Biosorption of Lead (II) and Copper (II) from Aqueous Solution

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Received : 18 September 2007
Accepted : 5 October 2007

ABSTRACT
In this study, the potential of biosorption of heavy metal ions by corncob and the natural fungi growing on corncob was investigated. Solutions containing lead (II) and copper (II) ions were prepared synthetically in single component and the time required for attaining biosorption equilibrium was studied. The effects of initial pH of heavy metal ions solutions and biosorbent dosages in respective ranges of 4.0 to 6.0 and 150 to 350 g (wet weight) on adsorption efficiency were also examined. Results showed the equilibrium time for biosorption of lead and copper ions from the solution to be approximately 90 minutes. The optimum initial pH for lead and copper adsorption by the natural fungi growing on corncob was 5.0. Under these conditions, the biosorption of lead and copper ions solution was 4.29 and 1.76 mg metal/g dry biomass, respectively. When using corncob alone as control, the corresponding values for the biosorption of lead and copper were 1.09 and 0.67 mg metal/g dry biomass, respectively, at initial pH level of 5. The adsorption equilibrium data were adequately characterized by both Langmuir and Freundlich equations. The maximum adsorption capacity based on the Langmuir isotherm, was found to be 14.75 and 1.77 mg metal per g dry weight biosorbent for lead and copper adsorption, respectively, at initial pH level of 5.0 by the natural fungi growing on corncob.

Keywords: Biosorption, Wastewater Treatment, Heavy Metal Ions.

1. INTRODUCTION
Rapid industrialization has led to increased disposal of wastewater into the environment. This often exceeds the admissible sanitary standards and results in the adverse impact on aquatic environment and consequently on human health. Wastewater treatment has received greater attention over the years due to the global awareness of the environmental deterioration. However, the application of various treatment techniques needs to agree with the wastewater characteristics. For example, the wastewater from food and beverage industries mainly consists of high organic compounds, which are commonly found in microbiological treatment processes such as activated sludge process. On the other hand, metallurgical industry, electroplating and metal finishing industries, tannery operations, chemical manufacturing, mine drainage and battery manufacturing are examples of the
industrial sources of heavy metals ions found in wastewater. A variety of suitable methods can be used for the removal of metal pollutants from such liquid wastes, including filtration, chemical precipitation, coagulation, solvent extraction, electrolysis, ion exchange, membrane process and adsorption. Ion exchange and adsorption are the most common and effective processes for the removal of heavy metal ions [1]. However, high operation cost and input of chemicals often make these processes impractical and result in further environment damage [2].

Treatment of effluents with heavy metals following biotechnological approaches is simple, comparatively inexpensive and friendly to environment [2-4]. Microbiological processes are of significance in determining metal mobility and have potential application in bioremediation of metal pollution [5]. Bioremediation of heavy metals, biooxidation of precious metal from ores, desulfurization of coal and oil, and biosorption of metal ions are examples of the wide variety of potential applications of microorganisms in mining and related fields [6, 7].

Biosorption is the uptake of heavy metal and radionuclides from aqueous solution by biological materials (i.e. biosorbents) [8]. A low cost sorbent is defined as one which is abundant in nature, or is a by-product or waste materials. Various waste biomaterials such as grape stalk waste [1], green coconut shell powder [9], chaff [2], and crab shell particles [4] have been studied for the removal of heavy metal ions from the effluents. In addition to biomaterials, microorganisms have also been used as metal sorbents. Bacteria, fungi, yeast and algae have been reported to remove heavy metals from aqueous solutions [10].

