



## Equilibrium and Kinetic Studies of Pb (II) Ions Biosorption by Immobilized Cells of *Pycnoporus sanguineus*

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### ABSTRACT

The biosorption of Pb (II) ions from aqueous solution onto immobilized cells of *Pycnoporus sanguineus* (*P. sanguineus*) was investigated by considering the effect of pH, initial lead (II) concentration and biomass loading at 150 rpm for 2 hr. Results showed that the uptake of Pb (II) ions increased with the increase of initial Pb (II) concentration and pH. The optimum pH for Pb (II) biosorption was at pH 4 with initial Pb (II) concentration of 3.12 mg/g. Langmuir, Freundlich and Redlich-Peterson isotherm models fitted the data well with correlation coefficients  $R^2 > 0.90$ . The change in biosorption capacity with time was found to fit the pseudo-second order followed by intraparticle diffusion equation at different temperatures.

**Keywords:** Biosorption, equilibrium, kinetics, lead, *Pycnoporus sanguineus*, immobilized cells, fungus, heavy metals

### ABBREVIATIONS

|           |  |                                    |
|-----------|--|------------------------------------|
| $a_{rp}$  | Redlich-Peterson isotherm constant                             | (dm <sup>3</sup> /mg) <sup>β</sup> |
| $\beta$   | Redlich-Peterson isotherm constant                             |                                    |
| $C_e$     | equilibrium concentration                                      | (mg/L);                            |
| $C_i$     | initial concentration  | (mg/L)                             |
| $C_f$     | final or equilibrium concentration                             | (mg/L)                             |
| $k_1$     | rate constant of first-order biosorption                       | (1/min)                            |
| $k_2$     | rate constant of second-order biosorption                      | (g/mg min)                         |
| $K_b$     | Langmuir equilibrium constant                                  | (dm <sup>3</sup> /mg)              |
| $K_f$     | Freundlich constant  |                                    |
| $K_{rp}$  | Redlich-Peterson isotherm constant                             | (dm <sup>3</sup> /mg)              |
| $n$       | Freundlich constant  |                                    |
| $q$       | metal ions biosorbed per g of biomass                          | (mg/g)                             |
| $q_{max}$ | maximum specific uptake corresponding to the site's saturation | (mg/g)                             |
| $q_e$     | amount of metal ions uptake at equilibrium                     | (mg/g)                             |
| $q_t$     | amounts of adsorbed Pb(II) ions on the biosorbent at time $t$  | (mg/g)                             |
| $V$       | volume of metal solution in the flask                          | (L)                                |
| $W$       | weight of biosorbent   | (g)                                |

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## INTRODUCTION

The presence of lead (Pb (II)) in the environment such as in soil and water poses serious problems to members of the ecological system, including humans. It may come from various industrial sources e.g. battery manufacturing, textile, mining and metal finishing (Tunali *et al.*, 2006). Removal of the Pb (II) ions from water and industrial wastewater have become a challenge to researchers as it has been classified the premier environmental poison among the toxic metals existing in the world (Rai and Amit, 2002). Exposure to this metal at high levels can damage the reproductive system, kidneys, nervous system and cause mental retardation (Sheng *et al.*, 2004). Conventional methods used to remove metal ions from industrial effluents, e.g. chemical precipitation, membrane separation, activated carbon adsorption and ion exchange (Beszedits, 1983; Metcalf and Eddy, 1991), may not be usable for removing lead due to inefficiencies, high operational costs at low concentrations of the metal ion in the treated water (Arica *et al.*, 2001) and difficulties in disposing of the metal sludge (Malkoc and Nuhoglu, 2005).

In the past few decades, biosorption has become an alternative method used to remove heavy metals from wastewater (Kim *et al.*, 2003). Biosorption may involve several chemical processes including adsorption, covalent binding and ion-exchange (Tobin *et al.*, 1994). Heavy metals biosorption that utilizes microorganisms as a biosorbent has received great attention due to its capability to remove metal ions from wastewater treatment or contaminated wastewater (Aksu and Acikel, 2000). Metal binding by microorganisms can be classified as extracellular accumulation, cell surface sorption and intracellular accumulation (Ahalya *et al.*, 2003; Veglio and Beolchini, 1997).

