BIOSORPTION OF Pb(II) - KINETICS, EQUILIBRIUM AND THERMODYNAMIC STUDY

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Heavy metals
Neem leaves
Hyacinth roots
Pseudo-second order model
Freundlich isotherm model

Paper presented in International Conference on Environment, Energy and Development (from Stockholm to Copenhagen and beyond)
December 10 - 12, 2010, Sambalpur University
The ability of neem leaves and hyacinth roots as low cost natural adsorbent was investigated for the adsorptive removal of Pb (II) ions from aqueous solutions. The effects of pH, metal ion concentration, contact time and adsorbent dosage on the adsorption process were studied in batch experiments. Results of the present study showed that the solution pH was the key factor affecting the adsorption characteristics. The optimum pH for adsorption was found to be 5 and equilibrium was achieved within 2 hr of contact time. Kinetics data were best described by pseudo-second order model for both the cases and equilibrium adsorption data were better fitted to Freundlich isotherm model. The maximum adsorption capacity \( q_{\text{max}} \) of neem leaves for Pb(II) ions in terms of monolayer adsorption was 22.326 mg/g and for hyacinth roots it was 24.937 mg/g. The value of sorption energy calculated using Dubinin-Radushkevich isotherm were 10.358 kJ/mol for neem leaves and 11.251 kJ/mol for hyacinth roots and it indicated that the adsorption processes were chemical in nature. The negative value of Gibbs free energy for the adsorption process reveal that the process was spontaneous. The standard enthalpy change indicated that the process was endothermic and also it indicated that the process was chemical in nature.

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INTRODUCTION

Environmentalists are primarily concerned with the presence of heavy metals due to their toxicity and impact on human health and environment. Lead poisoning in human causes severe damage to kidney, nervous system, reproductive system, liver and brain. Severe exposure to lead has been associated with sterility, abortion, stillbirths and neo-natal deaths (Amuda et al., 2007 and Manahan, 1984). Process industries, such as battery manufacturing, printing and pigment, metal plating and finishing, ammunition, soldering material, ceramic and glass industries, iron and steel manufacturing units generate large quantities of wastewater contaminated with lead. In drinking water lead contamination occurs due to the corrosion and leaching of lead pipes and Pb/Sn solder joints associated with copper service lines used in household plumbing (Goyer and Chisolon, 1972). The permissible level of lead in drinking water is 0.05 mg/L (WHO, 1984). The acceptable limit of lead in wastewater as set by Environment Protection Agency (EPA, 1990) is 0.05 mg/L and that of Bureau of Indian Standards (BIS) is 0.1 mg/L (BIS, 1981). Keeping in view the importance of the situation, specifically toxicity in children, it has diverted the global attention towards understanding its behavioral pattern in ecosystem and metabolism for adopting measures for its effective removal from such industrial and municipal waste effluents.

The safe and effective disposal of Pb(II) ions containing waste water is a challenging objective for industries because cost effective treatment alternatives are not readily available. Common cleaning methods comprise chemical precipitation, co-precipitation, and formation of volatile compounds such as hydride and alkylate, ion exchange, electrolysis, membrane filtration, solvent extraction, fertilization and sorption to metal oxide, clay, activated carbon, organic sorbents. These methods differ with respect to cost, complexity and efficiency (Bhattacharya et al., 2008). Among these technologies, adsorption is a user-friendly technique for the removal of heavy metal.

The present study deals with a series of batch adsorption experiments to investigate and explore the feasibility of neem leaves and hyacinth roots as low cost adsorbent for the removal of Pb(II) ions from aqueous solutions.

MATERIALS AND METHODS

Adsorbent preparation

Neem leaves and hyacinth roots were used as low cost natural adsorbent for the removal of Pb(II) ions from aqueous solution. All the adsorbents were collected from local area near Kolkata, West Bengal, India.

Neem leaves were treated with 0.1 N NaOH to remove lignin based color materials followed by 0.1 N H₂SO₄. Hyacinth roots were boiled for 6 hr to remove color materials. Finally all the adsorbents were washed with distilled water several times and dried at 105ºC for 6 hr to remove the adherent moisture. After drying, all the adsorbents were sieved to obtain particle size of 250-350 μm prior to use for adsorption studies.

