Biosorption of Pb(II) Ions onto Cocos Nucifera L.: Application of Two-Parameter Isotherm Models

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Abstract: The feasibility of Cocos nucifera leaf powder for the removal of Pb(II) from aqueous solutions is experimentally investigated in the present study and to understand the interaction among the operating variables – metal ion concentration, biosorbent dosage, initial solution pH and absolute temperature and by making constant of the adsorbent size and contact time. A 20 mg/L of Pb(II) solution, treated with 25 g/L of adsorbent at a pH of 5.0 and 303 K yielded 97.68 % removal of Pb(II). Freundlich isotherm proved to be better model to represent the equilibrium data compared to Langmuir, Temkin and Dubinin Rudishkevich, Flory-huggins and Halsey isotherm.

Keywords: Pb(II) removal; Biosorption; Cocos nucifera L.; Equilibrium

1. Introduction

Water is essential to all living bodies. Most of it is polluted due to the discharge of heavy metals like Co, Pb, Cr, Zn, Cd, Cu, Hg, As, Al and Ni, from various industrial units [1,2]; Pb(II) is one of the most toxic metal ion causing serious health issues related to liver damage, nervous system, kidneys, genetic disorder, neurological activity and also causes high hypertension [3, 4]. Among the conventional methods - chemical precipitation [5], reverse osmosis [6], ion exchange [7], coagulation [8], electrodialysis [9], ultrafiltration [10], were studied earlier, Adsorption is one of the best method for removal of heavy metals from synthetic and real systems.

In the present study, Cocos nucifera leaf powder is used to remove Pb(II) from aqueous solutions. The effects of operating parameters were initial solution pH, sorbent dosage, metal ion concentration and temperature and equilibrium parameters were determined to understand the adsorption mechanism.

2. Materials and Methods

2.1. Preparation of Stock Solution

All chemical compounds used are of analytical grade (Merck). A Stock solution of 500 ppm Pb(II) is prepared by dissolving 0.4055 mg of 98.5% Pb(NO₃)₂ in 500 ml of distilled water. It is diluted to different levels, appropriate to the study. The pH of the solution was measured with a digital pH meter using solid electrode calibrated with a standard buffer solution; pH of the solution is adjusted with 0.1 N Sodium Hydroxide and 0.1N Sulphuric acid. The final concentration of Pb(II) ion is obtained by inductively coupled plasma optical emission spectroscope (Perkin Elmer model Optima 8000).

2.2. Preparation and activation of biosorbent

Cocosnucifera leaves are collected in the University Campus, water washed thoroughly to clear the surface impurities, and is then sun dried. They are pulverized into a fine powder and 63 µm standard sieve size particles are collected. The particles are further washed with water to remove dirt particles, dried at room temperature and are stored in air tight bottles for further studies.

3. Results and Discussion

3.1 Effect of agitation time

Time required for metal ion concentration to reach a equilibrium during adsorption process and for the interaction time intervals between 1, 2, 3…. 150min. For 63 µm size of 25 g/L biosorbent dosage mixed in 50 mL of aqueous solution (Co = 20 mg/L) and at a particular pH. The % biosorption is increased briskly up to 70 min reaching 97.68%. Beyond 70 min, the % biosorption is nearly constant indicating the attainment of equilibrium conditions. The maximum biosorption of 97.68% is attained for 70 min of agitation time. The rate of adsorption is fast in the initial stages because adequate surface area of the biosorbent is available for the sorption of Pb(II). As time increases, more amount of Pb(II) getsbiosorbed onto the surface of the sorbent due to Vanderveaal’s forces of attraction and resulted in decrease of available surface area. So that biosorbateforms a thin one molecule thick layer over the
surface of adsorbent. When this monomolecular layer covers the surface, the biosorbent capacity is exhausted. The maximum removal of Pb(II) is attained at 70 minutes. The percentage biosorption of Pb(II) becomes constant after 70 min. Hence all other experiments are conducted at 70 minutes of agitation time.

