

Competitive biosorption of Cd(II), Pb(II) and Cr(III) using fungal biomass *Pycnoporus sanguineus*

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ORIGINAL RESEARCH ARTICLE

ABSTRACT

The growing population and industrial advancement caused a greater environmental contamination with toxic metals potentially affecting the soil and groundwater. Biosorption is an alternative treatment method for wastewater containing toxic metals. This work aims to use fungal biomass (*Pycnoporus sanguineus*) as biosorbent for Cd(II), Pb(II) and Cr(III) ions. The results demonstrate that fungal biomass exhibited good biosorption capacity towards studied metal ions. The modification of the biomass with NaOH and HCl influenced the biosorption process as well as the competition existing between the metal species. The adsorption isotherm was described using the competitive multi-element Langmuir model and the results indicated that the model fitted the experimental data. The model confirmed the competition between metal ions. The results also indicated that it was possible to improve the biosorption performance of fungal biomass through treatment with NaOH and HCl.

KEYWORDS

contamination; fungal biomass; HCl; NaOH; toxic metals

1. INTRODUCTION

The industrial and population growth resulted in greater generation of wastes potentially containing toxic metals (Purkayastha et al., 2014) such as Cd(II), Pb(II) and Cr(III) ions. These wastes when released into the environment without any treatment can contaminate the soil and the water sources (Bozic et al., 2013). The traditional techniques of physico-chemical treatment techniques such as coagulation, flocculation and decantation are reported to be costly as well as exhibit moderate removal efficiency (Spinelli et al., 2005).

An alternate cost-effective and better performing bioremediation method is biosorption (Elangovan et al., 2008). Biosorption utilizes inactive/dead biomass materials to sorb metal ions (Kumari et al., 2006). Several biomaterials were studied as metal

biosorbents and this includes orange peel, cashew bagasse, coconut husk, microalgae, wood sawdust, pequi peel, bacteria and fungi such as *Aspergillus niger* (Nascimento et al., 2014; Selatnia et al., 2004; Nguyen et al., 2013).

The process of biosorption is based on the passive adsorption of metal ions onto biomass. The removal of the metal species by biomass can occur through any or combination of natural chemical mechanisms such as complexation, ion exchange, adsorption and micro-precipitation (Veglio and Beolchini, 1997). The biosorptive process is commonly involves solid phase represented by the biosorbent and a liquid phase constitutes of metal species (adsorbate) dissolved in aqueous solution. The process of metal retention is potentially continuous until equilibrium attained between the adsorbate concentration present on the surface of the biosorbent and adsorbate concentration left in the solution.

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The process of biosorption exhibits several inherent advantages compared to traditional waste treatment techniques. This includes low-cost, operation over wide range of operating conditions and easy regeneration (Volesky, 1990). Considering that the process involves biomass, biosorption have easy regeneration process and this makes the process economically feasible, thereby biomass can be utilized for multiple sorption cycles. One of the fundamental conditions for the selection of biomass for metal biosorption purpose is their potential to be regenerated for successive cycles of sorption/desorption. After efficient utilization, the metal-stripped biomass can be subsequently incinerated and deposited in landfill sites (Nascimento and Oliveira, 2014).

Several authors investigated fungal biomass for biosorption of various metal ions and recommended that the fungal-based biosorptive process as a good option for the treatment of metal-bearing aqueous streams (Souza et al., 2008). Some studies also observed an improvement in biosorptive process when the biomass was modified with reagents such as NaOH, HCl and citric acid (Rodrigues et al., 2006; Nascimento 2014). This paper aims to evaluate the potential of raw and modified (NaOH and HCl) fungal biomasses in biosorption of multi-element (Cd(II) ions, Pb(II) and Cr(III)) ions from synthetic solutions.

2. MATERIALS AND METHODS

2.1. Preparation of raw and modified fungal biosorbents

The fungal biomass (*Pycnoporus sanguineus*) was dried at room temperature. After the drying process, the biomass was grounded and subsequently sieved using 0.045 mm sieve opening. For the surface modification, the biomass was contacted with 0.1 mol/L sodium hydroxide (Vetec) and 0.1 mol/L hydrochloric acid for 24 h. Later, biomass was washed with deionized water and buffer solution (pH 5.0) and subsequently dried at room temperature.

2.2. Production of multi-element synthetic solution

All reagents used were of analytical grade. The stock solutions of cadmium, lead and chromium were prepared from the salts of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Vetec), $\text{Pb}(\text{NO}_3)_2$ (Vetec) and $\text{Cr}(\text{NO}_3)_3$ (Vetec), respectively. Cadmium solutions, lead and chromium were

standardized with 0.1 mol/L Na_2EDTA . A multi-element solution of Cd(II) ions, Pb(II) and Cr(III) was also prepared for experimentation.