Synthetic Pb(II) ions solution preparation

The stock solution containing 1000 mg/L of Pb(II) was prepared by dissolving 1.61 g of lead nitrate (Pb(NO₃)₂) in 1000 ml of double distilled water. The range of Pb(II) ions concentration was varied from 5 mg/L to 300 mg/L by diluting stock solution.

Reagent and equipment

All the necessary chemicals used in the study were of analytical grade and obtained from E. Merck Limited, Mumbai, India. The pH of the solution was measured with a EUTECH make digital microprocessor based pH meter previously calibrated with standard buffer solutions. Analysis of heavy metal ions including Pb(II) ions were carried out using Atomic Absorption Spectrophotometer (AA 240 VARIAN, Australia).

Batch adsorption studies
Batch adsorption experiments were carried out to determine the optimum Pb(II) ions adsorption condition onto natural adsorbents in 250 mL stopper conical flask. The pHs of the solutions were adjusted by adding HCl or NaOH solution as per required at the beginning of the experiment and not controlled afterwards. Necessary amount of adsorbent was then added and content in these flasks were shaken for the desired contact time in an electrically thermostated reciprocating shaker at 110-125 strokes/minute at 30ºC. The time required to reach the equilibrium was estimated by drawing samples at regular intervals of time. After completion of the adsorption process adsorbent was separated from the solution using filter paper (Whatman No. 42) and supernatant was analyzed for residual Pb(II) ions concentration by Atomic Absorption Spectrophotometer (APHA, 1998). Three replicates were used for each Pb(II) ions adsorption experiments and the results given were the average values. The percentage of removed Pb(II) ions in solution was calculated using the following equation

\[
\% \text{ removal of Pb(II) ions} = \left(1 - \frac{C_t}{C_0}\right) \times 100\%
\]

Where \(C_0\) and \(C_t\) are the concentrations of Pb(II) ions at initially and any time \(t\) respectively.

**RESULTS AND DISCUSSION**

**Effect of initial pH**

Fig. 1 shows the effect pH on the removal of Pb(II) ions from aqueous solution using neem leaves and hyacinth roots. The results showed that the adsorption capacities of Pb(II) ions increased significantly as pH increased from 2.0 to 5.0 for all the adsorbents. At low pH (pH 2-3) less metal ions adsorption occur, may be explained on the basis of binding sites being protonated, resulting in a competition between H\(^+\) and Pb(II) ions for occupancy of binding sites (Hasana et al., 2010). As the pH increased and biosorbents surface functional groups activated, it resulting the increased Pb(II) ions sorption and sharpest increase in Pb(II) ions uptake. When pH > 5, Pb(II) ions started to precipitate out from the solution as lead hydroxide. At pH > 5, adsorption capacity increased may be a combination of both adsorption onto biosorbents surface and precipitation of lead hydroxide from the solution. Therefore experiments were not conducted at pH > 5 and pH 5.0 was considered as optimum pH.

**Effect of contact time**

The effect of contact time on the adsorption of Pb(II) ions onto different biosorbent is represented in Fig. 2. It seemed that the biosorption considered of two phase: a primary rapid phase and a second slow phase. Initial rapid phase indicated to give away a very slow approach to equilibrium and accounted for the major part in the total Pb(II) ions adsorption. Then adsorption reached a plateau value in approximately 120 min, which showed that the saturation of the active sites of the biosorbent. The time required to reach equilibrium for the adsorption of Pb(II) ions were 2.0 hr for all the cases.

**Effect of initial Pb(II) ions concentration**

Percent removal decreases with the increase in initial Pb(II) ions concentration from 5 mg/L to 300 mg/L. At the lower concentration, all the Pb(II) ions in the solution would react with the binding sites and thus facilitated almost complete adsorption. At higher concentration more Pb(II) ions left un-adsorbed in the solution due to the saturation of the binding sites. This indicates that the energetically less favorable sites become involve with increasing Pb(II) ions concentration in aqueous solution. Adsorption capacity increases when initial concentration of Pb(II) ions increases from 5 mg/L to 300 mg/L.

**Effect of adsorbent dosage**

The effect of adsorbent types and dosage for the removal of Pb(II) ions from aqueous solution using initial metal ion concentration at 25 mg/L are carried out. The removal efficiency was found to increase rapidly and decreases adsorption capacity at optimum pH for all the cases which may be attributed to increase surface area of the biosorbent and availability of more adsorption sites due to increase amount of biosorbent (Naiya et al., 2009).
Adsorption kinetics study
The mechanism of adsorption depends on the physical and chemical characteristics of the adsorbent as well as on the mass transfer process. The rate kinetics of Pb(II) ions adsorption onto neem leaves and hyacinth roots were analyzed using pseudo first-order, pseudo-second order and intraparticle diffusion models. The conformity between experimental data and the model predicted values were expressed by correlation coefficients ($r^2$) and chi-square ($\chi^2$) analysis.

