

Journal of Environmental Informatics 19(1) 51-57 (2012)

Journal of Environmental Informatics

www.iseis.org/jei

# Characteristics and Thermodynamics of Biosorption Copper by a Newly Isolated *Penicillium* sp. QQ Using a Response Surface Methodology

B. Yan<sup>1,\*</sup>, J. T. Zhou<sup>2</sup>, Y. G. Li<sup>1</sup>, Q. Shi<sup>1</sup>, H. Y. Fu<sup>1</sup>, T. Chai<sup>1</sup>, and J. F. Liu<sup>1</sup>

<sup>1</sup>Department of Environmental Engineering, Xiamen University of Technology, Xiamen 361024, P. R. China

<sup>2</sup>Key Laboratory of Industrial Ecology and Environmental Engineering (MOE), School of Environmental Science and Technology, Dalian

University of Technology, Dalian 116024, P. R. China

Received 27 December 2010; revised 9 November 2011; accepted 2 December 2011; published online 12 March 2012

**ABSTRACT.** The objective of this study was to investigate the potential for *Penicillium* sp. QQ to perform copper adsorption. The following optimal conditions were assigned for biosorption by a response surface methodology (RSM): a biomass concentration of 4.6% (w/v), pH of 5.6, initial copper concentration of 100 mg/L and an established biosorption equilibrium after a 30 min reaction. A copper removal efficiency of about 98% was achieved after 30 min. The kinetics of copper adsorption are discussed, and the experimental data are fit to a pseudo-second-order kinetic model. The experimental results were analyzed using the Langmuir and Freundlich isotherms. The equilibrium constant *b* and *n* value show copper has been favorably adsorbed by the QQ strain. The thermodynamic parameters such as the free energy ( $\Delta G^\circ$ ), enthalpy ( $\Delta H^\circ$ ) and entropy ( $\Delta S^\circ$ ) also prove the adsorption process was thermodynamically feasible and spontaneous. The results indicate *Penicillium* sp. QQ could be used as a promising candidate for removing heavy metal ions from aqueous environments.

Keywords: response surface methodology (RSM), penicillium sp. QQ, copper, isotherms, thermodynamics, biosorption

#### 1. Introduction

Heavy metal pollution has become a serious environmenttal problem. With the rapid development of industrial activity and technology, the amount of heavy metals released into the environment have been continuously increasing, posing a serious threat to the environment and public health due to their toxicity, bioaccumulation and bioaugmentation in the food chain and persistence in nature (Uluozlu et al., 2008). Many industries, such as mining and smelting of metalliferous, energy and fuel production, fertilizer and pesticide industry and application, metallurgy, iron and steel, electroplating, electrolysis, electro-osmosis, leatherworking, photography, electric appliance manufacturing, etc., have produced and discharged large quantities of wastewater containing various concentrations of heavy metals into the environment (Han et al., 2006). Copper is the most common pollution in industrial effluents and a major concern has arisen recently owing to their nonbiodegradability and toxicity to organisms even at very small concentrations (Nuhoglu et al., 2003; Wang et al., 2009). As reported previously, EPA regulated that copper in drinking water not exceed 1.3 mg/L (Sheng et al., 2004).

ISSN: 1726-2135 print/1684-8799 online

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Since heavy metals are non-renewable resources, it is necessary to remove and recover them from effluents. The conventional methods such as chemical precipitation, membrane technologies, ion exchange, electro-chemical treatment and adsorption on activated carbon, etc., have been suggested to remove metal ions from aqueous environments. However, most of them were costly and might cause secondary pollution (Aksu et al., 2002). For example, chemical precipitation and electrochemical treatment were found to produce a large quantity of sludge (Bhainsa et al., 2008). Compared with these methods, biological methods are more efficient, low-cost and environmental-friendly, which has become an important consideration in the field of metal pollution removal (Wang et al., 2006). Biosorption provides an alternative process, which can utilize various microbial materials including fungi, bacteria, yeast, algae, etc (Parvathi et al., 2007). Mechanisms of biosorption may include ion exchange, complexation, coordination, adsorption, electrostatic interaction, chelation and micro precipitation (Vijayaraghavan et al., 2008). Fungi can be considered for heavy metals removal from aqueous solution due to their good performance, low cost and large available quantities (Kumar et al., 2008). Penicillium sp. have been reported to remove a variety of heavy metal ions, such as  $Cu^{2+}$ ,  $Au^{2+}$ ,  $Zn^{2+}$ .  $Cd^{2+}$ ,  $Mn^{2+}$ ,  $U^{2+}$ ,  $Th^{4+}$  and so on, from aqueous solution (Ahluwalia et al., 2007; Deng et al., 2005).