Fungi in particular have demonstrated unique metal adsorption characteristics and are easy to cultivate [11]. Living and dead cells of fungi can be used for the removal of heavy metal ions [12]. In related studies, metal removal abilities of various species of fungi have been investigated such as *Phanerochaete chrysosporium* [13], *Trametes versicolor* [14], *Aspergillus niger* [12], *Phellinus badius* [8], and *Aspergillus oryzae* and *Phizopus oryzae* [11]. However, no previous study has reported the application of natural fungi for wastewater treatment purposes for heavy metal removal. It is well recognized that natural fungi can be easily grown in substantial amounts on biomaterial waste. Thus, there is potential for utilizing some vegetable wastes as alternative low cost metal sorbents. Corncob is one of such wastes generated in the community, which has been satisfactorily used for growing natural fungi. Therefore, a fungal biomass growing on corncob could serve as an economical means for the removal of metal ions from aqueous solutions.

The objective of this study was to investigate the potential of corncob and the natural fungi growing on corncob for absorbing lead (II) and copper (II) from aqueous solution. Also the influence of various parameters such as adsorption equilibrium contact time, initial pH and amount of biosorbent on adsorption potential of corncob was studied in detail.

2. MATERIALS AND METHODS

2.1 Biosorbent Preparation

Yellow corn on the cob was boiled in filtered water at 100°C for 30 minutes, and then corn was removed from corncob. Boiled corncob was next cut into cubical pieces of about 1.3 centimeter. All experiments were carried out in 1.5 liter round plastic drinking bottles containing corncob. The gas supply system was designed to accommodate ambient air through cotton wool. Based on the results obtained from cell dry weight of the natural fungi growing on corncob, the bottles were incubated outside the building.
under the shade for 7 days for optimal growth. The control experiments were set up by preparing a series of bottles with the same composition with no fungi present.

2.2 Copper (II) and Lead (II) Solutions
The chemicals used for the study were analytical grades lead nitrate (Pb(NO$_3$)$_2$) and copper sulphate (CuSO$_4$) purchased locally from BDH company, Bangkok. The copper (II) and lead (II) solutions with concentration of about 1000 mg/l were prepared by dissolving the respective amounts in distilled water. The exact heavy metal content of the solutions was analyzed by an atomic absorption spectrophotometer (AAS).

2.3 Equilibrium Contact Time
All experiments were carried out in 1.5 liter round plastic bottles containing 350 g (wet weight) of corncob to serve as control. Another identical plastic bottle contained similar amount of corncob with fungi growing on it naturally. Each bottle contained 0.5 liter of the copper (II) and lead (II) solutions with concentration of about 1000 mg/l. The initial pH levels of heavy metal ions solution were adjusted to 4.0, 5.0 and 6.0. Duplicate trials were conducted in all tests. For analysis, 5 ml sample was taken out from each bottle at regular time intervals of 30, 60, 90, 120, and 150 minutes. The heavy metal ions solution was passed through a filter paper (Whatman No. 1) to separate solid and liquid phases and the filtrate was used for analyzing the copper and lead concentrations.

2.4 Effects of Initial pHs on Adsorption Capacity
All experiments were conducted in duplicate in a 1.5 liter round plastic bottles containing 250 g (wet weight) of corncob with and without natural growth of fungi. Each bottle contained 0.5 liter of the copper (II) and lead (II) solutions with concentration of about 1000 mg/l. Three different level of initial pH (4.0, 5.0 and 6.0) were maintained in the solution. All samples were taken at optimal equilibrium contact time and filtered as described in previous section. The filtrate was subsequently analyzed for copper and lead concentrations. The solid part was dried at 60 °C until reaching a constant level and recorded as dry weight.

The metal concentrations adsorbed on the solid were calculated from the difference between heavy metal ions content (in mg per liter) in the liquid solution before ($C_i$) and after adsorption ($C_{eq}$). The following equations were used to compute the adsorption percentage (%Ad) and the absorption capacity by the adsorbent, $q_{eq}$ (mg metal per g dry biosorbent), respectively:

$$\% Ad = \left(1 - \frac{C_{eq}}{C_i}\right) \times 100$$  \hspace{1cm} (1)

$$q_{eq} = \left(1 - \frac{C_{eq}}{C_i}\right) \left(\frac{V}{w}\right)$$  \hspace{1cm} (2)

where $V$ (in liter) is the solution volume and $w$ (in gram) the amount of dry biosorbent used.

