The Effect of Phosphorus and Nitrogen Biofertilizers inoculation on the oily Sunflower to Adsorption of Pb (II) from Aqueous Solutions

Temer S. Ahmadi
Department of Chemistry, Villanova University, P.A., U.S.A.

Meisam Rahmatifard
Department of Chemistry, Boroujerd Branch, Islamic Azad University, Boroujerd, Iran

Zeinab Ghasemi
Department of Chemistry, Boroujerd Branch, Islamic Azad University, Boroujerd, Iran

Ahmad Seif
Department of Chemistry, Boroujerd Branch, Islamic Azad University, Boroujerd, Iran

Ali Goodarzi
Lab of Chemistry, Exir Pharma Inc., Boroujerd, Iran

Abstract — The effect of phosphorus and nitrogen biofertilizers inoculation on oily sunflower (var: iroflor) was studied for adsorption of Pb (II) from aqueous solutions. We used different types of phosphorus and nitrogen solubilizing bacteria as biological fertilizers. After inoculation of treated samples, we observed that the maximum adsorption was obtained by blank treatment in cases where no fertilizer was added to it (a,b). So irolf was applied as a biosorbent for Pb (II) adsorption. The effects of varying parameters such as: temperature, initial metal concentration, pH, and contact time on the adsorption process were determined. Adsorption equilibrium was established in 120 min and the maximum adsorption of Pb (II) on the biosorbent was observed to occur at a pH of 8.0. The Langmuir isotherm showed the best fit to the equilibrium data. The equilibrium parameter, R_L, indicated that this biosorbent is useful for Pb removal from aqueous solutions. The thermodynamic parameters were calculated which showed an exothermic adsorption process.

Keywords — Phosphorus and nitrogen Biofertilizers, solubilizing bacteria, sunflower, (var: iroflor), Pb (II) adsorption, Isotherm.

I. INTRODUCTION

The discharge of industrial waste water is a common source of heavy metal ions' pollution in the environment. Among the heavy metal ions, Pb (II) holds a special position and various processes such as metal electroplating, painting and coating, smelting, petrochemical, plumbing and battery manufacturing, make up the major sources of Pb in the environment. Lead can accumulate throughout the food chain and persist in nature without degradation. It is very toxic and can cause serious disorders such as anemia, kidney disease, mental retardation and nervous system damages [1]-[2]. Removal of metal ions from wastewater in an effective manner has become an important issue lately. The commonly used procedures for removing metal ions from wastewater include chemical precipitation, ion exchange, membrane separation, reverse osmosis, evaporation and electro dialysis. However, the application of these methods is often limited due to their inefficiency such as: high cost, generation of toxic sludge and high energy requirements. In contrast, adsorption techniques can be excellent method to treat industrial waste effluents, offering significant advantages such as low-cost, availability, profitability, ease of operation and efficiency [3]-[4].

There is a need for efficient and environmentally friendly methods to be developed to reduce heavy metal content despite many classical methods currently in use. Therefore, considerable attention has been focused upon the field of biosorption for the removal of heavy metal ions from aqueous solutions in recent years. Biosorption is a term used to describe the ability of biological materials to accumulate heavy metals from an aqueous solution through passive binding to dead biomass (such as: fiber, peat, rice hull, wool) or living plants and bacteria. The Plant materials are inexpensive, readily available and mainly comprised of cellulose and polyphenolic compounds that, under appropriate conditions of pH and temperature, are capable of adsorbing significant amounts of metal ions from solution [5]-[6].

In this work, the effect of phosphorus and nitrogen biological fertilizers inoculation on sunflower hybrid iroflor for Pb (II) adsorption was investigated. The sorption of lead from aqueous solutions by all of the treated samples in single metal solutions is examined and the sample which has a maximum adsorption is selected. This compound is subsequently employed as a biosorbent for Pb (II) adsorption.

The influence of experimental conditions such as pH, temperature, contact time, and initial concentration of pb (II) are studied. The Freundlich and Langmuir equations are used to fit the equilibrium isotherms. The thermodynamic parameters are also determined for the adsorption of Pb (II) on to biosorbent.

