The Biosorption of Pb(II) from Solution by Elephant Grass

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ABSTRACT

The biosorption of Pb(II) from dilute aqueous solution using elephant grass as the biosorbent has been studied. The biosorption study was carried out as a function of pH, contact time, initial metal ion concentration, and temperature. The residual Pb(II) in solution were determined using atomic absorption spectrophotometer (AAS). The FT-IR analysis of elephant grass biomass revealed the presence of bonded OH, -NH stretching, C-H stretching, and C=O stretching of COOH. The study on pH showed that the biosorption was pH dependent as maximum biosorption of Pb(II) was obtained in the range pH 3-5. The biosorption was also time dependent as maximum biosorption was obtained within 30 min of the process. Kinetic studies show that the biosorption of Pb(II) can be described by pseudo-second-order kinetic model. For the metal ions, the biosorption efficiency increased with increase in initial metal ion concentration. The free energy change obtained for the biosorption of Pb(II) at 303K with an initial Pb(II) concentration of 100 mgL⁻¹ was -11.887 KJmol⁻¹. The entropy change for the biosorption of Pb(II) was 104.84 Jmol⁻¹K⁻¹, while the enthalpy change was 19.88 KJmol⁻¹. These results indicate that the biosorption of Pb(II) by elephant grass is spontaneous and endothermic.

(Keywords: biosorption, Pb(II), lead, adsorption isotherms, elephant grass)

INTRODUCTION

The pollution of the environment by heavy metals has become one of the most serious environmental problems today (Anayurt et al., 2009). This is because they are highly toxic, non-biodegradable, and tend to accumulate causing different health problems in living organisms. Lead poisoning in humans causes severe damage to the kidneys, nervous system, reproductive system, liver, and brain (Naiya et al., 2009a). These metals get into the aqueous environment through effluents from various industrial operations such as mining, smelting, printing, dyeing, metal plating, and manufacturing of explosives.

The conventional methods of heavy metal removal from the environment include ion-exchange, reverse osmosis, chemical precipitation, chemical oxidation, evaporation, and electrochemical treatment. Unfortunately, the conventional methods are either economically expensive or technically problematic to handle. These limitations have led to the development of a "new technology" at little or no cost for the removal of the heavy metals from aqueous environment. This new method, called biosorption, has great merits of low cost, high efficiency, ease of operation, and the possibility of metal recovery. Biosorption is the binding and concentration of heavy metals from aqueous solutions by certain types of biomass of plant or animal origin.

The benefits of biosorption have led to several studies in the last decade and a half to determine the possibility of making use of different plant and animal materials especially agricultural wastes. Individuals and research groups with different backgrounds, from engineering to biochemistry, have been making significant contributions to the understanding of biosorption (Babarinde et al., 2007; de la Rosa et al., 2008; Anayurt et al., 2009; Babalola et al., 2009a, 2009b; Babarinde et al., 2009; Bankar et al., 2009; Fereidouni, 2009; Gok and Aytas, 2009; Gundogdu et al., 2009; Lakshmanraj et al., 2009; Liang et al., 2009; Mohan and Gandhimathi, 2009; Nadeem et al., 2009; Naiya et al., 2009a, 2009b; Özcimen and
Ersoy-Mericboyu, 2009; Qaiser et al., 2009; and Vimala and Das, 2009). These interdisciplinary efforts have been essential to exploit this technology commercially. A chemical engineering background is particularly useful for expanding the application of this technology in large-scale process industries. The objective of this study was to investigate the biosorption of Pb(II) by elephant grass from aqueous solution.

MATERIALS AND METHOD

Biomass Preparation

Elephant grass (Pennisetum purpureum) was obtained from within the premises of Obafemi Awolowo University mini-campus, Ago-Iwoye, Ogun State, Nigeria. The grass was rinsed with deionized water, sun dried, and cut into pieces of approximately 0.5 cm. The samples were kept dry until the time of usage.

Reagents and Equipment

All chemical reagents used in this study were of analytical grade. Deionized water was used for preparation and dilution of all solutions. Pb(II) stock solution was prepared as 1000 mg L\(^{-1}\) by dissolving appropriate amount of Pb(NO\(_3\))\(_2\) in a 1-Litre standard flask using deionized water. The stock solution was diluted to the required concentrations and appropriate pH with a dropwise addition of 0.1 M HNO\(_3\) and/or 0.1 M NaOH using a pH meter. Freshly diluted stock solutions were used for each experiment. Atomic Absorption Spectrophotometer (AAS) (Bucks scientific model 210 VGP) was used for analysis of residual metal ions in solution after each biosorption process. Fourier Transform Infrared (FT-IR) spectra of unloaded and metal-bound elephant grass samples were recorded using an FT-IR spectrophotometer (Shimadzu FT-IR 8400S) in wavenumber range of 400-4000 cm\(^{-1}\).