Fungi have been used as a biosorbent of heavy metals for years (Tunali *et al.*, 2006). Cell walls of fungi consists of three major biopolymers including polysaccharides, protein and nucleic acids (Aloysius *et al.*, 1999). These biopolymers carry many functional groups such as carboxylate, hydroxyl, amino groups and phosphate which provide active binding sites for metals biosorption to occur (Aloysius *et al.*, 1999; Tunali *et al.*, 2006). Both living and dead fungal cells can take up metal ions (Brady and Tobin, 1994). Although, several fungal biosorbents (*Aspergillus niger*, *Cephalosporium aphidicola*, *Pycnoporus sanguineus* and *Trametes versicolor*) have been evaluated as potential biosorbents for the removal of heavy metals from aqueous solutions (Bayramoglu *et al.*, 2003; Kapoor and Viraraghavan, 1997; Mashitah *et al.*, 1999; Tunali *et al.*, 2006), less studies were reported on Pb (II) biosorption by live immobilized cell system of *P. sanguineus* in a batch mode. Immobilized cell concept offers additional advantages over free cells including regeneration and reuse of the biosorbent, easier solid liquid separation, enhanced mechanical strength of microbials and minimal clogging problems in continuous operations (Ting and Sun, 2000; Arica *et al.*, 2001; Bayramoglu *et al.*, 2003; Annadurai *et al.*, 2007; Vijayaraghavan and Yan, 2007).

Hence, the main objective of this study was to determine the potential of immobilized living cells of *P. sanguineus* to adsorb Pb (II) ions in shake flask culture. Adsorption isotherms and kinetic models were also evaluated.

## MATERIAL AND METHODS

### *Microorganism and Production Medium*

*P. sanguineus* capable of adsorbing heavy metals was obtained from the Forest Research Institute of Malaysia (FRIM), Kepong, Selangor (Mashitah *et al.*, 1999). It was maintained

by weekly transfer on malt extract agar slants incubated at 30°C for 6 days, after which the slants were stored at 4°C until required. The composition of the production medium comprised of (g/L): glucose 20, yeast extract 10 and malt extract 10. The pH of the medium was adjusted to 9.0 prior to autoclaving at 121°C (1.5 bar) for 15 minutes.

#### *Immobilized Cell Preparation*

A cell suspension was prepared by inoculating a stock culture of *P. sanguineus* onto malt extract agar plates and incubating them at 30°C for 6 days. The mycelial mat formed was scraped off by using a sterile blade and mixed with 10 ml sterile Tween 20 solution prior putting it into a sterile sampling bottle (100 ml). The sampling bottle was vortexed for 3 minutes so that the mycelium was evenly distributed in the liquid.

Fifteen ml of the cell suspension was inoculated into an Erlenmeyer flask containing 135 ml of the production medium. The flask was incubated on a rotary shaker at 30°C, 150 rpm for 66 hr. The harvested sample was centrifuged at 3500 rpm for 4 minutes at 25°C and known as free cells of *P. sanguineus*. Immobilized cells of *P. sanguineus* beads were prepared by dropping a mixture of 1.5 % (w/v) sodium alginate solution and *P. sanguineus* mycelium into a 2% (w/v) CaCl<sub>2</sub> solution stirred slowly at room temperature, 25± 3.0°C. The beads were stirred slowly for 30 minutes, then collected by filtration, washed three times with sterile deionized water and stored in Tris-HCl buffer (pH 7) at 4°C until used.

#### *Preparation of Metal Ions*

Metal solutions were prepared by diluting 1000 mg/L of Pb (NO<sub>3</sub>)<sub>2</sub> (Mallinckrodt) solutions with deionized water to a desired range of 50 to 300 mg/L. For each solution, the initial metal concentrations and the concentrations in the samples after biosorption treatment were determined using an Atomic Absorption Spectrophotometer (Model Shimadzu AA 6650).