Pseudo first-order model
The integral form of the pseudo first-order (Lagergren, 1898) model generally expressed as follows,

$$ \log \left( q_e - q \right) = \log q_e - \frac{K_{ad} \cdot t}{2.303} \quad \text{...... (2)} $$

Where $q_e$ and $q$ are the adsorption capacity (mg/g) at equilibrium and at time t, respectively, $K_{ad}$ is the pseudo first-order rate constant (min$^{-1}$). The plot of $\log (q_e - q)$ versus $t$ give a linear relationship from which rate constant ($K_{ad}$) and statistical parameters are calculated. The result is shown in Table 1.

Pseudo second order model
The kinetics of adsorption process may also be analyzed by pseudo second order rate equation (Ho et al., 2000). The linearized form of the equation is expressed as

$$ \frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \cdot t \quad \text{...... (3)} $$

Where $K_2$ is the rate constant of pseudo second-order model (mg/g/min). The plot of ($t/q$) and $t$ should give a linear relationship from which $q_e$ and $K_2$ can be determined from the slope and intercept of the plot respectively. The values of pseudo second order rate constants along with statistical data is shown in Table 1.

Intraparticle diffusion model
The intraparticle diffusion model is based on the theory proposed by Weber and Moris (Weber and Morris1963) and can be expressed as,

$$ q = K_{id} \cdot t^{0.5} + C \quad \text{...... (4)} $$

Where $k_{id}$ and $C$ are intra-particle diffusion rate constant (mg/g/min$^{1/2}$) and a constant respectively. From the Eq. (4), the value of $K_{id}$ is calculated. The values of rate constants and statistical parameters for each model is shown in Table 1. The high correlation coefficients and low chi-square value indicated that the pseudo second-order model, an indication of chemisorptions mechanism fits better with experimental data than that of intra-particle diffusion model and Pseudo first-order model

Prediction of adsorption rate-limiting step
The prediction of adsorption rate-limiting step is an important aspect for the study of adsorption process. Generally, a solid-liquid adsorption process could be described by three steps as follows, (1) Transport of adsorbate from bulk solution through liquid film to the adsorbent exterior surface. This step is called film diffusion; (2) Transport of adsorbate from the adsorbent exterior surface to the pores of the adsorbent. This step is called intraparticle diffusion; (3) The adsorbate is adsorbed onto the active group in inner and outer surface of adsorbent. Generally, the adsorption rate is controlled by outer diffusion or inner diffusion or both (Kalavathy et al., 2005). The study tries to use Fick’s equation, Eq. (5) (Seeber et al., 1998; Zaki et al., 2000; Qin et al., 2007) to describe the diffusion process of Pb(II) ions on the exterior and interior surface of the microspheres.

$$ \frac{q}{q_e} = \frac{6}{R_s} \cdot \sqrt{\frac{D_c \cdot t}{\pi}} \quad \text{...... (5)} $$

Where, $R_s$ (m) is the radius of adsorbents and $D_c$ ($m^2/s$) is the diffusion coefficient. Plot of $q/q_e$ versus $\sqrt{t}$ is shown in Fig. 3 for hyacinth roots. The first linear portion indicated to the film diffusion, the second linear portion related the intraparticle diffusion and the last linear portion suggested adsorption-desorption equilibrium. Fig. 3 showed that diffusion took about 75 min while the intraparticle diffusion took 45 min. The ratio of the time taken by film diffusion to intraparticle diffusion was 5:3. Similar type of result also found for neem leaves and ratio of time taken by film diffusion to intraparticle was 1:1.
Table 1: Different kinetic model parameter

