

Full Length Research Paper

# Isotherm and thermodynamic studies of the biosorption of copper (II) ions by *Erythrodontium barteri*

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Accepted 24 October, 2007

The biosorption of Cu(II) from dilute aqueous solution using *Erythrodontium barteri* as a biosorbent has been studied as a function of pH, contact time and initial Cu(II) ion concentration at the temperature of 27°C. The residual Cu(II) in solution was determined using atomic absorption spectrophotometer. The pH study shows that pH dependence of biosorption and optimum pH was 5. The study on contact time shows that the biosorption is time dependent and maximum biosorption was obtained after 150 min. The adsorption isotherms obtained fitted well into the Freundlich and Langmuir isotherms. The

Freundlich equation obtained is  $\log \Gamma = 0.8549 \log C_e + 1.5566$  while the Langmuir equation is:  $\frac{1}{\Gamma} =$

$0.0254/C_e + 0.0026$  with correlation factors of 0.9917 and 0.9907, respectively. The standard deviations are 0.0159 and 0.0006, respectively. The free energy change ( $\Delta G^\circ$ ) obtained for the biosorption of Cu(II) at the temperature of 297K, initial Cu(II) concentration of 100 mgL<sup>-1</sup> and pH 5 is -11.108 kJmol<sup>-1</sup>. This result indicates that the biosorption process is highly spontaneous and therefore shows that *Erythrodontium barteri* biomass could be successfully used for the biosorption of Cu(II) from waste streams.

**Key words:** Biosorption, *Erythrodontium barteri*, copper(II), isotherm.

## INTRODUCTION

Heavy metals are groups of pollutants, which are not biodegradable and tend to accumulate in living organisms (Koby et al., 2005). Copper, which is of main interest in this study, is an important metal used in electroplating industries. It is not acutely toxic to human, but its extensive use and increasing levels in the environment may cause serious health hazards (Davis et al., 2003).

Conventional techniques for removing dissolved heavy metals include chemical precipitation, carbon adsorption, electrolytic recovery, ion-exchange, chelation and solvent extraction or liquid membrane separation (Vasudevan et al., 2003; Gökşungur et al., 2005; Júnior et al., 2003; Lodeiro et al., 2005; Liu et al., 2006; Sharma et al., 2006). These techniques are sometimes restricted because of technical or economic constraints as a result of high capital and operational cost. An alternative approach

to this technique is biosorption process, which offers potential advantages such as low operating cost, minimization of the volume of the chemical and biological sludge to be disposed off and high efficiency in detoxifying very dilute effluent.

Previous studies show that biomass of different plants and animals have been employed as biosorbents in the biosorption of metal ions from aqueous solutions. Such materials include baker's yeast (Vasudevan et al., 2003; Gökşungur et al., 2005), *Aspergillus niger* (Júnior et al., 2003); *Enterobacter sp.* J1 (Lu et al., 2006) and Pang Da Hai (Liu et al., 2006). Others are marine macroalgae (Lodeiro et al., 2005); *Moringa oleifera* (Sharma et al., 2006), coconut husk (Babarinde and Oyedipe, 2001), human scalp hair (Babarinde et al., 2002), crab shell (Kim, 2004; Vijayarghavan et al., 2006) and agricultural by-products (Abia et al., 2002; Abia et al., 2003), *Coco nucifera* (Conrad and Hansen, 2007), *Microcystis sp.* (Pradhan et al., 2007), wood sawdust (Sciban et al., 2007), Sgacane

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bagasse (Karnitz et al., 2007), palm shell activated carbon (Issabayeva et al., 2006) and water hyacinth (Hassan et al., 2007)

This study was carried out to investigate the biosorption of Cu (II) from aqueous solution using *Erythrodontium barteri* biomass. The effects of parameters such as pH, contact time, initial metal concentration and temperature were studied. The kinetics and thermodynamics of biosorption were systematically studied. The biosorption efficiency of the metal from loaded biosorbent was determined to further evaluate the feasibility of applying this biomass in practical Cu(II) removal process.

## MATERIALS AND METHODS

### Preparation of materials

The *E. barteri*, which was used as the biosorbent, was obtained from a tree in Saki, Oyo State, Nigeria. It was stored in a cooled dry place till the time of usage. The chemicals used for the study were analytical grades of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , NaOH and  $\text{HNO}_3$ . Stock solution of  $1000 \text{ mgL}^{-1}$  Cu (II) was prepared from  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . The solutions used for the study were obtained by dilution of the stock solution to the required concentrations. The initial pH of each of the solutions was adjusted to the optimum pH 5 by the addition of  $\text{HNO}_3$  or NaOH solution, except for the experiment on the effect of pH where the study was carried out at different pH values. Fresh dilution of the stock solution was carried out for each biosorption experiment.