2.5 Effects of Biosorbent Dosage on Adsorption Capacity
The experimental procedure described in the previous section was followed using different amounts of corncob (150, 200, 250, 300 and 350 g wet weight) and optimal initial pH level. The samples were taken out for analysis at optimal equilibrium contact time. The data was then used to compute %Ad, and $q_{eq}$ (mg metal per g dry biosorbent).

2.6 Analysis of the Copper (II) and Lead (II) Concentration
Copper and lead contents in the solution
were determined by an atomic absorption spectrophotometer (AAS). Calibration curves for each metal were determined using standardized metal solutions. The solutions were diluted with distilled water and later the same day the amounts of copper and lead were determined by AAS (3300 Perkin Elmer).

3. RESULTS AND DISCUSSION
3.1 Equilibrium Contact Time

Adsorption equilibrium is defined as the equilibrium distribution of a given component between an adsorbate and adsorbent. The equilibrium adsorption isotherm data can be characterized by a model such as the Langmuir equation.

$$\frac{1}{q} = \frac{1}{q_m b C_{eq}} + \frac{1}{q_m}$$  \hspace{1cm} (3)

where: q is the concentration of adsorbed metal per unit weight of biosorbent, $C_{eq}$ is the concentration of heavy metal ions in the liquid phase, $q_m$ is the maximum adsorption capacity per unit weight of biosorbent and b is the adsorption equilibrium constant.

Equilibrium data for the bacterial adsorption is plotted as $1/q$ vs $1/C_{eq}$ according to the Langmuir isotherm. The two constants $q_m$ and b are calculated from the slope ($1/q_m b$) and intercept ($1/q_m$) of the line, respectively.

The equilibrium isotherm data can also be characterized by a model such as the Freundlich equation.

$$q = K C_{eq}^{1/n}$$  \hspace{1cm} (4)

where: K and n are empirical constants indicative of sorption capacity and sorption intensity, respectively. The Freundlich parameters were obtained by fitting the experimental data to the linearized equation (plot of log q against log $C_{eq}$).

Figures 1 and 2 show the results on the adsorption of lead (II) and copper (II) ions from the solutions, respectively, at three different initial pH levels. The heavy metal ions concentration in the liquid-phase decreased rapidly with time apparently due to the adsorption of metal ions on the corncob and finally leveled off. The results presented in Figures 1 and 2 also showed that the amount of adsorbed heavy metal ions was dependent on the initial pH of the solution and the type of biosorption media.

The initial sharp decrease in heavy metal ions concentration in the liquid-phase implied higher rate of biosorption (Figures 1 and 2). The rate of biosorption was markedly influenced by the levels of initial pH in the solution. The overall results indicated that the adsorption of heavy metal ions was comparatively higher at initial pH of 5.0 irrespective of the presence of fungi on corncob. The biosorption by the natural fungi growing on corncob showed similar patterns to corncob without fungal growth. The reduction in heavy metal ion concentration in the liquid phase resulting from the natural fungi growing on corncob (Figures 1(b) and 2(b)) was much greater than the control experiments (Figures 1(a) and 2(a)). The adsorption of heavy metal ions was enhanced by the filamentous fungi present on the corncob surfaces.

Adsorption of lead (II) and copper (II) on corncob reached equilibrium levels both in presence of natural fungal growth and control samples as shown in Figures 1 and 2. Apparently, equilibrium adsorption levels were attained after about 90 minutes of exposure for all pH levels investigated in this study. The data beyond 90 minutes indicated only a little adsorption. The equilibrium adsorption trends of copper (II) were in good agreement with those of lead (II) solution. The short equilibrium adsorption contact time of about 90 minutes in lead (II)
and copper (II) ions solutions in general agreed with the other findings [4,14,15]. Taking into account these results, a contact time of 90 minutes was chosen for further experiments irrespective of initial pH level.

**Figure 1.** Biosorption of lead (II) ions as a function of time for (a) corncob alone and (b) in the presence of natural fungi growing on corncob.