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>Pseudo first-order model</th>
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<tr>
<td></td>
<td>$K_r$ (min$^{-1}$)</td>
<td>$r^2$</td>
<td>$\chi^2$</td>
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<tr>
<td>Neem leaves</td>
<td>0.0397</td>
<td>0.9476</td>
<td>6.5157</td>
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<tr>
<td>Hyacinth roots</td>
<td>0.0427</td>
<td>0.9869</td>
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<td>0.1527</td>
<td>0.9999</td>
<td>0.0026</td>
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<tr>
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<table>
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<tr>
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<td>$K_{id}$ (mg/g/min$^{1/2}$)</td>
<td>$r^2$</td>
<td>$\chi^2$</td>
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<tr>
<td>Neem leaves</td>
<td>0.0270</td>
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<td>0.0086</td>
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<tr>
<td>Hyacinth roots</td>
<td>0.0294</td>
<td>0.8478</td>
<td>0.0051</td>
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Table 2: Different adsorption isotherm constants with statistical parameters

<table>
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<tr>
<td></td>
<td>$q_{max}$ (mg/g)</td>
<td>$b$ (L/mg)</td>
<td>$r^2$</td>
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<tr>
<td>Neem leaves</td>
<td>22.3264</td>
<td>0.0207</td>
<td>0.8380</td>
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<tr>
<td>Hyacinth roots</td>
<td>24.9376</td>
<td>0.0701</td>
<td>0.9259</td>
</tr>
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<td></td>
<td>Freundlich isotherm model</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$K_f$ (mg/g)/$n$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Neem leaves</td>
<td>0.8322</td>
<td>1.5988</td>
<td>0.9901</td>
</tr>
<tr>
<td>Hyacinth roots</td>
<td>2.0363</td>
<td>1.7185</td>
<td>0.9977</td>
</tr>
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</table>

Table 3: Thermodynamic parameters for Pb(II) ions biosorption

<table>
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<tr>
<th>Temperature (K)</th>
<th>Neem leaves</th>
<th>Hyacinth roots</th>
</tr>
</thead>
<tbody>
<tr>
<td>Δ$G^\circ$ (KJ/mol)</td>
<td>303</td>
<td>-0.140</td>
</tr>
<tr>
<td></td>
<td>313</td>
<td>-0.237</td>
</tr>
<tr>
<td></td>
<td>328</td>
<td>-1.793</td>
</tr>
<tr>
<td>Δ$H^\circ$ (KJ/mol)</td>
<td>20.658</td>
<td>41.299</td>
</tr>
<tr>
<td>Δ$S^\circ$ (KJ/(mol K))</td>
<td>0.067</td>
<td>0.147</td>
</tr>
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</table>

So in case of hyacinth roots film diffusion was predominated over the intraparticle diffusion. Film diffusion and intraparticle diffusion was equally responsible for the biosorption of Pb(II) ions onto neem leaves.

Adsorption isotherms

The adsorption isotherm for the removal of metal ion was studied using initial concentration of between 5 and 300 mg/L at an adsorbent dosage level of 10.0 g/L for Pb(II) ions 30°C.

Langmuir isotherm model

Equilibrium adsorption of Pb(II) ions assuming monolayer adsorption onto a surface with a finite number of indentical sites is represented by Langmuir adsorption isotherm model (Langmuir, 1918)

$$\frac{C_e}{q_e} = \frac{1}{q_{max}b} + \frac{C_e}{q_{max}} \quad \text{......... (6)}$$

Where $C_e$ is the concentration of Pb(II) ions in solution at equilibrium (mg/L), $q_{max}$ is the maximum adsorption capacity (mg/g) and $b$ is the Langmuir constant (L/mg). Linear plots of $C_e/q_e$ vs. $C_e$ have been used to determine the value of $q_{max}$ (mg/g) and $b$ (L/mg). The equilibrium constants and statistical parameters are listed in Table 2. Linearity of the plots indicates the applicability of the adsorption isotherm.
Freundlich isotherm model
Freundlich adsorption model (Freundlich, 1906) assumed heterolayer adsorption onto adsorbent surface and linear form can be described by the following Equation
\[
\log q_e = \log K_f + \frac{1}{n} \log C_e
\]
......... (7)
The Freundlich isotherm constants \(K_f\) (mg/g) and \(n\) are constants incorporating all factors affecting the adsorption process such as adsorption capacity and intensity of adsorption. The constants \(K_f\) and \(n\) are calculated from Equation (7) and Freundlich plots (Fig.4). The values for Freundlich constants, \(r^2\) and \(R^2\), are presented in Table 2. From the value of \(r^2\) and, it can be concluded that the adsorption of Pb(II) ions onto neem leaves and hyacinth roots better follow Freundlich adsorption isotherm model than Langmuir isotherm model.