### Batch biosorption experiments

The initial experiments were conducted at  $27^\circ\text{C}$  to examine the effects of initial solution pH, contact time and initial Cu(II) concentration on biosorption of the copper ions. Each of these experiments was conducted in a thermostated water bath (Haake Wia). The biomass was separated from the residual sorbate solution by centrifugation and the analysis of residual metal ions was carried out using Atomic Absorption Spectrophotometer (Buck Scientific 210 VGP). The removal efficiency of Cu(II) and the mean value was also calculated using the expression:

$$\% \text{ Removal Efficiency} = 100 (C_i - C_e) / C_i \quad (1)$$

where  $C_i$  = initial metal ion concentration ( $\text{mg L}^{-1}$ );  $C_e$  = equilibrium metal ion concentration ( $\text{mgL}^{-1}$ )

### Effect of solution pH on biosorption

The effect of initial pH on the biosorption of Cu(II) using *E. barteri* biomass was investigated at  $27^\circ\text{C}$ . The effect of pH on the biosorption of metal ion was carried out within the range that would not be influenced by the metal precipitated (Pavasant et al., 2006). It has been reported that the suitable pH range for the sorption of Cu(II) ions should be pH 1 - 6. The procedure used is similar to those earlier reported (Vasudevan et al., 2003; Xu et al., 2006; Babarinde et al., 2006). The effect of initial pH on the biosorption of Cu(II) was done at the temperature of  $27^\circ\text{C}$  by contacting 0.2 g of *E. barteri* biomass with 25 ml of  $100 \text{ mg L}^{-1}$  Cu(II) solution in a glass tube.

The studies were conducted at pH values of 1, 2, 3, 4, 5, and 6. The glass tubes containing the solution mixture were placed in a thermostated water bath for 24 h. The biomass was later removed from the solution and the residual Cu(II) concentration in the solu-

tion was then analyzed. The residual concentration in the solution was performed in triplicates and the mean value was determined for each pH. Subsequent experiments were conducted at pH 5.

### Effect of contact time on biosorption

Batch biosorption tests were carried out at different contact time intervals (5 - 300 min) at initial Cu (II) concentration of  $100 \text{ mg L}^{-1}$ . This was done by contacting 0.2 g of *E. barteri* with 25 ml of the solution at the pH 5. The residual Cu (II) concentration in each solution was then analyzed using Atomic Absorption Spectrophotometer.

### Effect of initial Cu(II) concentration on biosorption

Batch biosorption study was carried out in the concentration range of 10 -  $100 \text{ mg L}^{-1}$ . 0.2 g of the *E. barteri* biomass was weighed into each of the tubes used and 25 ml of the Cu(II) solution was measured into each tube containing the biomass at pH 5. The biosorption mixture at temperature of  $27^\circ\text{C}$  was left in a water bath for 4 h. The *E. barteri* biomass was removed from the solution and the concentration of residual Cu(II) in each solution was determined. The results obtained were analyzed using both Freundlich (Freundlich, 1906) and Langmuir (Langmuir, 1918) isotherms. The Freundlich isotherm in the linearized form is

$$\log \Gamma = (1/n) \log C_e + \log K \quad (2)$$

The Langmuir isotherm in the linearized form is

$$\frac{1}{\Gamma} = \frac{1}{b_m} \frac{1}{C_e} + \frac{1}{\Gamma_m} \quad (3)$$

where  $b_m$  is a coefficient related to affinity between the sorbent and sorbate, and  $\Gamma_m$  is the maximum sorbate uptake under the given condition.