The purpose of this study was to investigate *Penicillium* sp. QQ as a novel biosorbent for the removal of copper from aqueous solution. The effect of biosorption conditions, bio-

<sup>\*</sup> Corresponding author. Tel.: +86 592 6291138; fax: +86 592 6291138. *E-mail address:* yanb@xmut.edu.en (B. Yan).

sorption equilibrium time, Langmuir and Freundlich isotherm, and thermodynamics were investigated with batch tests. The optimal biosorption conditions were predicted by response surface methodology (RSM) using a central composite design (CCD) method.

# 2. Materials and methods

#### 2.1. Microbial Strain, Medium and Chemicals

The microbial strain used in this study was fungus *Penicillium* sp. QQ, which was provided by the Dalian University of Technology. Spores of QQ strain from potato dextrose agar (PDA) was inoculated in a 250 mL Erlenmeyer flask containing 100 mL of growth medium and cultured at 30 °C and 150 r/min. The growth medium contained (g/L): 10.0 glucose, 1.0 (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, 1.0 K<sub>2</sub>HPO<sub>4</sub> and 0.5 MgSO<sub>4</sub>·7H<sub>2</sub>O (pH 7.0). The fungal biomass was harvested through filtration with nylon cloth after 5 days of cultivation, and then washed 3 times with 0.1 M of phosphate buffer (pH 7.0) to remove traces of medium components. The washed fungal pellets were pressed against filter paper to remove the bound water. CuSO<sub>4</sub>·5H<sub>2</sub>O and other reagents of analytical grade were purchased from Lianbang Co., Ltd., Shenyang, China.

### 2.2. Preparation of the Stock Copper Solution

The stock copper solution was prepared by dissolving the required amount of  $CuSO_4 \cdot 5H_2O$  (analytical grade) in distilled water to obtain a final concentration of  $1 \times 10^4$  mg/L. Further dilutions were made in batch experiments to obtain different concentrations as desired.

#### 2.3. Batch Biosorption Studies

Batch-sequential tests were performed in 50 mL Erlenmeyer flasks, each containing 20 mL of copper solution to achieve the desired concentration. The solution's pH was adjusted by 0.1 M HNO<sub>3</sub> and 0.1 M NH<sub>3</sub>·H<sub>2</sub>O, before adding the biomass. The amount of biomass (wet weight) was determined according to the CCD, and an equal amount of biomass was dried at 55 °C to obtain the dry weight. All the biosorption experiments were conducted on a rotary shaker (150 r/min) at 30 °C.

**Table 1.** Experimental Ranges and Levels of the Independent Variables

| Independent variables    | Ranges and levels |      |      |     |           |
|--------------------------|-------------------|------|------|-----|-----------|
|                          | -α                | -1   | 0    | +1  | $+\alpha$ |
| Biomass (A, g/L)         | 0                 | 1    | 3    | 5   | 6.36      |
| pH (B)                   | 1.81              | 3.00 | 4.75 | 6.5 | 7.69      |
| Initial copper (C, mg/L) | 65.91             | 100  | 150  | 200 | 234.9     |