2.3. Biosorption experimental procedure

Biosorption studies were conducted by contacting mixed metal solutions at concentrations of 2, 10, 15, 20, 30 and 40 mg/L with 1 g of raw or modified (NaOH and HCl) biomasses. The suspension was agitated at 200 rpm for 24 h. After the stirring, the samples were filtered with the aid of a vacuum pump in membrane filter (0.45 μm). The concentration of metal ions in the filtrate was analyzed using Atomic Absorption Spectrophotometer with flame (FAAS) VARIAN model Spectra AA / 55. The uptake capacity of biosorption and the metal removal efficiency were calculated using the following equations,

$$Q = V(C_i - C_e) / m \quad (1)$$

$$E = \frac{(C_i - C_e)}{C_i} \times 100 \quad (2)$$

where Q is the biosorption capacity (mg/g), C_i is the initial metal concentration in the solution (mg/L), C_e is the metal concentration at equilibrium (mg/L), m is the biosorbent mass (g), V is the volume of solution (L) and E is the metal removal or biosorption efficiency (%).

3. RESULTS AND DISCUSSION

Figure 1 shows the biosorption capacity of raw and modified fungal biomass towards Cd(II), Pb(II), and Cr(III), respectively, in relation to the initial concentration of metal ions. It should be noted that the pH of mixed solutions was adjusted to pH 5.0, owing to the fact that metals exists as divalent ions in solution at pH 5.0 (Veglio and Beolchin, 1997). The modification using NaOH and HCl improved the biosorption capacity of all metal ions. For instance, at 40 mg/L initial concentration, HCl-modified fungal biomass exhibited 6.49 mg Cd(II)/g compared to 5.99 mg Cd(II)/g of raw biomass. In particular, HCl modified biomass performed well compared to NaOH modified biomasses. Around 2.9–16.1% enhancement was observed on treatment with HCl compared to 1.7-8.9% enhancement by NaOH treatment. This enhancement by HCl was possibly due to opening up

of binding functional groups and removal of impurities from the biomass. From Figure 1, it was clear that fungal biomass exhibited highest Cd(II) biosorption capacity and competed successfully compared to other metal ions. At 40 mg/L initial concentration, the HCl-modified fungal biomass exhibited 6.49 mg Cd(II)/g compared to 6.25 mg Cr(III)/g and 4.1 mg Pb(II)/g. On the other hand, Cr(III) uptake capacity of all forms of fungal biomass was relatively good. However, the uptake of Pb(II) was severely affected and the recorded uptake values were significantly lower than that of Cd(II) and Cr(III) ions. It was also observed that the biosorption capacity was proportional to the increase of concentration of multi-element solution of studied metal species. For instance, uptake capacity of 0.354 mg/g observed at 10 mg/L for Cr(III) ions increased to 6.25 mg/g at 40 mg/L. The initial concentrations provide an important driving force to overcome all mass transfer resistances of the metal ions between the aqueous and solid phases which increase the uptake capacity (Premkumar and Vijayaraghavan, 2015).

Figure 2 represents the biosorption efficiency of raw and modified fungal biomass towards Cd(II), Pb(II), and Cr(III) ions. It was clear from Figure 2 that the removal efficiencies decrease with increase in initial metal concentration. This is due to decrease in availability of binding functional groups at higher metal concentrations. Similar to uptake values, all forms of fungal biomasses exhibited highest Cd(II) removal efficiencies and lowest Pb(II) removal efficiencies.

The isotherms obtained for multi-element biosorption of Cd(II), Pb(II), and Cr(III) ions onto raw and modified fungal biomass are shown in Figure 1. An important criterion for the selection of biosorbent is its uptake capacity towards particular metal ion. To explore the full saturation capacity of biosorbent, sorption isotherm is widely used. It is a plot of the sorption uptake (q) versus the final equilibrium concentration of residual sorbate remaining in the solution (C_e). The isotherms obtained were steep which indicate favorable isotherm, and the steepness were in the following order: Cd(II) > Cr(III) > Pb(II). It was clear from the experimental data that both raw and modified fungal biomass exhibited highest uptake for Cd(II) followed by Cr(III) and Pb(II).