3.2 Effect of biosorbent size

The variations in % removal of Pb(II) from the aqueous solution with biosorbent size are obtained. The percentage biosorption is increased from 82.43% to 97.68% as the biosorbent size decreases from 125 to 63 µm. This phenomenon is depicted, as the size of the particle decreases, surface area of the biosorbent increases; thereby the number of active sites on the biosorbent also increases. Adsorbent size of 63 µm was selected for further experimentation.

3.3 Effect of pH

pH controls sorption process by influencing the surface change of the sorbent, the degree of ionization and the species of sorbate. In the present study, Pb(II) sorption data are obtained in the pH range of 2 to 9 of the aqueous solution (C= 20 mg/L) using 25 g/L of 63 µm size sorbent. The % biosorption of Pb(II) is increased from 92.43% to 97.68% as pH is increased from 2 to 5 and decreased beyond the pH value of 6. % biosorption is decreased from pH 6 to 9 reaching 92.48% (figure is not presented). Since the pH of aqueous solution influences the metal ion concentration, the binding of metal ions by surface functional groups is strongly pH dependent. The increase in % removal when pH increases from 2 to 5 could be due to decrease in competition between hydrogen ions and metal species for appropriate sites on the biosorbent surface and also by the decrease in positive surface charge on the adsorbent. However, with increasing, pH> 5 Pb(II) tends to hydrolyse so that precipitation occurs instead of adsorption and adsorbent was deteriorated with accumulation of metal ions, in that cases true adsorption is unpredictable.

3.4 Effect of metal ion concentration

The effect of initial concentration of Pb(II) in the aqueous solution on the percentage biosorption of Pb(II). The percentage biosorption of Pb(II) is decreased from 97.68% to 93.12% with an increase in concentration of metal ion from 20 mg/L to 150 mg/L. Such behavior can be attributed to the increase in the amount of sorbate to limited number of active sites on the sorbent.

3.5 Effect of adsorbent dosage

The biosorption of Pb(II) increased from 79.54% to 97.68% with an increase in biosorbent dosage from 5 to 25 g/L; due to number of active sites available for Pb(II) biosorption. Percentage adsorption of Pb(II) ions is marginal from 97.56% to 97.68% even adsorbent dosage is increased from 35 to 45 g/L. Hence further experiments are conducted at 25 g/L adsorbent dosage.

3.6 Effect of temperature

The effect of temperature on the equilibrium metal uptake was significant. Adsorption processes are normally endothermic and as the temperature increases the % adsorption increases. The effect of changes in the temperature on the Pb(II) ion uptake marginally increased from 97.38 to 98.53% with increasing temperature from 283 - 323 K indicating that the adsorption of Pb(II) on to Cocos nucifera leaf powder. The reverse phenomena could occur for living biomass under moderate temperatures and increasing the temperature is known to increase the rate of diffusion of the sorbate molecules across the external boundary layer and in the internal pores of the sorbent particles, owing to increase the adsorption process.

3.7 Adsorption isotherm

Six standard isotherms were Langmuir, Freundlich, Temkin, Dubinin-Rudishkevich, Flory-Huggins and Halsey isotherm models are tried to characterize the adsorption equilibrium characteristics.

3.7.1. Langmuir isotherm model

This model is based on assumption of monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform energies of adsorption with no transmigration of adsorbate in the plane of the surface and sorption is reversible. The empirical equation can be expressed as in equation 3.

\[ \frac{c_e}{q_e} = \frac{1}{q_m b} + \frac{c_e}{q_m} \]

The Langmuir isotherm model [11] was applied for the estimation of maximum metal uptake capacity and homogeneous active sites on surface of sorbent and constant b. The applicability of the Langmuir isotherm depends on a dimensionless constant, expressed by separation factor.

\[ R_L = \frac{1}{1 + \left(\frac{C_m}{C_e}\right)} \]

The value of R_L should lie in between 0 – 1 for favorable adsorption. The R_L value is 0.924 was estimated from the metal ion concentration range of 10-150 ppm and the maximum adsorption capacity was 8.475 mg/g with R^2 of 0.964. Langmuir isotherm for adsorption of Cobalt(II) as in Figure 1.