#### 2.4. Optimization of Biosorption

The optimal conditions for copper adsorption by the QQ strain was estimated using response surface methodology. The biosorption conditions included the biomass concentration (factor A), pH (factor B) and initial copper concentration (fa-

ctor C). The ranges and levels of the three parameters were shown in Table 1. The optimal conditions were determined by the CCD with 20 groups of independent experiments (Table 2). The independent variables were calculated with Equation 1:

$$X_i = \frac{(U_i - U_0)}{\Delta U} \tag{1}$$

where  $X_i$  was the coded value of the independent variable.  $U_i$ ,  $U_0$  and  $\Delta U$  represented the real value of the independent variable, the center point of  $U_i$  and the step change in  $U_i$ , respectively. If the *P*-value (probability > *F*) was less than 0.05, the model and parameters were considered to be proper and could be used in further experiments (Kumar et al., 2008).

The following empirical second-order polynomial mode explained the behavior of system:

$$Y = \beta_0 + \sum \beta_i x_i + \sum \beta_{ii} x_i^2 + \sum \beta_{ij} x_i x_j$$
(2)

where *Y*,  $\beta_0$ ,  $\beta_i$ ,  $\beta_i$  and  $\beta_{ij}$  represented the predicted response, intercept term, linear effect, squared effect and interaction effect, respectively.

# 2.5. Effect of Contact Time and Biosorption Kinetics

The effect of contact time on copper adsorption was investigated. The samples were withdrawn at fixed time intervals from the flasks within  $5 \sim 60$  min.

#### 2.6. Adsorption Isotherms

To obtain biosorption isotherms, the biosorbents under optimal conditions were suspended with different initial copper concentrations ( $50 \sim 250 \text{ mg/L}$ ) and carried out at three different temperatures (20, 30 and 40 °C). The samples were withdrawn at equilibrium.

The equilibrium biosorption data could be described by several isotherm models such as Langmuir, Freundlich and Dubinin-Radushkevich (D-R) models (Wang et al., 2009). Langmuir and Freundich isotherms were used to describe the biosorption equilibrium in this study. The Langmuir isotherm was available to assume monolayer adsorption. In contrast to a Langmuir isotherm, the Freundlich isotherm offered no information on monolayer adsorption. The general Langmuir (3) and Freundlich (4) equations are listed as follows (Freundlich, 1906; Langmuir, 1918):

$$\frac{q_e}{q_m} = \frac{bC_e}{(1+bC_e)} \tag{3}$$

$$q_m = K_f C_e^{\frac{1}{n}} \tag{4}$$

and the equations may be linearized as follows:

**Table 2.** The Design with Experimental Values and Predicted Values of Removal \*

| No. | А               | В               | C (mg/L)          | Removal (%) |        |
|-----|-----------------|-----------------|-------------------|-------------|--------|
|     |                 |                 | -                 | Exp.        | Pred.  |
| 1   | +1(5.00)        | +1(6.50)        | +1(200.00)        | 83.80       | 88.08  |
| 2   | +1(5.00)        | -1(3.00)        | +1(200.00)        | 74.88       | 80.55  |
| 3   | 0 (3.00)        | 0(4.75)         | 0(150.00)         | 95.88       | 95.47  |
| 4   | -1(1.00)        | +1(6.50)        | -1(100.00)        | 64.95       | 57.59  |
| 5   | 0 (3.00)        | 0(4.75)         | -α(65.91)         | 94.46       | 99.22  |
| 6   | 0 (3.00)        | -α(1.81)        | 0(150.00)         | 28.86       | 44.03  |
| 7   | 0 (3.00)        | 0(4.75)         | 0(150.00)         | 95.93       | 95.47  |
| 8   | 0 (3.00)        | 0(4.75)         | 0(150.00)         | 95.29       | 95.47  |
| 9   | 0 (3.00)        | 0(4.75)         | $+\alpha(234.09)$ | 76.85       | 84.64  |
| 10  | -α(0.00)        | 0(4.75)         | 0(150.00)         | 0.00        | 18.78  |
| 11  | +1(5.00)        | +1(6.50)        | -1(100.00)        | 95.69       | 100.00 |
| 12  | 0 (3.00)        | $+\alpha(7.69)$ | 0(150.00)         | 80.00       | 76.37  |
| 13  | -1(1.00)        | -1(3.00)        | -1(100.00)        | 32.50       | 26.61  |
| 14  | 0 (3.00)        | 0(4.75)         | 0(150.00)         | 91.67       | 95.47  |
| 15  | 0 (3.00)        | 0(4.75)         | 0(150.00)         | 93.91       | 89.90  |
| 16  | -1(1.00)        | -1(3.00)        | +1(200.00)        | 40.63       | 27.91  |
| 17  | 0 (3.00)        | 0(4.75)         | 0(150.00)         | 94.56       | 95.47  |
| 18  | $+\alpha(6.36)$ | 0(4.75)         | 0(150.00)         | 93.83       | 89.90  |
| 19  | -1(1.00)        | +1(6.50)        | +1(200.00)        | 39.35       | 44.54  |
| 20  | +1(5.00)        | -1(3.00)        | -1(100.00)        | 91.67       | 84.85  |

