.10	0.05
320	0.16	0.47	0.16	0.18	0.16	0.08
400	0.18	0.51	0.20	0.21	0.20	0.09
500	0.19	0.56	0.25	0.25	0.245	0.115

Note: The meaning of $C_{0, \text{other metal}}$ is the same as Table 1.

sorption duration of more than 10 min. Simultaneous biosorption of Au(III) and Cu(II) ions with MTB has been investigated. It was found that Cu(II) has a "catalyzing" effect on Au(III) sorption with MTB. When the initial metal concentration were within $500\text{mg}\cdot\text{L}^{-1}$, the maximum adsorption capacities of MTB for Au(III) and Cu(II) ions were nearly equal in single component solutions, whereas in Au-Cu binary system the maximum adsorption capacity for Au(III) were nearly doubled as that in the single system, whereas that for Cu(II) were sharply dropped.

When the initial and coexisting metal-ion concentration were within $320\text{mg}\cdot\text{L}^{-1}$, the selective removal of Au(III) and Cu(II) in a mixture of Au(III) and Cu(II) ions by MTB was more than 95.87% and less than 8.83%, respectively. Freundlich and Langmuir model were used to describe the equilibrium isotherm and reflected that MTB had a high propensity to adsorb Au(III) selectively from the binary solution. The pseudo second-order kinetic model was suitable to describe the kinetic data in the single and binary component situations. All of the experimental data fitted well into the pseudo second-order kinetic model with a high correlation coefficient ($R^2 > 0.999$).

This unique finding indicates the high possibility to recover gold from wastewater containing Au(III) and Cu(II) using the method of "MTB biosorption and magnetic separation", which was simple, effective and environmentally friendly.

NOMENCLATURE

b	sorption constant related to the affinity of the binding sites, $\text{L}\cdot\text{mg}^{-1}$
C_{eq}	unadsorbed metal-ion concentration remaining in solution at equilibrium, $\text{mg}\cdot\text{L}^{-1}$
C_0	initial metal-ion concentration, $\text{mg}\cdot\text{L}^{-1}$
K_F	an indicator of the adsorption capacity of the adsorbent
k_1	rate constant of each component for the first-order biosorption, min^{-1}
k_2	rate constant of each component for the second-order biosorption, $\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$
m	biomass concentration (wet mass basis), $\text{g}\cdot\text{L}^{-1}$
n	adsorption intensity
Q^0	represents the maximum sorption capacity, $\text{mg}\cdot\text{g}^{-1}$
q_{eq}	metal uptake measured at equilibrium, $\text{mg}\cdot\text{g}^{-1}$
$q_{\text{eq}(\text{theo})}$	metal uptake calculated at equilibrium, $\text{mg}\cdot\text{g}^{-1}$
q_t	metal uptake per unit mass of cells at time t (min), $\text{mg}\cdot\text{g}^{-1}$
R^2	the correlation coefficient
t	point of time in the adsorption process, min
Y	adsorption yield, %