### Effect of temperature variation on biosorption of Cu(II)

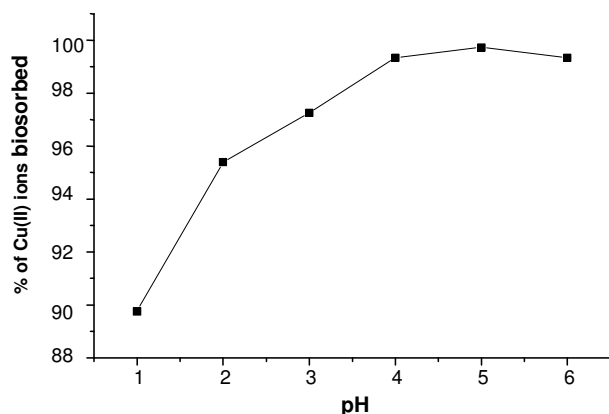
The batch biosorption process was studied at different temperatures of 24, 27, 34 and  $37^\circ\text{C}$  in order to investigate the effect of temperature on the biosorption process. This was done by contacting 0.2 g *E. barteri* with 25 ml of  $100 \text{ mg L}^{-1}$  Cu(II) solution at pH 5 for 180 min. The result was used to investigate the thermodynamics of the biosorption process.

## RESULTS AND DISCUSSION

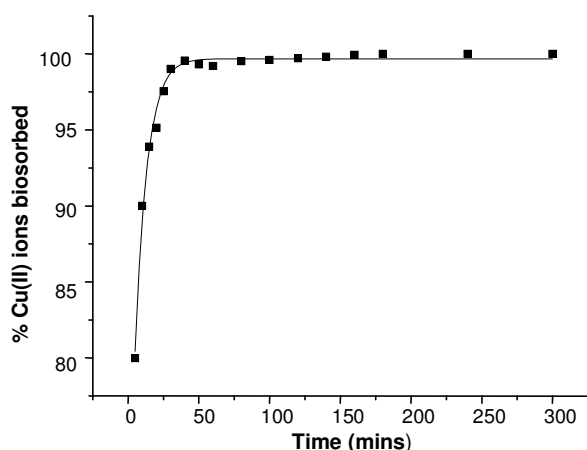
### Effect of pH on biosorption of Cu(II)

The result of the pH study is shown in Figure 1. It shows that the maximum biosorption was obtained at pH 5. The percentage Cu(II) ions adsorbed are slightly lower at other pH values. This result confirms the earlier reports that biosorption of Cu(II) is pH-dependent. It reveals that the optimum biosorption of Cu(II) is obtained at pH 5 and that initial pH is very essential in the removal of Cu(II) from aqueous solution using *E. barteri*.

As a result of net negative charge on the cell wall of the biosorbent above the isoelectric point the ionic state of the ligands such as carbonyl, phosphate and amino gro-



**Figure 1.** Effect of pH on the biosorption of Cu(II) using *E. barteri* at 27°C and initial metal ion concentration of 100 mgL<sup>-1</sup>

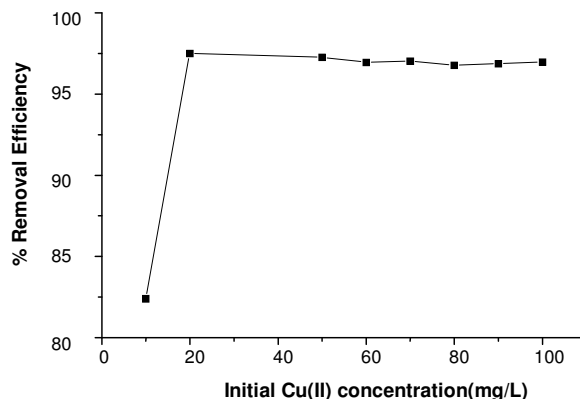


**Figure 2.** Time course for the biosorption of Cu(II) using *Erythrodontium barteri* at 27°C, pH 5 and initial metal ion concentration of 100 mgL<sup>-1</sup>

groups favours reaction with Cu<sup>2+</sup>. On the other hand, on decreasing pH, the net charge on the cell wall is positive thereby inhibiting the approach of positively charge ions (Göksungur et al., 2005). As the pH increased, the ligands in biomass would be exposed, increasing the attraction of metal ions with positive charge and allowing the biosorption on the biomass surface. The result suggests that optimum biosorption is obtained at pH 5.0 that initial pH would play a vital role in the removal of Cu<sup>2+</sup> from aqueous solutions using *E. barteri*.

#### Effect of contact time on biosorption of Cu(II)

The result of the effect of contact time on the biosorption of Cu(II) from aqueous solution is shown in Figure 2. It is observed that the biosorptive capacity of Cu(II) metal ion increases with contact time. The biosorption of Cu(II) by the biomass was rapid for the first 30 min as a result of the free binding sites on the biomass. The biosorption ap-



**Figure 3.** Removal Efficiency of the biosorption of Cu(II) using *Erythrodontium barteri* at 27°C, pH 5 and initial metal ion concentration of 100 mgL<sup>-1</sup>

proach equilibrium within 100 min as the binding sites on the biomass were being used up. Equilibrium was attained after 250 min. The period of 300 min was therefore used for the biosorption of Cu(II) by *E. barteri*.