Batch Biosorption Procedure

Biosorption was carried out using batch method. In order to optimize the experimental conditions, the batch biosorption studies were performed for different pH 1-5, contact times (0-300 min), metal concentrations (10-100 mg L\(^{-1}\)), and temperature (27-50°C). Each batch biosorption study was carried out by contacting 2.5 g of the elephant grass with 25 ml of a given concentration of metal ion solution in a thermostated water bath (Haake Wia model) for temperature regulation. In each case, a parameter was varied while others were kept constant. At the end of the contact time, the solution was decanted into sample bottle and analyzed for the residual metal ions in solution using AAS. Each experiment was repeated and the mean value calculated.

Statistical Analysis

The curve fittings of all the data obtained were performed using Microcal Origin\textsuperscript{®} 6.0 software.

RESULT AND DISCUSSION

FT-IR Analysis

The FT-IR spectroscopy method was used to obtained information about the nature of the functional groups responsible for the biosorption of the metal ions on the binding sites of the grass (Elangovan et al., 2008; Ertgay and Bayham, 2008; and Bueno et al., 2008). Figure 1 shows the FT-IR spectra of unloaded and Pb(II)-loaded elephant grass. The assignment of the functional groups responsible for bands are shown in Table 1.

![Figure 1: FT-IR Spectra of the Unloaded and Pb-Loaded Elephant Grass Biomass.](image-url)

The IR spectra indicate that the cell wall of elephant grass possesses different surface structures and functional groups with lone pairs of electron that are available to bind to the positively divalent metal ions. The reaction involved the biosorption of metal ion (represented as M\(^{2+}\) for a divalent metal ion) from the liquid phase to the
solid phase, the adsorbent with lone pair of electron (represented as $\text{Ä}$), and can be
considered as a reversible reaction with an
equilibrium being made between the two phases
as schematically shown in Equation (1).

$$\text{Ä} + M^{2+} \rightleftharpoons A^- M$$

(1)

Table 1: IR Absorption Bands and the Corresponding Possible Functional Groups.

<table>
<thead>
<tr>
<th>Wave number (cm$^{-1}$)</th>
<th>Functional group</th>
</tr>
</thead>
<tbody>
<tr>
<td>3300-3400</td>
<td>OH, NH stretch</td>
</tr>
<tr>
<td>2920-2850</td>
<td>C – H stretch</td>
</tr>
<tr>
<td>2360.95</td>
<td>O – H carboxylic acids</td>
</tr>
<tr>
<td>2121.77</td>
<td>C ≡C</td>
</tr>
<tr>
<td>1710-1690</td>
<td>C =O</td>
</tr>
<tr>
<td>1519.96-1516.10</td>
<td>N = O Nitro (R – NO$_2$)</td>
</tr>
<tr>
<td>1423.51-1431.23</td>
<td>C – H bend</td>
</tr>
<tr>
<td>1324.48-1246.06</td>
<td>C – X</td>
</tr>
<tr>
<td>1050</td>
<td>S – O sulphuroxides</td>
</tr>
<tr>
<td>895.00</td>
<td>C – H Aromatic (out of plane)</td>
</tr>
<tr>
<td>783.13-775.41</td>
<td>C – H Aromatic (out of plane)</td>
</tr>
</tbody>
</table>

Figure 2: Effect of pH on the Biosorption of Pb(II) by Elephant Grass at Metal Concentration of 100 mg L$^{-1}$ and Temperature of 300K.

At low pH, the solution is highly acidic thereby making the net charge on the active sites to be positive. Also, the metal ions compete with protons for the active sites on the cell wall of the biomass. Consequently, the result is reduction in the uptake of the metal ions by the sorbent. In addition, the protonation of the active sites on the cell wall of the biomass reduces the number of negatively charged sites needed for the metal ions to bind. As the pH increases, the functional groups in the cell wall become deprotonated and free for the metal to bind. Therefore, the competition between metal ions and protons is reduced, thus the increase in the biosorption with increase in pH. Similar results have been reported for different biomass in the biosorption of Cd(II) and Pb(II) (Anayurt et al., 2009; Vimala and Das, 2009).