Dubinin-Radushkevich (D-R) isotherm model
The Dubinin-Radushkevich (Dubinin et al., 1947) isotherm model was used to predict the nature of adsorption processes as physical or chemical. The linear form of the model was described as,
\[
\ln C_{abs} = \ln X_m - \lambda \varepsilon^2
\]
......... (8)
Where \(C_{abs}\) is the amount of Pb(II) ions adsorbed onto neem leaves and hyacinth roots (mol/g) and \(X_m\) represents the maximum adsorption capacity of adsorbent (mmol/g), \(\lambda\) is constant related to sorption energy, while \(\varepsilon\) is the Polanyi potential (Polanyi, 1932) which is equal to,
\[
\varepsilon = R T \ln (1 + \frac{1}{C_e})
\]
......... (9)
Plot of \(\ln C_{abs}\) vs. \(\varepsilon^2\) give a straight line from which the values of \(\lambda\) was calculated. Using the value of \(\lambda\), the mean sorption energy, \(E\), were evaluated as
\[
E = \frac{1}{\sqrt{-2\lambda}}
\]
......... (10)
The estimated values of \(E\) were 10.358 KJ/mol and 11.251 KJ/mol for neem leaves and hyacinth roots respectively which suggested the adsorption process was chemical in nature.

Thermodynamic study
To study the thermodynamic behavior of Pb(II) ions biosorption, thermodynamic parameters such as change in Gibbs free energy (\(\Delta G^0\)), enthalpy (\(\Delta H^0\)) and entropy (\(\Delta S^0\)) are calculated. The thermodynamic equilibrium constant () are obtained by calculating apparent equilibrium constant () at different temperature and initial Pb(II) ions concentration for each system and extrapolating to zero (Naiya et al., 2009).
\[
K_e = \frac{C_a}{C_e}
\]
......... (11)
Where \(C_a\) is the concentration of Pb(II) ions on the adsorbent at equilibrium (mg/L) and \(C_e\) is the concentration of Pb(II) ions in solution (mg/L). The change Gibbs free energy (\(\Delta G^0\)), enthalpy (\(\Delta H^0\)), and entropy (\(\Delta S^0\)), for the biosorption processes are calculated using the following equations
\[
\ln K_e^0 = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}
\]
......... (12)
\[
\Delta G^0 = -RT \ln K_e^0
\]
......... (13)
From the slope and intercept of the plot vs. \(1/T\), the values of \(\Delta H^0\) and \(\Delta S^0\) had been computed, while \(\Delta G^0\) was calculated using Eq. (13) and reported in Table 3. The results indicated that the biosorption processes are endothermic in nature. The heat of adsorption value between 20 and 400 KJ/mol indicates the process are chemical in nature. The negative value of \(\Delta G^0\) at all temperatures indicated the feasibility of biosorption process. The positive value of \(\Delta S^0\) indicated the increased randomness at the solid/solution interface during
the Pb(II) ions adsorption process.

CONCLUSIONS

The obtained results can be summarized as,

1. Maximum Pb(II) ions adsorption occur at pH 5 and at higher pH precipitation of hydroxyl species get started.
2. The equilibrium time for adsorption of Pb(II) ions from aqueous solutions was achieved within 2 hr of contact time.
3. The experimental data were better described by pseudo 2\textsuperscript{nd} order model as evident from statistical data.
4. Film diffusion of Pb(II) ions was predominated over the intraparticle diffusion onto hyacinth roots. But film diffusion and intraparticle diffusion was equally responsible for the onto neem leaves.
5. The maximum monolayer adsorption capacity was 22.326 mg/g and 24.937 mg/g onto neem leaves and hyacinth roots respectively.
6. The sorption energy was 10.358 KJ/mol and 11.251 KJ/mol for neem leaves and hyacinth roots respectively which suggested the adsorption process was chemical in nature.
7. The thermodynamic parameters indicated that the adsorption process is endothermic, spontaneous and chemical in nature.

ACKNOWLEDGEMENT

B. Singha wishes to thanks the University of Calcutta for the Project Fellow (UPE /Science and Technology), Ref. No. UGC/489/Fellow UPE (SC/T), dated the 16/ 4/ 2009. The authors acknowledge to AICTE for financial support (Project no. F. No.: 8023 /BOR /RID/RPS-72/2008-09).

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