REFERENCES

- Celaya, R.J., Noriega, J.A., Yeomans, J.H., Ortega, L.J., Ruiz-Manriquez, A., "Biosorption of Zn (II) by *Thiobacillus ferrooxidans*", *Bioprocess Eng.*, **22**(6), 539—542(2000).
- Veglio, F., Beolchini, F., "Removal of metals by biosorption: A review", *Hydrometallurgy*, **44**(3), 301—316(1997).
- Su, H.J., Wang, L.J., Tan, T.W., "Adsorption of heavy metal ions by adsorbent from waste mycelium chitin", *Chin. J. Chem. Eng.*, **10**(6), 650—652(2002).
- Meng, Q., Lv, D.W., "Biosorption of Ni^{2+} and Fe^{3+} by fungal cell wall sacchrides", *Chin. J. Chem. Eng.*, **8**(2), 123—127(2000).
- Ting, Y.P., Sun, G., "Use of polyvinyl alcohol as a cell immobilization matrix for copper biosorption by yeast cells", *J. Chem. Technol. Biotechnol.*, **75**(7), 541—546(2000).
- Blackmore, R.P., "Magnetotactic bacteria", *Science*, **19**(2), 377—379(1975).
- Heyen, U., Schöler, D., "Growth and magnetosome formation by microaerophilic magnetospirillum strains in an oxygen-controlled fermentor", *Appl. Microbiol. Biotechnol.*, **61**(5/6), 536—544(2003).
- Tatyana, P., Vitalii, Z., "Magnetization processes in magnetotactic bacteria systems", *J. Magn. Magn. Mater.*, **293**(1), 365—370(2005).
- Wei, Y.B., Zhang, H.X., Jiang, W., Qiu, J.F., "Studies on magnetotactic bacteria I. Morphological characteristics of magnetotactic bacterium from the East Lake in Wuhan and isolation of its strain WD-1", *J. Wuhan University (Natural Science edition)*, (6), 115—120(1994). (in Chinese)
- Chemla, Y.R., Grossman, H.L., Lee, T.S., Clarke, J., Adamkiewicz, M., Buchanan, B.B., "A new study of bacterial motion: Superconducting quantum interference device microscopy of magnetotactic bacteria", *Biophys. J.*, **76**(6), 3323—3330(1999).
- Bahal, A.S., James, P.A.B., Mosechler, F.D., "Wastewater treatment by bio-magnetic separation: A comparison of iron oxide and iron sulphide biomass recovery", *Water Sci. Technol.*, **38**(6), 311—317(1998).
- Bahal, A.S., James, P.A.B., Mosechler, F.D., "Low magnetic-field separation system for metal-loaded magnetotactic bacteria", *J. Magn. Magn. Mater.*, **177-181**(2), 1453—1454(1998).
- Bahal, A.S., James, P.A.B., "Metal uptake and separation using magnetic bacteria", *IEEE Trans. Magn.*, **30**(6), 4707—4709(1994).
- Wu, Z.H., Sun, J.S., Song, H.P., Li, X.G., "Studies on adsorption of palladium(II) by magnetotactic bacteria(MTB)", *Ion Exchange and Adsorption(China)*, **22**(5), 385—391(2006).
- Shin-ichi, I., Kyoze, S., Keizo, A., Makoto, I., "Uptake and recovery of gold ions from electroplating wastes using eggshell membrane", *Bioresour. Technol.*, **81**(3), 201—206(2002).
- Blackmore, R.P., Maratea, D., Wolfe, R.S., "Isolation and pure culture of a freshwater magnetic spirillum in chemically defined medium", *J. Bacteriol.*, **140**(2), 720—729(1979).
- Matsunaga, T., Kamiya, S., "Use of magnetite particles isolated from magnetotactic bacteria for enzyme immobilization", *Appl. Microbiol. Biotechnol.*, **26**(4), 328—332(1987).
- Zümriye, A., Hanife, G., "Binary biosorption of iron(III) and iron(III)-cyanide complex ions on *Rhizopus arrhizus*: Modeling of synergistic interaction", *Process Biochem.*, **38**(2), 161—173(2002).
- Nasernejad, B., Esslam, Z.T., Bonakdar, P.B., Esmaail, B.M., Zamani, A., "Comparison for biosorption modeling of heavy metals (Cr(III), Cu(II), Zn(II)) adsorption from wastewater by carrot residues", *Process Biochem.*, **40**(3/4), 1319—1322(2005).
- Gamez, G., Gardea-Torresdey, J.L., Tiemann, K.J., Parsons, J., Dokken, K., "Recovery of gold (III) from multi-elemental solutions by alfalfa biomass", *Adv. Environ. Res.*, **7**(2), 563—571(2003).
- EPS, Overview of the Canadian Surface Finishing Industry: Status of the Industry and Measures for Pollution Control. Environment Canada, EPS 2/SF/1 (1987).
- Hayward, D.O., Trapnell, B.M.W., Chemisorption, 2nd Ed., Butterworths, London, 67—107(1964).
- Canan, E.D., Kadir, T., Goksel, A., Ali, A., "Biosorption of Au(III) and Cu(II) from aqueous solution by a non-living *Cetraria islandica* (L.)", *Ach. Annali di Canada*, **96**(3/4), 229—236(2006).
- Pethkar, A.V., Kulkarni, S. K., Paknikar, K. M. "Comparative studies on metal biosorption by two strains of *Cladosporium cladosporioides*", *Bioresour. Technol.*, **80**(3), 211—215(2001).
- Kapoor, A., Viraraghavan, T., "Fungal biosorption - An