<sup>\*</sup>Adsorption conditions: biomass concentration (factor A), pH (factor B), and initial copper concentration (factor C).

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m}$$
(5)

$$\ln q_e = \ln K_{\rm f} + \frac{1}{n} \ln C_e \tag{6}$$

where  $q_e$  and  $q_m$  represent the observed and maximum adsorption capacities (mg/g), respectively.  $C_e$  is the equilibrium concentration (mg/L), *b* is the equilibrium constant (L/mg),  $K_f$  is a measurement of biosorption capacity and *n* is the intensity of biosorption.

# 2.7. Thermodynamic Parameters

In order to confirm the spontaneity of the process, the energy and entropy factors should be considered. In this study, the change in free energy ( $\Delta G^{\circ}$ ), enthalpy ( $\Delta H^{\circ}$ ) and entropy ( $\Delta S^{\circ}$ ) were investigated as thermodynamic parameters to describe the thermodynamic behavior of the QQ strain and calculated by the following equations (Dundar et al.,2008):

$$\Delta G^{\circ} = -RT \ln b \tag{7}$$

$$\ln b = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT}$$
(8)

where *R*, *T* and *b* represent the gas constant (8.314 J/(mol·K)), solution temperature (K) and Langmuir equilibrium constant, respectively.

#### 2.8. Analytical Methods

The samples were withdrawn at equal time intervals except for special requirements and filtered through 0.45  $\mu$ m filters. The filtered samples were analyzed for residual copper concentration in the aqueous solution with an atomic absorption spectrophotometer (Analyst 700, USA). Before measuring the copper solutions with the AAS, the solutions were diluted with deionized water to ensure the heavy metal concentrations in the samples were linearly dependent on the absorbance detected. Removal rate ( $\eta$ , %) and copper biosorption ( $q_e$ , mg/g, dry weight) were calculated with the following formulas:

$$\eta = \frac{(C_0 - C_t)}{C_0} \times 100\%$$
(9)

$$q_e = \frac{(C_0 - C_e)V}{W} \tag{10}$$

where  $C_0$ ,  $C_t$  and  $C_e$  are referred to as the initial, residual and equilibrium copper concentrations (mg/L), respectively. *V* is the volume of copper solution (L) and *W* represents the dry weight (g) of the biomass. All of the experiments were duplicated and the average values were used in the calculations.

# 3. Results and discussions

# 3.1. Optimization of Biosorption

The design of the CCD in coded levels of the three independent variables is shown in Table 2 and the central point has been replicated six times. A quadratic second order polynomial equation (11) is expressed by the model and represents the relation among removal efficiency and biomass concentration (factor A), pH (factor B) and initial copper concentration (factor C). The removal rate of copper was used as the response (Y, %):

$$Y = -142.41 + 43.59A + 52.36B + 0.30C - 0.65AB - 0.014AC - 0.0418BC - 4.28A^2 - 4.08B^2 - 0.0005C^2$$
(11)

