

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 spectroscopy (Perkin Elmer model Optima 8000).

2.2. Preparation and activation of biosorbent

Cocsnucifera 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.

2.3. Biosorption Procedure

A set up of flasks, containing 50 ml solution of 20mg/L Pb(II) are taken and the solution pH adjusted with 0.1N NaOH and 0.1N H₂SO₄. A known quantity of adsorbent is added and the flasks are agitated at constant speed and at room temperature, on orbital shaker. Flask are withdrawn at suitable intervals, the content filtered and Pb(II) estimation in the sample is made. Similarly the procedure is repeated with different quantities of adsorbent and other parameters to make the study complete. Percentage removal Pb(II) and equilibrium metal uptake capacity are calculated using the formulae

$$\frac{C_0 - C_e}{C_0} * 100 \quad (1)$$

$$q_e = \frac{C_0 - C_e}{m} * V \quad (2)$$

3. Results and Discussion

3.1 Effect of agitation time

Time required for metal ion concentration to reach an 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 (C₀ = 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) gets biosorbed onto the surface of the sorbent due to Vanderwaal's forces of attraction and resulted in decrease of available surface area. So that biosorbent forms 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.

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \quad (3)$$

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.

$$R_L = \frac{1}{1 + (K_L C_e)} \quad (4)$$

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.

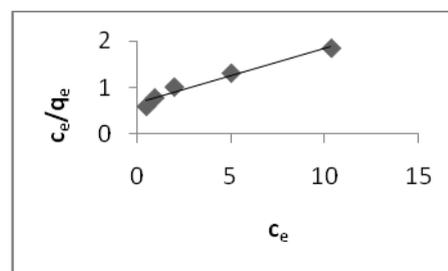


Figure 1: Langmuir isotherm for adsorption of Pb(II)

3.7.2. Freundlich isotherm model

$$q_e = K_f C_e^n$$

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.

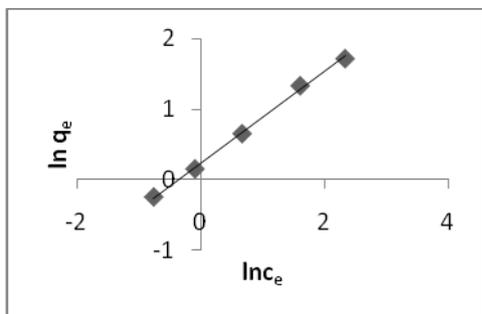


Figure 2: Freundlich isotherm for adsorption of Pb(II)

3.7.3. Temkin isotherm model

Temkin model considered the effects of indirect

$$q_e = \frac{RT}{b_T} \ln A_T + \frac{RT}{b_T} \ln c_e \quad (5)$$

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

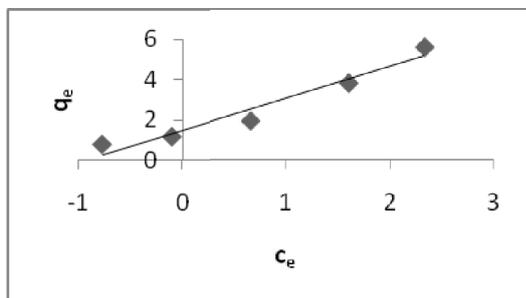


Figure 3: Temkin isotherm for adsorption of Pb(II)

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 plot 4. T is absolute temperature.

$$\ln q_e = \ln q_m - K \varepsilon^2 \quad (6)$$

$$\varepsilon = RT \ln \left(1 + \frac{1}{c_e} \right) \quad (7)$$

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

$$E = \frac{1}{\sqrt{2K}} \quad (8)$$

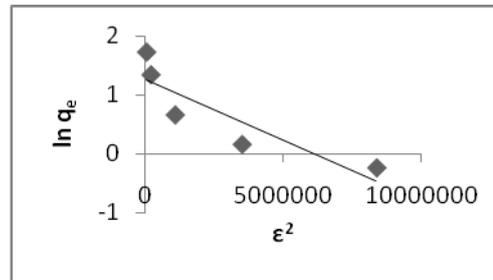


Figure 4: D-R model isotherm for adsorption of Pb(II)

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

$$\log \left(\frac{\theta}{c_e} \right) = \log K_{FH} + \eta_{FH} \log(1 - \theta) \quad (8)$$

c_e is residual metal concentration, mg/L, K_{FH} is Flory – Huggins model equilibrium constant and $\theta = (1 - c_e/c_0)$, is the degree of surface coverage, K_{FH} & η_{FH} are calculated from slope and intercept. The higher R^2 shows the excellent applicability of the model and model plot as shown in fig.5.

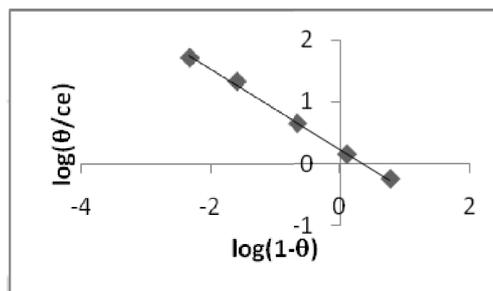


Figure 5: Flory–Huggins isotherm for adsorption of Pb(II)

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.

$$\ln q_e = \frac{1}{n_H} \ln K_H + \frac{1}{n_H} \ln \frac{1}{c_e} \quad (9)$$

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

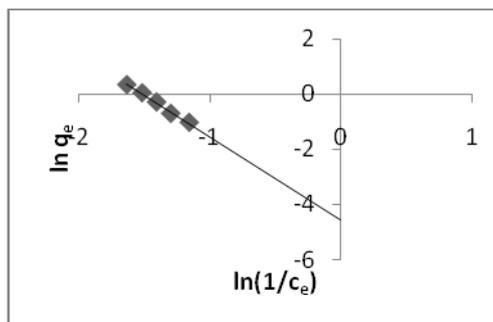


Fig.6 Halsey isotherm model for adsorption of Pb(II).

Table 1: Isotherm equations and constants

Isotherm Models	Equation	Parameters
Langmuir	$c_e/q_e = 0.1183c_e + 0.6679$	$q_{max}=8.475\text{mg/g}$ $K_L=b=0.1769\text{L/g}$ $R^2=0.964$
Freundlich	$\ln q_e = 0.6482 \ln c_e + 0.2382$	$K_F=1.269\text{mg/g}$ $n=0.648$ $R^2=0.998$
Temkin	$q_e = 1.5617 \ln c_e + 1.4836$	$b_T=1613.8$ $A_T=2.5858 \text{ L/g}$ $R^2=0.948$
D-R model	$\ln q_e = -2E-07\varepsilon^2 + 1.2683$	$K=2e^{-7}$ $q_m=3.56\text{mg/g}$ $E=16.5$ $R^2=0.781$
Flory-Huggins	$\log\left(\frac{\theta}{c_e}\right) = -2.9894 \log(1-\theta) - 4.5449$	$n_{FH}=-2.9894$ $K_{FH}=2.83 \times 10^{-5}$ $R^2=0.9941$
Halsey	$\ln q_e = 0.648 \ln(1/c_e) + 0.2381$	$K_H=0.692, n_H=.64$ $R^2=0.9981$

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 isothermal 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.

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