#### *Batch Biosorption Procedures*

The biosorption of Pb (II) ions by the immobilized *P. sanguineus* from aqueous solution was evaluated in batch biosorption equilibrium experiments. Effects of initial Pb (II) ion concentration, pH, biomass loading and temperature on the biosorption rate and capacity were examined.

The effect of solution pH between 2 and 4 on the biosorption of Pb (II) by the immobilized *P. sanguineus* preparation was evaluated in cultures kept at 150 rpm, 30°C for 2 hr. For initial Pb (II) concentration, the biosorption studies were conducted at pH 4 as described above, but the concentration of Pb (II) varied from 58 to 300 mg/L. The effect of biomass loading was evaluated at 1 to 6 g with other procedures as described previously. For the equilibrium study, the initial Pb (II) concentration was 100 mg/L and the working pH was 4. The contact time varied from 15 to 120 min at 30°C (303 K), 35°C (308 K) and 40°C (313 K), respectively.

The amount of Pb (II) bound by the biosorbent was calculated as:

$$q = \frac{V(C_i - C_f)}{W} \quad (1)$$

where  $q$  is mg of metal biosorbed per g of biomass (mg/g),  $C_i$  (mg/L) is the initial concentration,  $C_f$  (mg/L) is the final or equilibrium concentration,  $V$  (L) is the volume of metal solution in the flask and  $W$  (g) is the weight of the biosorbent. Each experiment was repeated three times and the results given are average values. Samples taken after the desired incubation period were measured with an Atomic Absorption Spectrophotometer (Model Shimadzu AA 6650).

Kinetics experiments were carried out at known Pb (II) concentrations with various biosorbent loadings and shaking at 150 rpm. At pre-determined interval times, samples were withdrawn, filtered and the Pb (II) concentration measured with an Atomic Absorption Spectrophotometer (Model Shimadzu AA 6650).

#### *Equilibrium Isotherm and Kinetics Studies*

##### i. Equilibrium isotherm models

Langmuir, Freundlich and Redlich-Peterson models have all been used to determine the sorption equilibrium between a solid biosorbent and metal ions. The Langmuir model assumes that a monomolecular layer is formed when biosorption occurs and that the adsorbed molecules do not interact with one another (Langmuir, 1916; Malkoc and Nuhoglu, 2003).

The Langmuir equation is:

$$q_e = \frac{q_{\max} K_b C_e}{1 + K_b C_e} \quad (2)$$

where  $q_{\max}$  is the maximum specific uptake corresponding to the site saturation,  $K_b$  is an equilibrium constant ( $\text{dm}^3/\text{mg}$ ) and both parameters can be determined from a linearised form of Eq. (3) as followed:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} K_b} + \frac{C_e}{q_{\max}} \quad (3)$$

where  $C_e$  is the equilibrium concentration (mg/L);  $q_e$  is the amount of metal ion uptake at equilibrium (mg/g),  $q_{\max}$  is  $q_e$  for a complete monolayer (mg/g) and  $K_b$  is the equilibrium constant ( $\text{dm}^3/\text{mg}$ ).

The Freundlich isotherm model (Freundlich, 1906) is

$$q_e = K_f C_e^n \quad (4)$$

and the equation may be linearised and described as:

$$\ln q_e = \frac{1}{n} \ln C_e + \ln K_f \quad (5)$$

where  $q_e$  is the amount of metal ion uptake (mg/g);  $C_e$  is the equilibrium concentration (mg/L);  $K_f$  and  $n$  are Freundlich constants and can be determined by plotting  $\ln q_e$  versus  $\ln C_e$ .

The Redlich-Peterson isotherm (Redlich and Peterson, 1959) has three parameters and incorporates features from both the Langmuir and the Freundlich isotherms. It can be described as:

$$q_e = \frac{K_{rp}C_e}{1 + a_{rp}C_e^\beta} \quad (6)$$

where  $K_{rp}$ ,  $a_{rp}$  and  $\beta$  ( $0 < \beta < 1$ ) are the Redlich-Peterson isotherm constants. These isotherms can be evaluated from a linear plot of

$$\ln\left(K_{rp} \frac{C_e}{q_e} - 1\right) = \beta \ln(C_e) + \ln a_{rp} \quad (7)$$

using a nonlinear regression method.