![Figure 1: Langmuir isotherm for adsorption of Pb(II)](image)

3.7.2. Freundlich isotherm model

\[ q_e = K_f c_e^n \]

![Figure 1: Langmuir isotherm for adsorption of Pb(II)](image)
The Freundlich isotherm model [12] assumes heterogeneous surface energies in which the energy term in the Langmuir equation varies as a function of surface coverage, \( n \) and \( K_f \) were empirical constants, 0.648 and 1.269 mg/g with \( R^2 \) of 0.998 and Freundlich isotherm for adsorption of Pb(II) as shown in Figure 2.

![Figure 2: Freundlich isotherm for adsorption of Pb(II)](image2.png)

### 3.7.3. Temkin isotherm model
Temkin model considered the effects of indirect adsorbate/adsorbate interactions on adsorption isotherms. The heat of adsorption of all molecules in the layer would decrease linearly rather than logarithmically with coverage due to adsorbate/adsorbate interactions. \( A_T \) and \( b_T \) are empirical constants of 2.5858 L/g and 1613.8 with \( R^2 \) of 0.948, gas constant \( R=8.314J/mol-K \) and Temkin isotherm for adsorption of Pb(II) as shown in Figure 3.

![Figure 3: Temkin isotherm for adsorption of Pb(II)](image3.png)

### 3.7.4. Dubinin–Radushkevich isotherm
D-R model [15] is used for the analysis of isotherms of a high degree of rectangularity and the sorption curve depends on the porous structure of the sorbent and \( q_m \) and \( K \) can be calculated from slope and intercept of the equation and as shown in Figure 4.

The mean free energy \( E \) of sorption per molecule of the sorbate when it is transferred to the surface of the solid from infinity in the solution and can be computed by using the equation

\[
E = \frac{1}{\sqrt{2k}}
\]

![Figure 4: D-R model isotherm for adsorption of Pb(II)](image4.png)

### 3.7.5. Flory–Huggins isotherm
This model was applied to assess the degree of surface coverage of the sorbate on the sorbent. The linearized form of the model [16] is

\[
\log\left(\frac{c_s}{c_e}\right) = \log K_{FH} + \eta_{FH}\log(1 - \theta)
\]

where \( c_s \) is residual metal concentration, mg/L, \( K_{FH} \) is Flory–Huggins model equilibrium constant and \( \theta = (1 - c_s/c_e) \), is the degree of surface coverage. \( K_{FH} \) and \( \eta_{FH} \) are calculated from slope and intercept. The higher \( R^2 \) shows the excellent applicability of the model and model plot as shown in Figure 5.

![Figure 5: Flory–Huggins isotherm for adsorption of Pb(II)](image5.png)

### 3.7.6. Halsey isotherm model
Halsey isotherm model [17] can be used to evaluate the multilayer adsorption system for metal ions adsorption at a relatively large distance from the surface [18] and which can be calculated by using the empirical equation and as shown in Figure 6.

\[
\ln q_e = \frac{1}{\eta_H} \ln K_H + \frac{1}{\eta_H} \ln \left(\frac{1}{c_s}\right)
\]

where \( K_H \) and \( \eta_H \) are the Halsey constants and obtained from the slope and the intercept of the linear plot based on ln\( (1/c_s) \) versus ln\( (q_e) \), respectively and isotherm model equations and constants were in Table 1.

![Figure 6: Halsey isotherm model for adsorption of Pb(II)](image6.png)

Fig. 6 Halsey isotherm model for adsorption of Pb(II).
4. Conclusion

The experimental investigations clearly suggest that abundantly available and low-cost materials like Cocos nucifera L is effective in removing Pb(II) from aqueous solution. Six standard equilibrium isotherm sorption experiments suggested that maximum removal of Pb(II) at optimum conditions of sorbent dosages of 25g/L of Cocos nucifera L, pH of 5.0, metal ion concentration of 20mg/L and temperature of 303. The time to reach equilibrium was observed to be 70 minutes. Freundlich model well fitted to experimental equilibrium data.

5. Acknowledgements

One of the authors (D. Hymavathi; RGNF-SC-AND-11087) is thankful to University Grants Commission (UGC), New Delhi, India, for the financial support under Rajiv Gandhi National Fellowship scheme.

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