II. SAMPLE PREPARATION

The seeds of oily sunflower hybrid iroflor were inoculated with different types of phosphorus and nitrogen biofertilizers. As is shown in Table 1, two sets of biofertilizers were used from which 16 combinations were obtained, as in Table 2.
The sunflower leaves were washed with distilled water to remove the surface adhered particles and water soluble materials. 1.0g of a,b,c treated leaves was added to 100 mL of Pb (II) solution with initial concentration of 400 mg/L at pH=5. The mixture was agitated for 60 min on a shaker at 24°C. At the end of agitation, the mixtures were separated by filtration. The equilibrium concentration of the metal ion remaining in the solution was measured by flame atomic absorption spectroscopy. The same procedure was repeated for other samples. The results are shown in Table 2. It was found that the blank sample (a,b,c) adsorbed a maximum of Pb (II) ions from the solution. So this sample due to its physical and chemical stability, relatively lower cost, non-toxicity, and high adsorption capacity can be used as an alternative sorbent for removal of heavy metals such as lead. In addition, iroflor is readily available in large quantities and its adsorption process is rapid. So the present investigation has been carried out to explore the sorptive potential of this treatment for removal of Pb (II) from aqueous solutions in the absence of other metals.

Table 1: the different types of biofertilizer that were used.

<table>
<thead>
<tr>
<th>Nitrogen Biofertilizers</th>
<th>Phosphorus Biofertilizers</th>
</tr>
</thead>
<tbody>
<tr>
<td>b₁ : Super Nitro Plus</td>
<td>a₁ : Barvar – 2(^{30})</td>
</tr>
<tr>
<td>b₂ : Nitroxin</td>
<td>a₂ : Barvar – 3(^{30})</td>
</tr>
<tr>
<td>b₃ : Nitro Kara</td>
<td>a₃ : Bio phosphorus</td>
</tr>
<tr>
<td>b₄ : Blank Treatment (no biofertilizer)</td>
<td>a₄ : Blank Treatment (no biofertilizer)</td>
</tr>
</tbody>
</table>

Table 2: The results of Pb(II) % adsorption by 16 samples that were obtained from inoculation of treatments together.

<table>
<thead>
<tr>
<th>Treatment Samples</th>
<th>Pb(II) Adsorption%</th>
</tr>
</thead>
<tbody>
<tr>
<td>a₁b₁ : (Barvar – 2(^{30}) + Super Nitro Plus)</td>
<td>23.3</td>
</tr>
<tr>
<td>a₁b₂ : (Barvar – 2(^{30}) + Nitroxin)</td>
<td>4.8</td>
</tr>
<tr>
<td>a₁b₃ : (Barvar – 2(^{30}) + Nitro Kara)</td>
<td>10.84</td>
</tr>
<tr>
<td>a₁b₄ : (Barvar – 2(^{30}) + Blank Treatment)</td>
<td>7.98</td>
</tr>
<tr>
<td>a₂b₁ : (Barvar – 3(^{30}) + Super Nitro Plus)</td>
<td>12.22</td>
</tr>
<tr>
<td>a₂b₂ : (Barvar – 3(^{30}) + Nitroxin)</td>
<td>27.03</td>
</tr>
<tr>
<td>a₂b₃ : (Barvar – 3(^{30}) + Nitro Kara)</td>
<td>10.63</td>
</tr>
<tr>
<td>a₂b₄ : (Barvar – 3(^{30}) + Blank Treatment)</td>
<td>15.08</td>
</tr>
<tr>
<td>a₃b₁ : (Bio phosphorus+ Super Nitro Plus)</td>
<td>4.66</td>
</tr>
<tr>
<td>a₃b₂ : (Bio phosphorus + Nitroxin)</td>
<td>6.36</td>
</tr>
<tr>
<td>a₃b₃ : (Bio phosphorus + Nitro Kara)</td>
<td>24.41</td>
</tr>
<tr>
<td>a₃b₄ : (Bio phosphorus + Blank Treatment)</td>
<td>7.61</td>
</tr>
<tr>
<td>a₄b₁ : (Blank Treatment + Super Nitro Plus)</td>
<td>9.05</td>
</tr>
<tr>
<td>a₄b₂ : (Blank Treatment + Nitroxin)</td>
<td>5.5</td>
</tr>
<tr>
<td>a₄b₃ : (Blank Treatment + Nitro Kara)</td>
<td>17.10</td>
</tr>
<tr>
<td>a₄b₄ : (Blank Treatment + Blank Treatment)</td>
<td>49.53</td>
</tr>
</tbody>
</table>
III. MATERIALS and INSTRUMENTAL

A stock solution (1000 mg/L) of Pb (II) was prepared by dissolving appropriate amounts of Pb(NO₃)₂ (Merk) in double-distilled water. An appropriate volume of CH₃COOH and CH₃COONa were used to adjust pH of the solution. All chemicals were of analytical grade and were used as received. The concentration of lead ions were determined by an atomic absorption spectrometer (VARIAN, AA240) equipped with air-acetylene flame. The operating parameters were: lamp current, 10.0 mA; slit width, 1 mm; wavelength, 217 nm. A portable pH meter equipped with a combined glass electrode was used for all the pH measurements.