#### ii. Kinetic modeling

Kinetic models such as pseudo first-order, pseudo second-order and intraparticle diffusion equations have been used to evaluate the mechanisms of biosorption and potential rate controlling steps such as mass transport and chemical reaction processes. The first-order rate expression of Lagergren (Lagergren, 1898) based on solid capacity was used:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t \quad (8)$$

where  $q_e$  and  $q_t$  are the amounts of Pb(II) ions adsorbed at equilibrium and at time  $t$  (respectively mg/g), and  $k_1$ , is the rate constant of first-order biosorption ( $\text{min}^{-1}$ ). The pseudo second-order equation is also based on the sorption capacity of the solid phase and can be obtained from (Arica et al., 2001):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e^2}t \quad (9)$$

where  $k_2$  is the rate constant of second-order biosorption (g/mg min) and  $q_e$  is the biosorption capacity calculated by the pseudo-second order kinetic model (mg/g).

The intraparticle diffusion equation was introduced to indicate the behaviour of intraparticle diffusion as the rate limiting step in the biosorption (Sharma and Foster, 1994). The equation is given as:

$$R = K_s t^b \quad (10)$$

where  $R$  is the percent metal adsorbed,  $t$  is the contact time (min),  $b$  is the gradient of linear plots and  $K_s$  is the intraparticle diffusion constant.

## RESULTS AND DISCUSSION

### *Effect of Initial Pb (II) Ions Concentrations*

The effect of initial Pb (II) ion concentration on Pb (II) uptake was studied in a range from 58 to 300 mg/L (Fig. 1). Increasing the initial Pb (II) concentration increased the amount of Pb (II) taken up. The increase in initial Pb (II) concentration could increase the mass transfer driving force of the ions between the aqueous and solid phases (Aksu, 2002; Fawzi and Sameer, 2000; Malkoc and Nuhoglu, 2005). However, at a higher concentration the percentage of Pb (II) ions removed decrease. For an initial Pb (II) ion concentration of 58 mg/L, 96% of the ions were removed within 2 hours, whereas only 39% of the ions were removed from a 300 mg/L solution in the same time period. Thus, at higher metal concentrations, the available sites at which the biosorption process occurs are limited and the biosorption yield decline (Malkoc and Nuhoglu, 2005).

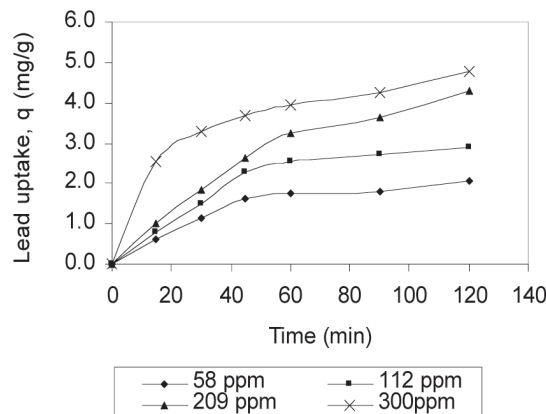


Fig. 1: Effect of initial metal concentration on the biosorption of Pb (II) ions by immobilized cells of *P. sanguineus* (Condition: pH 4.0; biomass loading 3 g; agitation 150 rpm)

### *Effect of pH*

Heavy metals biosorption was found to be significantly dependent on pH (Malkoc and Nuhoglu, 2005). To determine the effect of pH on Pb (II) removal by immobilized cells of *P. sanguineus*, biosorption studies were carried out at pH 2.0, 3.0 and 4.0. Previous studies stated that at lower pH, the surface charge on the cells became positive and that metal cations and protons compete for binding sites on cell walls, which results in lower Pb (II) uptake from the medium (Malkoc and Nuhoglu, 2005). At pH above the isoelectric point, the surface charges are negative and the ionic state of ligands such as amino groups, carboxyls and phosphates promote reactions with the Pb (II) ions, resulting in rapid efficient binding (Arica *et al.*, 2001). In most of Pb (II) ion removal studies, the optimum pH for Pb (II) ions biosorption was in the range pH 3.0 to 7.0 as presented in Table 1. In this study, the percent removal of Pb (II) by immobilized cells of *P. sanguineus* was more than 90% within 2 h at pH 4. No experiments were conducted at pH above 4 as the Pb (II) ions precipitate.