The statistical significance of the quadratic model, factors and their interactions at the factor levels were evaluated with analysis of variance (ANOVA) (Table 3). The significance of each factor was tested with an F-value and P-value. Generally, with a higher F-value and lower P-value, the corresponding factor is considered more significant. The determination of the coefficient  $R^2$  was used to check the fit of the model (Dwevedi et al., 2009). In this case, the F-value was 14.73 (corresponding to P-value 0.000), which indicated that the model was adequate. For the biosorption conditions, the Pvalue of A, B,  $A^2$ , and  $B^2$  were less than 0.05 (Table 3), which suggested that they were more significant factors than C, AB, AC, BC and  $C^2$ . The value of the determination coefficient  $R^2$ was found to be 0.930, which revealed that 93.00% of the response variability could be explained by the model. A larger  $R^2$  value indicated a better fit with the full quadratic equation

| Source | D.F.* | SS       | Mean Square | F-value | P-value    |
|--------|-------|----------|-------------|---------|------------|
|        |       |          |             |         | (Prob > F) |
| Model  | 9     | 14784.67 | 1642.74     | 14.73   | 0.000      |
| А      | 1     | 8396.19  | 8396.19     | 75.26   | 0.000      |
| В      | 1     | 1239.73  | 1239.73     | 11.11   | 0.008      |
| С      | 1     | 420.45   | 420.45      | 3.77    | 0.081      |
| AB     | 1     | 41.47    | 41.47       | 0.37    | 0.556      |
| AC     | 1     | 15.70    | 15.70       | 0.14    | 0.715      |
| BC     | 1     | 103.86   | 103.86      | 0.93    | 0.357      |
| $A^2$  | 1     | 3591.55  | 3591.55     | 32.19   | 0.000      |
| $B^2$  | 1     | 2263.01  | 2263.01     | 20.29   | 0.001      |
| $C^2$  | 1     | 31.04    | 31.04       | 0.28    | 0.609      |

Table 3. ANOVA Analysis for Full Quadratic (Eq. 11)

<sup>\*</sup>D.F.: degrees of freedom; SS: sum of squares



**Figure 1**. Response surface plot of biosorption: effects of biomass concentration (factor A) and pH (factor B) on biosorption.



**Figure 2**. Response surface plot of biosorption: effects of pH (factor B) and initial copper concentration (factor C) on biosorption.

(Equation 11) under the given experimental domain (Pan et al., 2008). The value of the adjusted determination coefficient was 0.867, which also showed more significance.

Response surface plots were used to determine the copper removal efficiency over different interactive variables, such as biomass concentration (factor A) with pH (factor B) (Figure 1), and pH (factor B) with initial copper concentration (factor C) (Figure 2). As shown in Figure 1, the copper removal efficiency increased with the increased biomass concentration from 1 to 4.6% (w/v). However, when the biomass concentration was greater than 4.6% (w/v), the copper removal efficiency decreased. The maximal removal efficiency was about 98%, which could be explained by the fact a higher concentration of biomass could provide a larger surface area as well as more binding sites. Otherwise, when the added biomass concentration was above the optimal dosage, the removal efficiency decreased due to the aggregation of biomass in the form of pellets, which reduced the exposed surface area of biomass and limited the accessibility of copper to the binding sites. Such results have been observed in previous reports (Bhainsa et al., 2008; Iqbal et al., 2004).

The P-value of pH was 0.008, which indicated that pH was the most important variable in copper biosorption (Figure 1). With a pH value increasing from 3 to 5.6, the removal efficiency of copper increased from 80% to 100% with a biomass concentration of 4.6%. The maximum removal efficiency of copper was observed at a pH of 5.6. At low pH, large quantities of hydrogen ions compete strongly with metal ions for biosorption sites (Özcan et al., 2005). As pH value increases, more biosorption sites could be exposed and carry negative charges for complexation with metal ions. Removal efficiency of copper decreased when pH was above 5.6. However, it was possible to observe the precipitation of copper, which interfered with the accumulation when pH was above 6.5 (Dursun, 2006). Similar results were also obtained from copper biosorption by immobilized Phanerochaete chrysosporium (Iqbal et al., 2004).