The Influence of Contact Time

The biosorption of Pb(II) by elephant grass as a function of time is shown in Figure 3.

The biosorption of the two metal ions from solution increased rapidly with increase in time within the first 30 min. The 30 min was taken as the optimum time for the biosorption of Pb(II). The rapidity in the biosorption of the ions from solution at the initial state reflects the availability of abundant active binding sites on the cell wall of the biomass. The rate of biosorption slows down with time as the available binding sites on the cell wall were used up.
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Figure 3: Time Course for the Biosorption of Pb(II) by Elephant Grass at Metal Ion Concentration of 100 mg L⁻¹ and Temperature of 300K.

The results of this kinetic study were tested with three kinetic models. The pseudo-first-order, pseudo-second-order and the intraparticle diffusion equations were applied to the kinetic study as shown in Equations (2) – (4), respectively.

\[
\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (2)
\]

\[
t = \frac{1}{k_2 q_e} + \frac{1}{q_e} t \quad (3)
\]

\[R = K_i t^b \quad (4)
\]

where \(k_1\) is the Lagergren rate constant of the biosorption (min⁻¹); \(k_2\) is the pseudo-second order rate constant (g mg⁻¹ min⁻¹); \(q_e\) and \(q_t\) are the amounts of metal ions sorbed (mg g⁻¹) at equilibrium and at time \(t\), respectively.

In the linear form, Equation (4) turns to Equation (5).

\[
\log R = b \log t + \log K_i 
\]

Only the pseudo-second-order model fits the biosorption of Pb(II) with elephant grass. The plot of \((t/q)_t\) versus \(t\) gives a linear graph for pseudo-second-order kinetics. The pseudo-second-order rate constant of the biosorption \((k_2)\) was calculated from the intercept of the plot. The linearity of the plot as indicated by \(R^2 \approx 1\) shows the applicability of the model for this biosorption process. Therefore, the kinetic parameters are shown in Table 2.

Figure 4: Pseudo-Second-Order Plot for the Biosorption of Pb(II) by Elephant Grass at Metal Concentration of 100 mg L⁻¹ and Temperature of 300K.

Table 2: Pseudo-Second-Order Kinetic Model Parameters for the Biosorption of Pb(II) by Elephant Grass at 100 mg L⁻¹, 300K.

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>(q_e) (mg g⁻¹)</th>
<th>(k_2) (g mg⁻¹ min⁻¹)</th>
<th>(R)</th>
<th>S.D.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb(II)</td>
<td>97.8774</td>
<td>7.36 \times 10⁻⁷</td>
<td>0.9999</td>
<td>0.0152</td>
</tr>
</tbody>
</table>

The Influence of Initial Metal Ion Concentration

The initial concentration of metal ion in solution determines the amount of the metal ions biosorbed by the sorbent when there are available binding sites. This is evident in the results shown in Figure 5.

The increase in uptake capacity with increase in initial metal concentration has been accounted for in terms of higher availability of metal ions for sorption (Vimala and Das, 2009). The increase in concentration leads to increase in collision between the metal ions and the sorbent which is a major factor in kinetics for increase in the rate of chemical reactions.

The biosorption efficiency for each metal was calculated using Equation (6).
Effect of Initial Metal Ion Concentration on the Biosorption of Pb(II) at Initial Concentration of 10 - 100 mgL⁻¹.

\[ E = 100 \left( \frac{C_i - C_f}{C_i} \right) \]  

(6)

where \( C_i \) and \( C_f \) are the initial and final metal ion concentrations, respectively. The result is shown in Figure 6.

This trend of increase in efficiency with increase in initial metal ion concentration is similar to earlier reports (Babarinde et al., 2009). The trend of initial rapid increase in efficiency is due to the availability of binding sites on the biomass which reduces with increase in concentration of metal ions. Consequently, the sorption approached saturation stage as the fixed number of binding sites were exhausted.

**Biosorption Isotherm Models**

The equilibrium sorption isotherms provide vital data to understand the mechanism of the biosorption process. Out of the different isotherms used to explain the nature of sorbent/sorbate interface in biosorption, the most common of them are Freundlich and Langmuir isotherms.