**Figure 2.** Biosorption of copper (II) ions as a function of time for (a) corncob alone and (b) in the presence of natural fungi growing on corncob.
3.2 Effects of initial pHs on adsorption capacity

The pH of metal solution has been identified as one of the most important variables governing the biosorption process. Based on the finding of optimum pH levels in several studies [1,8,12-14,16] the range of pH selected in this study was between 4 and 6.

The absorption capacity and the adsorption percentage of lead (II) and copper (II) ions solutions for different initial pH levels are shown in Figures 3 and 4, respectively. The adsorption capacity of lead (II) ions in case of control corncob sample (Figure 3) increased slightly with increasing initial pH from 0.8 to 1.3 mg metal per g dry weight biosorbent with corresponding adsorption percentage ranging from 23 to 38, respectively. The adsorption capacity of lead (II) ions by the natural fungi growing on corncob was relatively higher in the range of 2.0 to 2.6 mg metal per g dry weight biosorbent corresponding to the adsorption percentage of about 67 to 77, respectively. The optimum initial pH for lead adsorption by the natural fungi growing on corncob was found to be 5.0.

Figure 3. Comparison of the absorption capacity (q) and the adsorption percentage (%Ad) of lead (II) ions by corncob alone and in the presence of natural fungi growing on corncob for different initial pH levels.

The adsorption capacity of lead (II) ions solution in the presence of fungi was much greater than the control experiments. The natural fungi growing on corncob at initial pH 5 resulted in the maximum adsorption capacity of 2.6 mg metal per g dry weight biosorbent in lead (II) solution as compared to about 0.9 mg metal per g dry weight biosorbent by the corncob alone. This clearly demonstrated that an increase in the adsorption capacity of lead (II) ions because of the influence of fungi.

As shown in Figure 4, no significant
difference was found in the values of the absorption capacity and percentage in case of copper (II) ions solution by corncob. The adsorption capacity in copper (II) ions solution was found to be about 0.6, 0.6 and 0.7 mg metal per g dry weight biosorbent corresponding to the same adsorption percentage of about 19 for initial pH level of 4.0, 5.0 and 6.0, respectively. Although the effect of initial pH on metal adsorption in the control experiments was not significantly different, it had a noticeable effect in the presence of the natural fungi growing on corncob. The corncob with fungi showed adsorption capacity of copper (II) ions to be 1.0, 1.2 and 0.7 mg metal per g dry weight biosorbent corresponding to the adsorption percentage of about 34, 38 and 24 for initial pH of 4.0, 5.0 and 6.0, respectively. Thus, the optimum initial pH of 5.0 for copper adsorption by the natural fungi growing on corncob was found to be similar to the case of lead (II) adsorption.

Overall results indicated the adsorption capacity of copper (II) ions solution to be very low in comparison to that of lead (II) adsorption experiments in case of both biosorbents. This may be probably due to the difference in natural affinity between the type of heavy metal and biosorbent. A direct comparison of these findings is not possible with the values reported in literature due to different study conditions, metal ions and fungus strains used in various studies. However, the results on the adsorption of lead (II) and copper (II) ions are in agreement with the previous studies [12,14] by the live cells showing comparatively higher adsorption of lead (II) ions from the solution.

3.3 Effects of biosorbent dosage on adsorption capacity

Biosorbent dosages may have a significant influence on the adsorption capacity and percentage. Vijayaraghavan et al. [4] found that the percentage of copper and cobalt removal by crab shell particles increased with increase in biosorbent dosage, however, biosorption efficiency (mg metal per g biosorbent) decreased with increase in biosorbent dosage. The small number of published papers available does not allow researchers to draw a sound conclusion; the present study may contribute to fill this apparent gap in knowledge.