TABLE 1  
pH for Pb (II) ions biosorption by different biosorbent

| Biosorbent material                | pH      | Reference                         |
|------------------------------------|---------|-----------------------------------|
| <i>Streptomyces noursei</i>        | 6.1     | (Mattuschka and Straube, 1993)    |
| <i>Penicillium chrysogenum</i>     | 4.5     | (Niu <i>et al.</i> , 1993)        |
| <i>Rhizopus arrhizus</i>           | 5.0-7.0 | (Sag and Kutsal, 2000)            |
| <i>Rhizopus arrhizus</i>           | 4.0-5.0 | (Fourrest and Roux, 1992)         |
| <i>Zoogloea ramigera</i>           | 4.0-5.0 | (Sag and Kutsal, 2000)            |
| <i>Saccharomyces cerevisiae</i>    | 5.0     | (Cabuk <i>et al.</i> , 2007)      |
| <i>Phanerochaete chrysosporium</i> | 6.0     | (Say <i>et al.</i> , 2001)        |
| <i>Cephalosporium aphidicola.</i>  | 5.0     | (Tunali <i>et al.</i> , 2006)     |
| <i>Aspergillus niger</i>           | 4.0     | (Dursun, 2005)                    |
| <i>Trametes versicolor</i>         | 4.0-6.0 | (Bayramoglu <i>et al.</i> , 2003) |
| <i>Pycnoporus sanguineus</i>       | 4.0     | This study                        |

#### Effect of Biosorbent Loading

The biosorption capacity for Pb (II) ions varies with the biosorbent loading (Fig. 2). Pb (II) ion removal increased from 23% to 99% when the amount of immobilized cells of *P. sanguineus* increased from 1.0 to 6.0 g. This increase could be attributed to the presence of more binding sites for binding the Pb (II) ions (Malkoc and Nuhoglu, 2005). However, the Pb (II) uptake decreased from 2.89 to 1.95 mg/g as the biosorbent dosage increased. The maximum metal uptake capacity occurred at 3.0 g of immobilized cells (Fig. 2). The high biosorbent loading may produce a 'screen' effect on the cell wall, protecting the binding sites and thus lowering the Pb (II) uptake (Malkoc and Nuhoglu, 2005; Mashitah *et al.*, 1999; Pons and Futse, 1993).

#### Equilibrium Isotherms

The linearised Langmuir, Freundlich and Redlich-Peterson equilibrium isotherm constants for Pb (II) ion biosorption were obtained at 30°C (303 K), 35°C (308 K) and 40°C (313 K) (Table 2). Biosorption of the metals by the immobilized cells of *P. sanguineus* could

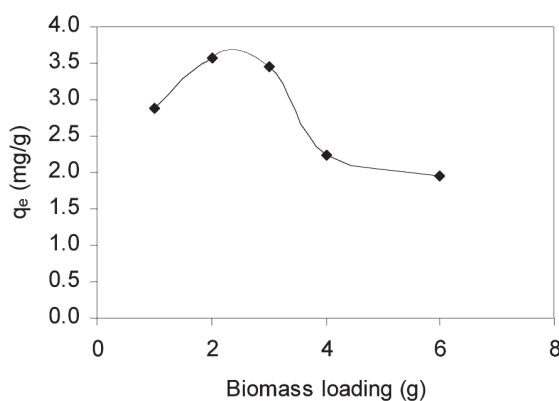


Fig. 2: Effect of biomass loading on the uptake of Pb (II) ions by immobilized cells of *P. sanguineus* (Condition: pH 4.0; 100 mg/L Pb (II) ions; agitation 150 rpm)



be represented well by any of the three isotherm models, as all had a correlation coefficient ( $R^2$ ) of approximately 1. The Langmuir constants  $K_b$  and  $q_{max}$  were determined using Eq. (3). The equilibrium sorption capacity,  $q_{max}$  increased from 3.62 to 4.43 mg/g when the temperature increased from 30 to 40°C. The higher the  $K_b$  value, the higher the affinity for binding metal ions. The highest  $K_b$  occurred at 313 K. The increase in  $K_b$  with temperature shows that a chemical interaction occurs between the metal ions and the biosorbent (Malkoc and Nuhoglu, 2005).