- alternative treatment option for heavy metal bearing wastewaters: A review", *Bioresour. Technol.*, **53**(3), 195—206(1995).
- 26 Kuyucak, N., Volesky, B., "Biosorbents for recovery of metals from industrial solutions", *Biotechnol. Lett.*, **10**(2), 137—142(1988).
- 27 Mack, C., Wilhelmi, B., Duncan, J.R., Burgess, J.E., "Biosorption of precious metals", *Biotechnol. Adv.*, **25**(3), 264—271(2007).
- 28 Palmieri, M.C., Garcia, O.J., Melnikov, P., "Neodymium biosorption from acidic solutions in batch system", *Process Biochem.*, **36**(5), 441—444(2000).
- 29 Chiou, M.S., Li, H.Y., "Equilibrium and kinetic modeling of adsorption of reactive dye on cross-linked chitosan beads", *J. Hazard. Mater.*, **B93**(2), 233—248(2002).
- 30 Aksu, Z., "Equilibrium and kinetic modelling of cadmium(II) biosorption by *C. vulgaris* in a batch system: Effect of temperature", *Sep. Purif. Technol.*, **21**(3), 285—294(2001).
- 31 Ho, Y.S., McKay, G., "Pseudo-second order model for sorption processes", *Process Biochem.*, **34**(5), 451—465(1999).
- 32 Ayla, Ö., Dursun, Ö., Hibrâhîm, E., "The equilibrium and kinetic modelling of the biosorption of copper(II) ions on *Cladophora crispate*", *Adsorption*, **10**(4), 317—326(2004).
- 33 Yeşim, S., Burak, A., Tülin, K., "Evaluation, interpretation, and representation of three-metal biosorption equilibria using a fungal biosorbent", *Process Biochem.*, **37**(1), 35—50(2001).
- 34 Stumm, W., Morgan, J.J., *Aquatic Chemistry: An Introduction Emphasizing Chemical Equilibria in Natural Water*, 2nd Ed., John Wiley and Sons, New York, 78 (1981).
- 35 Michael, H. J., Ayebacmi, I. S., "Equilibrium sorption study of Al^{3+} , Co^{2+} and Ag^{+} in aqueous solutions by fluted pumpkin (*Telfairia Occidentalis* HOOK f) waste biomass", *Acta Chim. Slov.*, **52**(2), 174—181(2005).
- 36 Yeşim, S., Burak, A., Tülin, K., "Ternary biosorption equilibria of chromium(VI), copper(II), and cadmium(II) on *Rhizopus arrhizus*", *Sep. Sci. Technol.*, **37**(2), 279—309(2002).

AUTHOR'S LETTERS

A Statement of Withdrawing Paper

In my paper "Modeling of Turbulent Nonpremixed CH_4/H_2 Flame Using Second-Moment Turbulent Closure Models"[2005, **13**(1), 1–8] published in your journal, due to reporting different aspects of the same project results, there are some similar expressions in some parts of the paper compared to a paper published in another journal. I would like to withdraw this paper with a rigorous scientific attitude. Please accept my sincere apology to your journal and readers.

LI Guoxiu
October 2007