The multi-element isotherms were described using the extended Langmuir model with a constant interaction factor (Al-Duri and McKay, 1991), which can be represented for quaternary mixtures, as follows:

$$Q_i = \frac{Q_i^0 b_i (C_i / \eta_i)}{1 + \sum_{j=1}^4 [b_j (C_j / \eta_j)]} \quad (3)$$

where C_i and Q_i are the unadsorbed concentration of each component at equilibrium (mg/L) and biosorbed quantity of each component per gram of biomass at equilibrium (mg/g), respectively; Q_i^0 and b_i are the single component Langmuir parameters of the i component; η_i is the interaction factor for the i component.

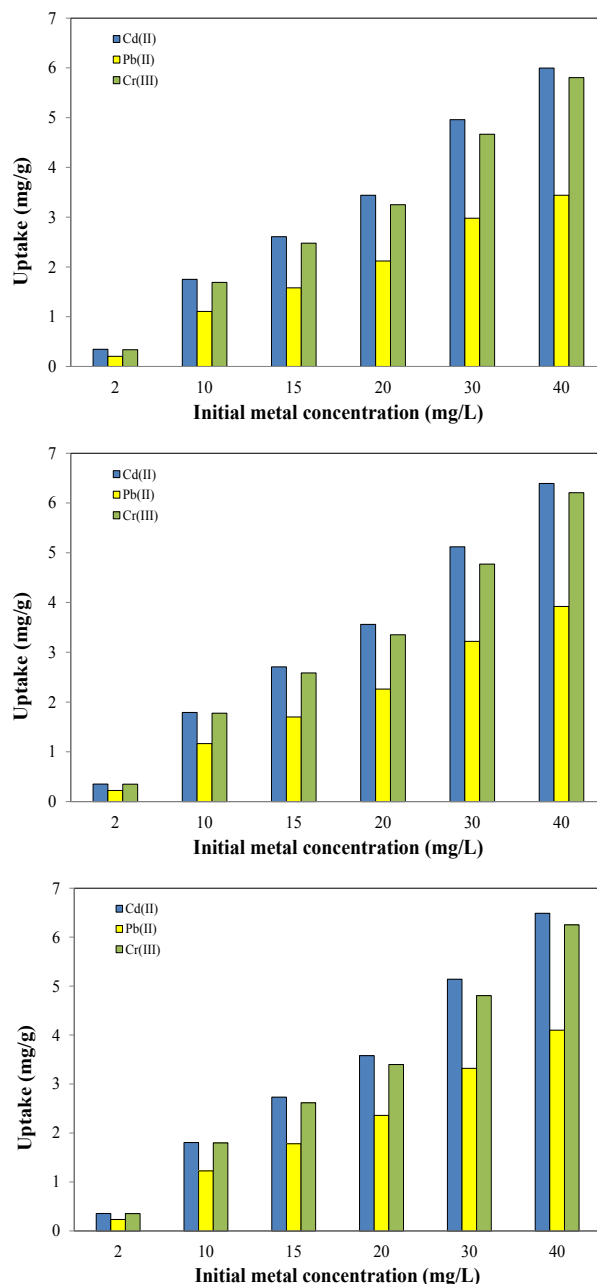


Figure 1. Biosorption capacities of raw biomass (top image); biomass modified with NaOH (middle image); and biomass modified with HCl (bottom image)