IV. ADSORPTION METHOD

Batch adsorption tests were carried out at room temperature (25°C), in each experiment 100 ml of Pb(II) solution of known initial concentration (400 mg/L) was treated with 1.0 g of a,b₂ treated wet leaves at pH=8. The mixture was shaken on a thermostated shaker bath operating at 100 rpm for duration of 120 min. After the equilibrium was reached, the adsorbent was separated from the metal solution. Then the filtrate was analyzed in an Atomic Absorption Spectrophotometer. All experiments were performed at least three times and average values of the results are given here.

The sorption percentage (Ads. %) was calculated as:

\[ A\% = \frac{C_0 - C_e}{C_0} \times 100 \]  (1)

Where \( C_0 \) is the initial concentration and \( C_e \) is the equilibrium concentration, mg/L.

The metal ion uptake capacity at adsorption equilibrium \( q_e \) was obtained using the equation:

\[ q_e = \frac{(C_0 - C_e) \times V}{S} \]  (2)

where \( q_e \) (mg/g) is the equilibrium adsorption capacity, \( C_0 \) and \( C_e \) are the initial and equilibrium concentration (mg/ L) of Pb(II) ions in solution, \( V \) (L) is the volume and \( S \) (g) is the weight of adsorbent.

V. RESULT and DISCUSSION

A. Effect of pH

Effect of initial pH of solution on adsorption was determined at various pH values ranging from 4 to 9. The pH of each solution was adjusted by addition of CH₃COOH / CH₃COONa, buffer solution. As Fig. 1 shows, adsorption of Pb (II) onto biosorbent increased from 4.04% to 80.03% when pH of the solution was increased from 4 to 8. This phenomenon can be explained by the surface charge of the adsorbent and the H⁺ ions present in the solution. At low pH, the cations compete with the H⁺ ions in the solution for the active sites and therefore, they have a lower adsorption. The surface charge of the biomass materials is a strong function of the pH. Therefore at high pH values surface of the adsorbent has a higher negative charge which results in a higher attraction for cations. At pH > 9.0 the adsorption of lead becomes slightly low which may be attributed to the formation of hydroxyl species such as [Pb (OH)]⁺ or Pb (OH)₂.

Since maximum adsorption occurs at pH= 8, pH of the solutions for the rest of the reactions were kept at this value [7]-[8].

![Fig.1. Effect of pH on the Pb (II) adsorption.](image)

B. Effect of contact time

The amount of metal adsorbed also depends on contact time if other parameters like initial concentration, temperature, pH, etc. are kept constant. Fig. 2 shows the effect of the contact time on the adsorption capacity of the Pb (II) metal ions on a,b₂ adsorbent. It was found that the amount of adsorbed ions increased rapidly at the first time, which indicates that there were enough adsorption sites for the ions to be accommodated. Adsorption percentage of Pb (II) increased with contact time up to 120 min. After this time, there is no considerable change in Pb (II) ion removal, which shows that the adsorption sites became saturated gradually and subsequently a constant value at about 180 min. Therefore, one can conclude that the system attains equilibrium value at 120 min; this time is used for all equilibrium studies that follow.

![Fig. 2. Effect of contact time on the adsorption of Pb (II) by a,b₂ treatment.](image)

C. The effect of initial metal ion concentration

The amount of Pb⁺⁺ adsorbed for different initial concentrations (200 – 600 mg/L) of lead solutions onto biosorbent was measured and the results are shown in Fig. 3. The following parameters were kept constant in the
process: adsorbent dose of 1.0 g, pH=8, and temperature at 25 °C. The experimental data indicate that the % adsorption of Pb (II) ions decreases from 87.35 % to 76.32 % with an increase in the initial Pb²⁺ concentration from 200 to 600 mg/L due to lack of binding sites for the adsorption of Pb (II) ions. However the metal uptake capacity is increased from 17.47 mg/g to 45.79 mg/g as the concentration of Pb (II) solution is increased, as shown in Fig. 4. This increase in loading capacity of the adsorbent in relation with the concentration of the metal ions can be explained with a high driving force for mass transfer [9]-[10].