Figure 2 showed that the removal efficiency of copper decreased with the initial copper concentration increasing from 100 to 200 mg/L. It was observed from Table 3 that initial copper concentration had little effect on the response (P-value = 0.081), which was the same with the previous report (Kiran et al., 2007). It should be due to competition among metal ions for limited biosorption sites and the saturation of biosorption sites (Dőnmez et al., 2002). The predicted optimal conditions of copper biosorption were obtained by the regression analysis (Equation 11) using the response optimizer method. The optimal conditions were obtained as follows: a biomass concentration of 4.6% (w/v), a pH of 5.6 and an initial copper concentration of 100 mg/L. Validation experiments were performed in triplicate tests to verify the predicted results. Under the optimal conditions, the removal efficiency was 97% within 30 min, which was in good agreement with the predicted values.

#### 3.2. Effect of Contact Time and Biosorption Kinetics

The copper biosorption by the QQ strain at different contact times was displayed in Figure 3(a). Strain QQ had a strong adsorptive capacity for copper, and the biosorption of Copper was rapid for the first 15 min as a result of available binding sites on the biomass. On the other hand, Figure 3(a) showed that the biosorption equilibrium was approached within 30 min. Therefore, 30 min was confirmed as the optimum contact



**Figure 3**. (a) Effects of contact time on copper biosorption by Penicillium sp. QQ; (b) pseudo second-order kinetics for copper biosorption by Penicillium sp. QQ.

time for further experiments. Furthermore, biosorption of metal ions has previously been reported to be biphasic, which suggests the initial rapid phase was owing to the surface adsorption and the subsequent slow phase was due to the diffusion of metal ions into the inner part of the biomass (Pan et al., 2008; García-Rosales et al., 2010).

In order to analyze the biosorption kinetics of Copper onto the cells of the QQ strain, the pseudo-second-order kinetic model was adapted in this study. The kinetic rate equation is given as follows:

$$\frac{t}{q_{\rm t}} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \tag{12}$$

where  $q_t$  and  $q_e$  are the amounts of ion adsorbed at time t and at equilibrium (mg/g), respectively.  $K_2$  (g/(mg·min)) represented the rate constant of the pseudo-second-order adsorption reaction.

Figure 3(b) represents a very good compliance with the pseudo-second order equation for its high correlation coefficient (0.9521). The rate constant ( $K_2$ ) and  $q_e$  of the plot value are 0.002 (g/(mg·min)) and 29.67 (mg/g), respectively. The



**Figure 4**. Langmuir isotherm for copper biosorption by Penicillium sp. QQ:  $\blacksquare$ : 20 (°C);  $\triangleright$ : 30 (°C); •: 40 (°C).



**Figure 5**. Freundlich isotherm for copper biosorption by Penicillium sp. QQ:  $\blacksquare$ : 20 (°C);  $\blacktriangleright$ : 30 (°C);  $\bullet$ : 40 (°C).

results suggest the biosorption of copper onto the QQ strain follow the pseudo second-order kinetic reaction.

# **3.3.** Biosorption Isotherms and Thermodynamics of Copper Adsorption by the QQ Strain

The linearized Langmuir and Freundlich isotherms of copper adsorption by the QQ strain at different temperatures are given in Figure 4 and 5. The correlation coefficient values  $(R^2)$  and constant parameters were calculated and displayed in Table 4. Comparing the  $R^2$  values listed in Table 4, it could deduced the Freundich equation better fits the experimental data than the Langmuir equation, and also indicates the heterogeneity of the adsorption sites on the QQ strain (Sari et al., 2007). As seen in Table 4, the  $q_{max}$  from the Langmuir isotherm increased with an increase in temperature, which indicated the process was endothermic. A comparison of the copper biosorption capacity of the QQ strain with other biosorbents is shown in Table 5. It is clear the adsorption capacity of the QQ strain is higher than most of other biosorbents.