Biosorption of metal ions has been reported to be biphasic (Liu et al, 2006). The initial fast phase occurs due to surface adsorption on the biomass. The subsequent slow phase occurs due to diffusion of the metal ions into the inner part of the biomass. It is observed in Figure 2 that the metal biosorption rate is high at the beginning but plateau values were obtained in 250 min, similar to what was reported by Liu and coworkers (Liu et al., 2006).

#### Effect of initial Cu(II) concentration on biosorption

The effect of initial Cu(II) ion concentration on the biosorption capacity shows that up to 97.50% of the metal ion was biosorbed at the initial metal ion concentration of 100 mg L<sup>-1</sup> within the first 300 min. As shown in Figure 3 the efficiency increases as the initial metal ion concentration increases. The result implies that the gradual increase in the efficiency of the biomass shows nearness to saturation of the available binding sites.

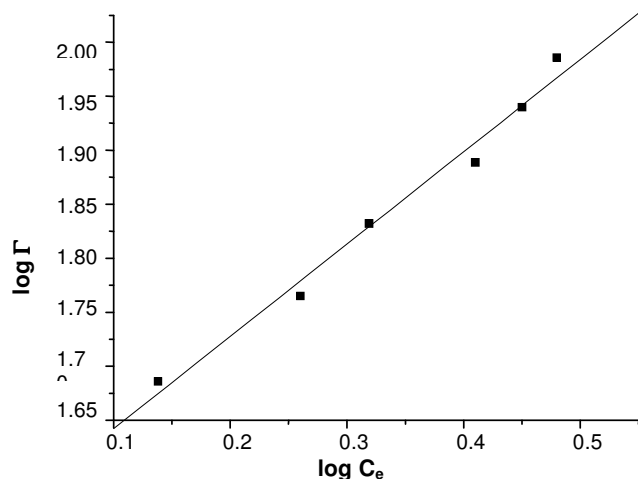
The experimental data fitted well into both Freundlich and Langmuir isotherm models as presented in Figures 4 and 5, respectively. The isothermal biosorption parameters for these isotherms are shown in Table 1. These Freundlich and Langmuir parameters compare well with those of other sorbents that have been reported (Pavasant et al., 2006). These isothermal biosorption parameters show that *E. barteri* is a good biosorbent for the uptake of Cu(II) from aqueous solution and can therefore be recommended for the uptake of Cu(II) from industrial waste waters.

#### Effect of temperature on the biosorption of Cu(II) by *Erythrodontium barteri* biomass

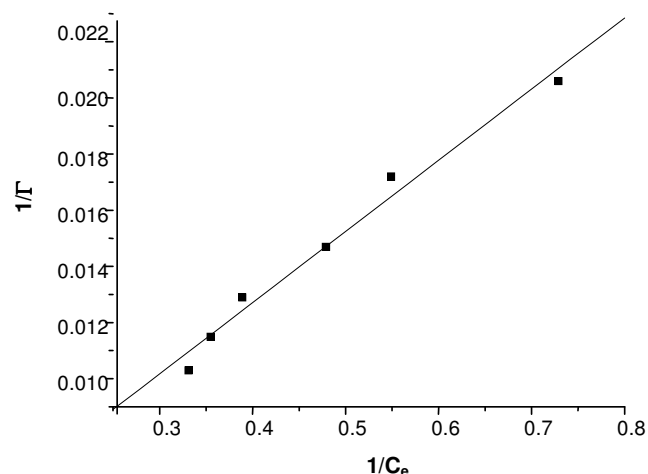
The biosorption experiment can be regarded as a hetero-

**Table 1.** Freundlich and Langmuir isothermal biosorption parameters for the biosorption of Cu(II) at 27°C and pH 5 using *Erythrodontium barteri* biomass.

Freundlich Parameters				Langmuir Parameters			
n	K	R	S.D.	b <sub>m</sub>	Γ <sub>m</sub>	R	S.D.
1.1697	36.022	0.9917	0.0159	39.432	390.625	0.9907	0.0006



**Figure 4.** Freundlich isotherm for the biosorption of Cu(II) using erythrodontium barteri at 27°C, pH 5 and initial metal ion concentration of 100 mgL<sup>-1</sup>.