![Fig.3. Effect of initial concentration on the Lesd’s % adsorption](image)

![Fig.4. Effect of initial concentration on the adsorption capacity of Pb(II) by a,b_i treatment’s leaves.](image)

**D. Effect of temperature**

The effect of temperature on the Pb (II) adsorption from aqueous solutions by a,b_i biosorbent was studied in the range of 298 and 328 K under optimized conditions. Fig. 5 shows that the sorption of metal ions by adsorbent reduces with an increase in temperature, indicating an exothermic nature of the sorption processes. A decrease in the adsorption of Pb (II) ions with the rise in temperature maybe explained by being more active adsorbing sites at low temperature. Also an increase in temperature results in mobility of the ions being increased and a decrease in the retarding forces acting on the adsorption ions [11].

![Fig.5. Effect of temperature on the adsorption percentage of Pb (II) ions.](image)

**I. EQUILIBRIUM ADSORPTION ISOTHERMS**

Adsorption isotherm at constant temperature shows the relation between the amount adsorbed and the equilibrium concentration of ions in the liquid phase. In this study, the isotherm data was analyzed using the Langmuir and Freundlich equations.

**A. Freundlich isotherm**

The Freundlich isotherm expresses multilayer adsorption on energetically heterogeneous surfaces. The widely used empirical Freundlich equation is given by:

\[ \log q_e = \log K_F + \frac{1}{n} \log C_e \]  

where \( q_e \) is the equilibrium concentration of Pb(II) ions on the adsorbent (mg/g), \( K_F \) is the equilibrium concentration of Pb (II) ion in solution (mg/L), and \( n \) are Freundlich isotherm constants, which are related to the adsorption capacity (or the bonding energy) and intensity of the sorbent, respectively [12].

The Freundlich plot for the adsorption of Pb (II) onto a,b_i biosorbent is shown in Fig. 6. It is seen that the model gives a good fit to the experimental data with the correlation coefficient of \( R^2 = 0.909 \).

The magnitude of \( 1/n \) quantifies the favorability of adsorption and the degree of heterogeneity on the surface of adsorbent. If \( 1/n \) is less than unity – suggesting favorable adsorption, then the adsorption capacity increases and new adsorption sites form [13]. The \( 1/n \) value obtained for Pb (II) ions was 0.539, indicating that heterogeneous binding sites were involved for the adsorption of Pb (II) ions.

**B. Langmuir isotherm**

The linear form of Langmuir isotherm is expressed as:

\[ \frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L \cdot q_m} \]  

where \( C_e \) is the equilibrium concentration of metal ions in the solution (mg/L), \( q_e \) is the adsorbed value of metal ions at equilibrium concentration (mg/g), \( q_m \) is the maximum adsorption capacity (mg/g), and \( K_L \) is the
Langmuir binding constant which is related to the energy of adsorption (L/mg). Plotting \( C/q_e \) vs. \( C \) gives a straight line with slope and intercept equal to \( 1/q_m \) and \( 1/(K_L q_m) \), respectively. The Langmuir isotherm assumes monolayer adsorption with maximum adsorption occurring when adsorbed molecules on the surface of the adsorbent form a saturated layer [14]. The Langmuir isotherm is shown in Fig. 7, indicating that adsorption of lead fits this model well with \( R^2 = 0.968 \). The values of Freundlich and Langmuir constants obtained from the plots are given in Table 3, for comparison. The values obtained from the Langmuir curve indicate a monolayer adsorption.

The Langmuir isotherm can be expressed in terms of a dimensionless constant called equilibrium parameter, \( R_L \) which is defined as:

\[
R_L = \frac{1}{1 + K_L \cdot C_0}
\]

(5)

Where \( C_0 \) is the initial metal concentration. The value of \( R_L \) indicates the type of isotherm to be favorable (0 < \( R_L < 1 \)), unfavorable (\( R_L > 1 \)), linear (\( R_L = 1 \)), or irreversible (\( R_L = 0 \)) [15]. Fig. 8 shows that the calculated values of are in the range of 0 < \( R_L < 1 \) which indicates that adsorption of Pb (II) onto biosorbent is favorable.