TABLE 2  
Biosorption equilibrium constant obtained from Langmuir, Freundlich and Redlich-Peterson isotherms for the biosorption of Pb (II) ions onto immobilized cells of *P. sanguineus*

| T<br>(°C) | Langmuir            |                                | Freundlich |       |       | Redlich-Peterson |                                   |   |         |       |
|-----------|---------------------|--------------------------------|------------|-------|-------|------------------|-----------------------------------|---|---------|-------|
|           | $q_{max}$<br>(mg/g) | $K_b$<br>(dm <sup>3</sup> /mg) | $R^2$      | $K_f$ | $n$   | $R^2$            | $K_{rp}$<br>(dm <sup>3</sup> /mg) | $a_{rp}$<br>(dm <sup>3</sup> /mg) <sup><math>\beta</math></sup> | $\beta$ | $R^2$ |
| 30        | 3.62                | 1.341                          | 1.000      | 1.553 | 4.713 | 0.933            | 3.928                             | 1.075   | 1.000   | 1.000 |
| 35        | 4.00                | 1.416                          | 0.999      | 1.840 | 5.025 | 0.962            | 9.955                             | 2.630   | 0.990   | 0.999 |
| 40        | 4.43                | 1.569                          | 0.999      | 2.179 | 5.313 | 0.949            | 25.234                            | 7.059   | 0.950   | 0.999 |

The  $K_f$  values for the Freundlich isotherms also increased with increase in temperature (Table 2). Since the  $n$  values obtained were  $> 1.0$ , the Pb (II) ions were favorably adsorbed by the biosorbent at all temperatures studied (Dursun, 2005). For the Redlich-Peterson constant  $K_{rp}$ , the values also increased with reaction temperature and most values of  $\beta$  were between 0.95-1.0.

#### Biosorption Kinetics Modeling

To evaluate the biosorption kinetics of Pb (II) ions, the pseudo-first order, pseudo-second order and intraparticle diffusion equations were applied to the experimental data. The corresponding constants for all three models obtained are presented in Table 3. The pseudo-second order model fitted the experimental data better than the intraparticle diffusion and pseudo-first order models with correlation coefficients ( $R^2$ ) of approximately 1.

TABLE 3  
Kinetic constants of pseudo first, pseudo second-order and intraparticle diffusion models for the biosorption of Pb (II) ions onto immobilized cells of *P. sanguineus* at different temperatures

| T (°C) | First-order kinetic model  |       | Second-order kinetic model |       | Intraparticle diffusion |       |
|--------|----------------------------|-------|----------------------------|-------|-------------------------|-------|
|        | $k_1$ (min <sup>-1</sup> ) | $R^2$ | $k_2$ (g/mg min)           | $R^2$ | $K_s$                   | $R^2$ |
| 30     | 0.039                      | 0.988 | 0.147                      | 0.947 | 1.515                   | 0.916 |
| 35     | 0.035                      | 0.979 | 0.198                      | 0.972 | 1.556                   | 0.907 |
| 40     | 0.008                      | 0.768 | 0.333                      | 0.990 | 1.717                   | 0.873 |



## CONCLUSIONS

Live immobilized cells of *Pycnoporus sanguineus* revealed a potential as a biosorbent for the removal of Pb (II) ions from an aqueous solution. The ability of immobilized cells of *P. sanguineus* to adsorb Pb (II) ions from aqueous solution was evaluated in batch studies. The initial Pb (II) concentration, pH and biomass loading all affected Pb (II) biosorption. The Langmuir, Freundlich and Redlich-Peterson isotherms fitted well with the experimental data at  $R^2 \geq 0.90$ . The kinetics of Pb (II) ions sorption at different temperatures was best described with a pseudo second order model.

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