These isotherms are generally used to establish the relationship between the amount of metal ion sorbed and its equilibrium concentration in solution. The Freundlich isotherm model assumes that the removal of metal ions occurs on a heterogeneous adsorbent surface and can be applied to multilayer biosorption of the metal ions. The linearized Freundlich isotherm is expressed in Equation (7):

\[ \log \Gamma = \frac{1}{n} \log C_e + \log K_f \]  

(7)

where \( K_f \) is a constant related to the biosorption capacity (mg g⁻¹) and \( 1/n \) is an empirical parameter related to the biosorption intensity. The Freundlich isotherm for the biosorption of Pb(II) is shown in Figure 7. The Freundlich isothermal parameters for this study are given in Table 3.

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Table 3: Freundlich and Langmuir Isothermal Biosorption Parameters for the Biosorption of Pb(II) by Elephant Grass at Initial Concentration of 10-100 mgL⁻¹, pH4, 300K.

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>Freundlich Isotherm Model</th>
<th>Langmuir Isotherm Model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>n</td>
<td>Kf</td>
</tr>
<tr>
<td>Pb(II)</td>
<td>2.4878</td>
<td>22.88</td>
</tr>
</tbody>
</table>

The Langmuir isotherm model is used for monolayer sorption onto a surface containing a finite number of identical binding sites on the sorbent. The linearized form of the Langmuir isotherm model is given in Equation (8).

\[
\frac{1}{\Gamma} = \frac{1}{b_m} \frac{1}{C_e} + \frac{1}{\Gamma_m}
\]  

(8)

where \(b_m\) is a coefficient related to the affinity between the sorbent and sorbate, \(\Gamma_m\) is the maximum sorbate uptake under the given condition. The Langmuir isotherm for the biosorption of Pb(II) is shown in Figure 8 and the Langmuir isothermal parameters are given in Table 3. In view of the values of the linear regression coefficients (R²) given in Table 3, it is observed that the Freundlich isotherm model exhibited better fit to the biosorption data for Pb(II). The value of \(n\) is greater than unity, indicating favorable biosorption (McKay et al., 1982).

The Freundlich equation obtained is:

\[
\log\Gamma = 0.402\log C_e + 1.36
\]

while the Langmuir equation:

\[
\frac{1}{\Gamma} = 205.9657 \frac{1}{C_e} - 0.7128
\]

Thermodynamics of the Biosorption Process

The effect of temperature on the biosorption of the metals was investigated and the thermodynamic parameters (changes in standard Gibbs free energy, \(\Delta G^\circ\), enthalpy, \(\Delta H^\circ\), and entropy change, \(\Delta S^\circ\)) were calculated using Equations (9) – (11).

\[
\Delta G^\circ = -RT \ln K_{ad}
\]

(9)

\[
K_{ad} = \frac{C_{ad}}{C_e}
\]

(10)

\[
\Delta G^\circ = -\Delta S^\circ(T) + \Delta H^\circ
\]

(11)

where \(R\) is the universal gas constant (8.314 Jmol⁻¹K⁻¹) and \(T\) is the absolute temperature (K). The profiles for the change in free energy with temperature for the biosorption of Pb(II) is shown in Figure 9.

The high value of \(R^2 = 0.9795\) (≈ 1) shows the agreement between the change in free energy and the temperature of the biosorption process. The value of the change in entropy, \(\Delta S^\circ = 104.84\) J mol⁻¹K⁻¹, and the change in enthalpy, \(\Delta H^\circ = 19.88\) kJ mol⁻¹, are obtained from the slope and the intercept, respectively.
The positive value of change in entropy for the biosorption of the Pb(II) show that the sorption process is highly disordered. The positive value has been reported to be associated with increase in the dehydration steps of the sorbate ions, which are known to possess relatively high energies of solvation thereby resulting in the stabilization of water sheaths in the absence of the sorbent. The positive values of $\Delta S^o$ obtained in this study implies that there would be an increase in the number of steps involved in the biosorption of Pb(II) by elephant grass. Similarly, the enthalpy change is positive, indicative of endothermic process. Consequently, it is expected that increase in temperature favors the process.

CONCLUSION

Elephant grass has much potential as an efficient and useful biosorbent for the removal of Pb(II) from wastewaters. The FT-IR study demonstrated the involvement of functional groups with lone pairs of electrons for binding with the metal ions. The pH study shows that the parameter is an important factor in the biosorption of the metal ions from solutions. The kinetic study revealed that pseudo-second-order kinetic model describes the biosorption process. The Freundlich and Langmuir isotherm models fit the biosorption of both metals. The thermodynamic study shows that the process was endothermic with positive change in entropy of biosorption.

REFERENCES


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