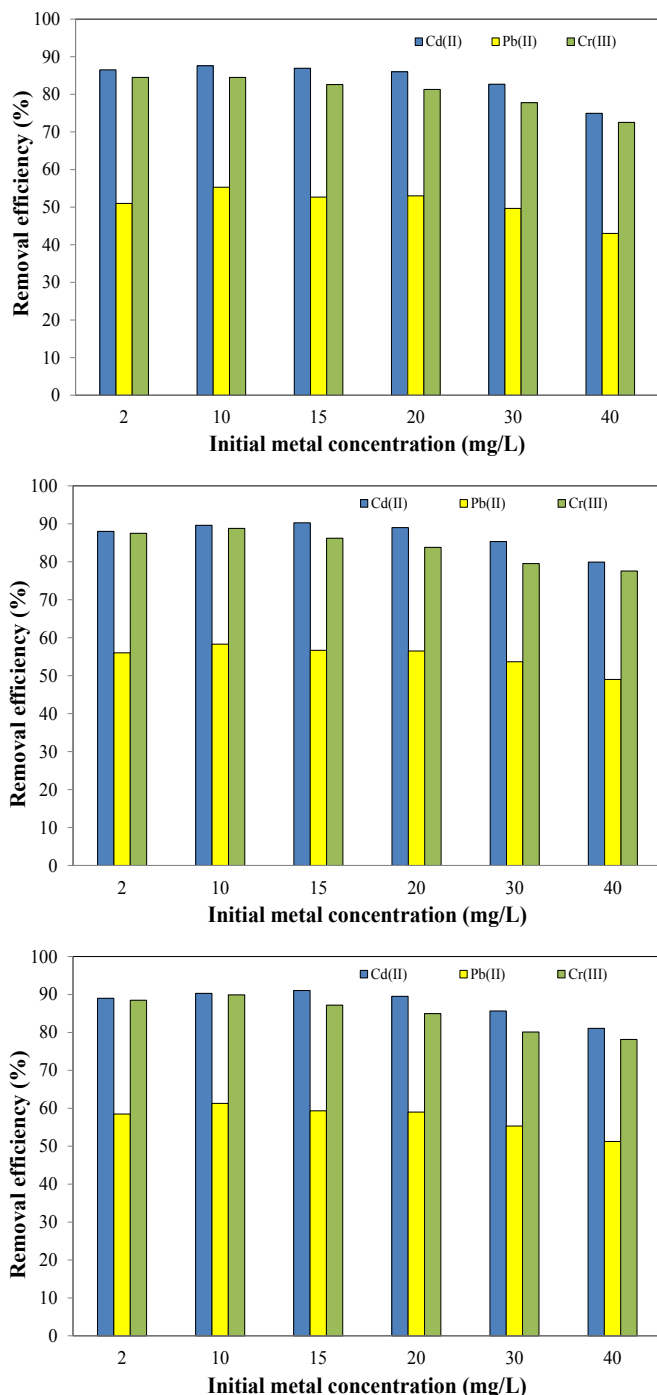


Figure 2. The efficiency of biosorption for raw biomass (top image); biomass modified with NaOH (middle image) and biomass modified with HCl (bottom image)

The calculation of the interaction factor is based on minimizing the following error function:

$$\frac{100}{n-p} \sum_{i=1}^n \left[\frac{(Q_{i,meas} - Q_{i,cal})^2}{Q_{i,meas}} \right]_i \quad (4)$$

where n and p are the number of data points and parameters, respectively. All model parameters were evaluated using non-linear regression employing the Sigma Plot (version 4.0, SPSS, USA) software. The traditional extended Langmuir equation assumes no interaction between solutes, which is not valid in real conditions. To incorporate sorbate interactions and competitions, an interaction factor (η) has been introduced into the extended Langmuir equation (McKay and Al-Duri, 1987). In the present study, η was assumed to be constant and specific for each metal ion in the multi-element system. The model was able to predict the multi-element biosorption isotherm with relative success using the single-component parameters. According to single-component Langmuir prediction, raw fungal biomass exhibited maximum uptake values of 9.88, 8.95 and 7.11 mg/g for Cd(II), Cr(III) and Pb(II), respectively, whereas 10.3, 9.7 and 9.6 mg/g, respectively, were observed for NaOH-modified fungal biomass. On the other hand, HCl-modified fungal biomass recorded 9.75, 9.7 and 9.68 mg/g for Cd(II), Cr(III) and Pb(II), respectively. With these single-component data, the multi-component isotherms were predicted. The interaction factor (η) values are given in Table 1. High correlation coefficients in the range of 0.935–0.981 were obtained. As already proven in our experiments, the magnitude of Cd(II) competition over other metal ions was significant, and these data were confirmed by the extended Langmuir equation yielding low η value for Cd(II) over other metal ions.

4. CONCLUSIONS

The competitive study on biosorption of potentially toxic metals Cd (II), Pb (II) and Cr (III) onto raw and

Table 1. The competitive Langmuir isotherm model parameter values during biosorption of metal ions onto fungal biomass

	Raw biomass			NaOH-modified biomass			HCl-modified biomass		
	Cd(II)	Pb(II)	Cr(III)	Cd(II)	Pb(II)	Cr(III)	Cd(II)	Pb(II)	Cr(III)
η	0.32	1.12	0.41	0.28	1.08	0.39	0.25	1.04	0.38
R^2	0.961	0.974	0.968	0.981	0.965	0.935	0.977	0.942	0.965

modified fungal biomass (*Pycnoporus sanguineus*) revealed that modification improved the biosorption performance towards all metal ions. The analysis of the results clearly revealed competition among the ions studied for the active sites on the surface of the biomass. Among metal ions examined, both raw and modified fungal biomass biosorbed more Cd(II) and Cr(III) compared to Pb(II) ions. The multi-element biosorption isotherms were modeled using the extended Langmuir model with a constant interaction factor. The model described the isotherms well with high correlation coefficients in the range of 0.935-0.981. The interaction factor (η) values were found low for Cd(II), indicating the magnitude of Cd(II) competition over other metal ions was highest.

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