Figure 4. Comparison of the absorption capacity (q) and the adsorption percentage (%Ad) of copper (II) ions by corncob alone and in the presence of natural fungi growing on corncob for different initial pH levels.
Figure 5. Comparison of the absorption capacity ($q$) and the adsorption percentage ($\%Ad$) of lead (II) ions by corncob alone and in the presence of natural fungi growing on corncob for different biosorbent dosages.

Figures 5 and 6 present typical set of results obtained by varying biosorbent dosages from 150 to 350 g (wet weight) during lead and copper biosorption, respectively. The adsorption of lead (II) ions by the corncob (Figure 5) showed only a little change in the value of $q$ ranging from 1.23 to 0.78 mg metal per g dry weight biosorbent. In addition, the percentage adsorption of lead (II) ions by the corncob increased from about 20 to 44 % when the biosorbent dosage was increased from 150 to 350 g.

In contrast, the adsorption of lead (II) ions by the natural fungi growing on corncob as shown in Figure 5 was markedly decreased from 4.3 to 2.0 mg metal per g dry weight biosorbent with an increase in biosorbent dosage from 150 to 350 g. However, an increase in the adsorption percentage of lead (II) absorption from about 75 to 84 % by the natural fungi growing on corncob appeared to be gradual with a corresponding increase in biosorbent dosage from 150 to 350 g.

The changes in the adsorption of copper (II) ions followed the trends similar to lead (II) ions as shown in Figure 6. The absorption capacity of copper (II) ions by corncob alone indicated a mean value of about 0.64 mg metal per g dry weight biosorbent for two replications and different dosages of biosorbent. However, there was a decrease in the absorption capacities of copper (II) ions in case of the natural fungi growing on corncob when biosorbent dosage increased from 150 to 350 g. For 150 g of corncob with the natural fungi, there was approximately a two-fold decrease in the copper adsorption as compared to 350 g of the same biosorbent.
Figure 6. Comparison of the absorption capacity (q) and the adsorption percentage (% Ad) of copper (II) ions by corncob alone and in the presence of natural fungi growing on corncob for different biosorbent dosages

An increase in adsorption percentage was observed in both experiments. The adsorption percentage increased from 12 to 28% for corncob used as control and from 27 to 43% for the natural fungi growing on corncob. These results are in good agreement with Vijayaraghavan et al. [4] who reported overall similar trends in an increase in the adsorption percentage with increasing biosorbent dosage despite the different type of biosorbent. The highest adsorption percentage of about 43% was achieved for 350 g of corncob with natural fungal growth.

In general, the absorption capacity and the adsorption percentage for copper (II) solution were much lower than those of lead (II) solution. This was an approximately two-fold decrease in the copper adsorption compared to the lead adsorption. Again, the nature of biosorbent particles might have played an important role in the adsorption of different metal ions.

The equilibrium adsorption isotherms data for lead and copper by the natural fungi growing on corncob at initial pH of 5.0 are characterized in Figures 7 and 8, respectively, based on Equations 3 and 4 when the biosorbent dosage varied between 150 and 350 g. For each biosorbent dosage, the concentration of adsorbed metal per unit weight of biosorbent (q) and the concentration of heavy metal ions in the liquid phase (C_{eq}) were determined for equilibrium time of 90 minutes. The equilibrium data for
the lead adsorption was plotted as $1/q$ vs $1/C_{eq}$, and $\log q$ vs $\log C_{eq}$, according to Equations 3 and 4, respectively. Subsequently, the equation parameters for Langmuir equation ($q_m$ and $b$) and Freundlich equation ($K$ and $n$) were determined from the slope and intercept of the least-squares fits. Similar analysis was carried out to determine parameters ($q_m$, $b$, $K$ and $n$) for copper adsorption from the plots of equilibrium data as shown in Figure 8.

Figure 7. Plots for determining the parameters of Langmuir and Freundlich equations for the adsorption of lead (II) ions by natural fungi growing on corncob (solution pH 5.0).

Figure 8. Plots for determining the parameters of Langmuir and Freundlich equations for the adsorption of copper (II) ions by the natural fungi growing on corncob (solution pH 5.0).