**Figure 5.** Langmuir isotherm for the biosorption of Cu(II) using erythrodontium barteri at 27°C, pH 5 and initial metal ion concentration of 100 mgL<sup>-1</sup>.

geneous and reversible process at equilibrium. The apparent equilibrium constant for the process has been shown to be

$$K_c = C_{ad}/C_e \quad (4)$$

The Gibbs free energy of the biosorption process (Khan et al., 2005) is thus given as

$$\Delta G^\circ = -RT \ln K_c \quad (5)$$

where  $\Delta G^\circ$  is the standard Gibbs free energy change for the biosorption process in J mol<sup>-1</sup>; R, the universal gas constant (8.314 J mol<sup>-1</sup>K<sup>-1</sup>) while T is the temperature in K. The effect of temperature on the biosorption of Cu(II) by *E. barteri* is reported in Table 2 and shown in Figure 6.

The free energy change ( $\Delta G^\circ$ ) obtained for the biosorption of Cu(II) at 297 K, initial Cu(II) concentration of 100 mg L<sup>-1</sup>, and pH 5 is -11.108 kJ mol<sup>-1</sup>. The large negative value of  $\Delta G^\circ$  obtained for the biosorption of Cu(II) shows spontaneity of the biosorption process at that temperature. However, the result in Table 2 shows that the free energy values increase positively with increase in temperature. This implies that the spontaneity of the biosorption process reduces with increase in temperature. Consequently, the biosorption of the Cu(II) using *E. barteri*

**Table 2.** Free energy values obtained from the biosorption of Cu(II) using *Erythrodontium barteri* biomass at different temperatures

Temperature (K)	$\Delta G^\circ$ (kJmol <sup>-1</sup> )
297	-11.108
300	-10.150
307	-9.149
310	-8.626

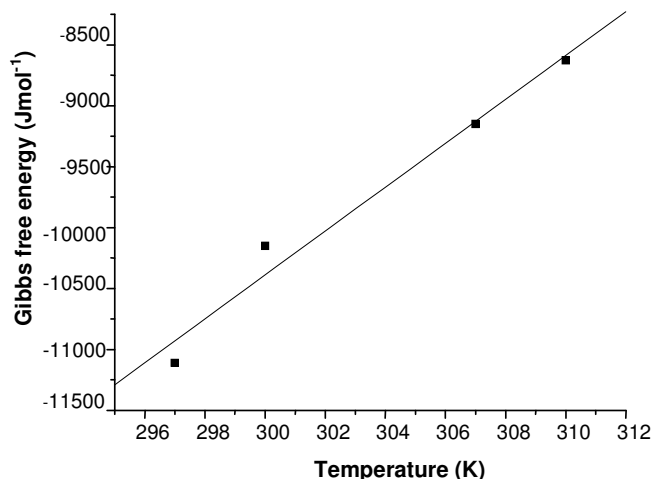
biomass is exothermic hence the process is better carried out at low temperature. From thermodynamics,

$$\Delta G^\circ = \Delta H - T \Delta S \quad (6)$$

Or

$$\Delta G^\circ = -\Delta S (T) + \Delta H \quad (7)$$

A plot of T against  $\Delta G^\circ$  gives a straight line with slope  $-\Delta S$  and an intercept of  $\Delta H$ . In Fig. 6, the slope is 0.18017 J mol<sup>-1</sup> while the intercept is -64.4397 J mol<sup>-1</sup>. Therefore, the values of the entropy and enthalpy are -0.18017 J mol<sup>-1</sup> and -64.4397 J mol<sup>-1</sup>, respectively. The increase in the value of the free energy with increase in temperature indicates that the biosorption process is exothermic and it



**Figure 6.** The free energy plot for the biosorption of Cu(II) using erythrodontium barteri at pH 5 and initial metal ion concentration of 100 mgL<sup>-1</sup>

is thereby favoured with decrease in temperature.

## Conclusions

The results of various studies show that *E. barteri* biomass has some capacity to biosorb Cu(II) from solution. Different variables such as solution pH, contact time and temperature influenced the adsorptive capacity. This study therefore shows that *E. barteri* biomass could be prescribed as a biosorbent in the treatment of waste water containing Cu(II) ions.

## ACKNOWLEDGEMENTS

The authors are grateful to Dr. Remi Ogunfowokan of Obafemi Awolowo University, Ile-Ife and Mr J. Adegoke of the Department of Chemical Sciences, Olabisi Onabanjo University, Ago-Iwoye for technical assistance.

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