| Т    | Langmuir parameters   |        | Freundlich parameters |             |       |       |
|------|-----------------------|--------|-----------------------|-------------|-------|-------|
| (°C) | q <sub>m</sub> (mg/g) | b      | $R^2$                 | $K_f(mg/g)$ | 1/n   | $R^2$ |
|      |                       | (L/mg) |                       |             |       |       |
| 20   | 46.08                 | 0.031  | 0.981                 | 0.514       | 1.517 | 0.993 |
| 30   | 50.33                 | 0.030  | 0.979                 | 0.656       | 1.454 | 0.988 |
| 40   | 52.49                 | 0.048  | 0.977                 | 0.832       | 1.386 | 0.985 |

**Table 4.** Constants Simulated with Langmuir and Freundlich

 Models for Biosorption

**Table 5.** Comparison of Copper Biosorption Capacity ofStrain QQ with Other Biosorbents Copper

| Biosorbent                      | Capacity | Reference                |
|---------------------------------|----------|--------------------------|
|                                 | (mg/g)   |                          |
| Rhizopus oryzae                 | 19.40    | (Bhainsa et al., 2008)   |
| PEI-modified biomass            | 92.00    | (Deng et al., 2005)      |
| Natural trembling poplar forest | 29.76    | (Dundar et al., 2008)    |
| Phanerochaete chrysosporium     | 102.80   | (Iqbal et al., 2004)     |
| Enterobacter sp.                | 32.50    | (Lu et al., 2006)        |
| Bacillus sp.                    | 16.30    | (Tunali et al., 2006)    |
| Pseudomonas putida              | 15.80    | (Chen et al., 2005)      |
| Thiobacillus ferrooxidans       | 39.80    | (Liu et al., 2004)       |
| Sphaerotilus natans             | 5.40     | (Beolchini et al., 2006) |
| Strain QQ                       | 52.49    | This study               |

Table 6. The Thermodynamic Constants of Biosorption

| T (°C) | $\Delta G (KJ/mol)$ | Mean $\Delta H$ (KJ/mol) | $\Delta S$ (KJ/mol) |
|--------|---------------------|--------------------------|---------------------|
| 20     | -18.744             |                          |                     |
| 30     | -19.762             | 11.144                   | 0.102               |
| 40     | -21.134             |                          |                     |
|        |                     |                          |                     |

The thermodynamic parameters such as free energy  $(\Delta G^{\circ})$ , enthalpy  $(\Delta H^{\circ})$  and entropy  $(\Delta S^{\circ})$  are summarized in Table 6. The  $(\Delta H^{\circ})$  and  $(\Delta S^{\circ})$  are calculated from the slope and intercept of the plot in Figure 6, respectively. As shown in Table 6, the values of free energy  $(\Delta G^{\circ})$  are all negative, which confirms the biosorption process is spontaneous. The positive value of enthalpy  $(\Delta H^{\circ})$  demonstrated that the adsorption process was endothermic in nature. Positive values of  $\Delta S^{\circ}$  suggest increased randomness at the solid-solution interface, when copper is fixed on the active sites of the biosorbents (Bulut et al., 2007).

#### 4. Conclusions

The adsorption properties of *Penicillium* sp. QQ were studied for copper removal from aqueous solution.,The optimal adsorption conditions and the maximum removal efficiency were consistent with the model prediction determined by response surface methodology. The kinetics of the adsorption processes were best described by the pseudo-second-order kinetic model. Moreover, the Langmuir and Freundlich isotherms were used to represent the experimental data, and the models fit the data well. Meanwhile, the negative value of  $\Delta G^{\circ}$  and positive value of  $\Delta S^{\circ}$  showed that the copper adsorption on strain QQ was feasible and spontaneous. The positive value of  $\Delta H^{\circ}$  confirmed the endothermic nature of biosorption



Figure 6. Variation of ln b with reciprocal of temperature.

by strain QQ. The present work showed that *Penicillium* sp. QQ could be utilized as a highly efficient adsorbent in the field application of heavy metal removal.

Acknowledgments. This work was supported by the Talented Youth Project (2008F3106) and Science Project of the Education Department of Fujian Province (JA08224).

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