Table 1 presents the results of regression analysis for determining the parameters of Langmuir and Freundlich equations (Equations 3 and 4). The coefficient of determination ($R^2$) ranged from 0.70 to 0.74 and 0.88 to 0.91 for adsorption of lead and copper, respectively. These results indicated that the equilibrium adsorption data of lead and copper conformed reasonably well to the Langmuir and Freundlich equations. Table 2 presents a general comparison of the results of this study with other published work for adsorption of lead and copper by different fungal species. In particular, there is reasonable agreement with the work of Kapoor et al. [12] and Yetis et al. [13] Yan and Viraraghavan [16].
Table 1. Regression parameters of Langmuir and Freundlich equations for biosorption of lead and copper by the natural fungi growing on corncob at initial pH of 5.0.

<table>
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<th>Metal adsorption</th>
<th>Langmuir equation</th>
<th>Freundlich equation</th>
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<tr>
<td></td>
<td>$q_m$ (mg metal per g dry weight biosorbent)</td>
<td>$b$</td>
</tr>
<tr>
<td>lead</td>
<td>14.75</td>
<td>$7.03 \times 10^{-4}$</td>
</tr>
<tr>
<td>copper</td>
<td>1.77</td>
<td>$6.92 \times 10^{-4}$</td>
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Table 2. Comparison of the parameters of Langmuir and Freundlich equations reported in literature.

<table>
<thead>
<tr>
<th>References</th>
<th>Adsorbent</th>
<th>Heavy metal ions</th>
<th>Langmuir equation</th>
<th>Freundlich equation</th>
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<tr>
<td></td>
<td></td>
<td></td>
<td>$q_m$</td>
<td>$b$</td>
</tr>
<tr>
<td>[1]</td>
<td>Aspergillus niger (Live cell)</td>
<td>Pb</td>
<td>598.0</td>
<td>$4 \times 10^{-4}$</td>
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<tr>
<td></td>
<td>NaOH pretreated Aspergillus niger pH = 5</td>
<td>Pb</td>
<td>10.19</td>
<td>7.8</td>
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<tr>
<td></td>
<td>Cu</td>
<td>4.69</td>
<td>0.30</td>
<td>0.88</td>
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<tr>
<td>[14]</td>
<td>Immobilized Trametes versicolor (Live cell)</td>
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<td>$6.13 \times 10^{-4}$</td>
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<td>This work</td>
<td>The natural fungi growing on corncob</td>
<td>Pb</td>
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<td>$7.03 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>Cu</td>
<td>1.77</td>
<td>$6.92 \times 10^{-4}$</td>
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</table>
The parameters in Langmuir and Freundlich equations ($q_m$, $b$, $K$ and $n$) have been reported to depend on several factors such as the experimental conditions, types of metal ions and fungus strains used as biosorbents. Specifically, the values of both $q_m$ and $K$ in case of lead adsorption were significantly higher than in copper adsorption, which agrees with the findings of other researchers. Also the decrease in the values of $q_m$ and $K$ for copper adsorption could be explained by the lower affinity due to the nature of biosorbent.

4. CONCLUSION

Adsorption of lead (II) and copper (II) in the presence of natural fungi growing on corncob attained equilibrium after about 90 minutes of exposure for initial pH ranging from 4.0 to 6.0. The optimum pH level for lead and copper adsorption by the natural fungi growing on corncob was found to be 5.0. The overall adsorption percentage increased with an increase in the biosorbent dosage, but the biosorption efficiency (mg metal per g biosorbent) was decreased. Results showed maximum adsorption capacity per unit dry weight of biosorbent based on Langmuir isotherm to be 14.75 and 1.77 mg metal per g dry weight biosorbent for lead and copper adsorption, respectively, by the natural fungi growing on corncob.

ACKNOWLEDGEMENTS

I wish to thank the Faculty of Engineering, Mahidol University for the project grant. This work was supported by the equipment in the Department of Chemical Engineering, the Faculty of Engineering, Mahidol University.

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