**II. DETERMINATION OF THERMODYNAMIC PARAMETERS**

The thermodynamic parameters such as: standard Gibb’s free energy (\( \Delta G^\circ \)), standard enthalpy (\( \Delta H^\circ \)) and standard entropy (\( \Delta S^\circ \)) were evaluated from the following equations [16].

\[
K_c = \frac{q_m}{C_e}
\]

(6)

\[
\Delta G^\circ = -RT \ln K_c
\]

(7)

\[
\ln K_c = -\frac{\Delta H^\circ}{R} \times \frac{1}{T} + \frac{\Delta S^\circ}{R}
\]

(8)

Where \( R \) is the universal gas constant (8.314 J/K mol), and \( T \) is the absolute temperature (K). Fig. 9 shows a plot of \( \ln K_c \) vs. \( 1/T \) that yields a straight line with a slope = - \( \Delta H^\circ / R \) and intercept = \( \Delta S^\circ / R \). The calculated values for \( \Delta G^\circ, \Delta H^\circ \) and \( \Delta S^\circ \) were shown in Table 4.

![Fig.6. Freundlich plot of Pb(II) adsorption onto a\textsubscript{b} treatment’s leaves.](image)

![Fig.7. Langmuir isotherm for biosorption of Pb(II).](image)

![Fig.8. Separation factor for Lead sorption by a\textsubscript{b} treatment’s leaves.](image)

![Fig.9. Vant Hoff plot of Ln Kc against 1/T for Pb (II) adsorption on a\textsubscript{b}.](image)

Table 3: Constants of isotherm models for Pb(II) sorption by biosorbent at 298K.

<table>
<thead>
<tr>
<th>Model</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>( K_L = 0.016 \text{ L/mg} )</td>
</tr>
<tr>
<td></td>
<td>( q_m = 66.66 \text{ mg/g} )</td>
</tr>
<tr>
<td></td>
<td>( R^2 = 0.968 )</td>
</tr>
<tr>
<td></td>
<td>( K_v = 3.45 \text{ (mg/g)/(mg/L)^{1/2}} )</td>
</tr>
<tr>
<td>Freundlich</td>
<td>( 1/n = 0.539, n = 1.84 )</td>
</tr>
<tr>
<td></td>
<td>( R^2 = 0.909 )</td>
</tr>
</tbody>
</table>

Copyright © 2012 IJAIR, All right reserved
The spontaneity of the biosorption is demonstrated further by the increase in free energy change with temperature. The increase in $\Delta G^\circ$ value with an increase in temperature indicates that the biosorption of Pb (II) is less favorable at higher temperatures. The negative value of $\Delta H^\circ$ indicates the biosorption is exothermic. The positive values of $\Delta S^\circ$ show that the freedom of metal ions is not too restricted on the biosorbent and also suggests some structural change in metal ions and adsorbent [5]-[17].

III. CONCLUSION

The effect of phosphorus and nitrogen biological fertilizers’ inoculation on the oily sunflower hybrid iroflor confirmed that the $a_b$ treated leaves with any biofertilizer could remove the maximum amount of lead ions from aqueous solutions. The sorption performances were strongly affected by parameters such as: contact time, initial Pb (II) concentration, initial pH of solution and temperature. The isotherm adsorption data were well fitted by the Langmuir model. Based on the thermodynamic parameters ($\Delta G^\circ$, $\Delta H^\circ$ and $\Delta S^\circ$), it was concluded that the adsorption process is exothermic in nature. The increase in $\Delta G^\circ$ value with an increase in temperature indicates that the biosorption of Pb (II) is less favorable at high temperatures and the positive $\Delta S^\circ$ values suggest an increase in the randomness at the solid/solution interface during the adsorption process. It is suggested that incorporating this treatment in the environment can be an effective low-cost biosorbent for Pb (II) ions and is particularly suitable for heavy metal adsorption application in small industries and developing countries.

REFERENCES


AUTHOR’S PROFILE

Temer S. Ahmadi
Department of Chemistry, Villanova University, P.A.,U.S.A.

Meisam Rahmatifard
Department of Chemistry, Boroujerd Branch, Islamic Azad University, Boroujerd, Iran

Zeinab Ghasemi
Department of Chemistry, Boroujerd Branch, Islamic Azad University, Boroujerd, Iran

Ahmad Seif
Department of Chemistry, Boroujerd Branch, Islamic Azad University, Boroujerd, Iran

Ali Goodarzi
Lab of Chemistry, Exir Pharma Inc., Boroujerd, Iran

Copyright © 2012 IJAIR, All right reserved