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Removal of Pb (II) from aqueous solution by using Custard apple (*Annona squamosa*) bark powder: Kinetics and equilibrium studies

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ABSTRACT

A new adsorbent was prepared from Custard apple (Annona squamosa) and applied to remove Pb (II) ions from aqueous solution. The present studies were conducted in a batch adsorption process. The biosorbent was characterized by FTIR spectroscopy, scanning electron microscopic analysis, elemental analysis and X-ray diffraction analysis. The influence of P^{H} , adsorbent dose, contact time, initial concentration of the adsorbate has been determined. The optimum pH for the removal of lead ions from aqueous medium is found to be pH=5. Kinetic parameters of adsorption such as Lagergren pseudo-first order, pseudo-second order and intraparticle diffusion model were determined. The sorption system follows pseudo-second-order kinetic model and equilibrium time is obtained after 50 min. The equilibrium data were analyzed by using Langmuir, Fruindlich and Dubinin-Radushkevich isotherm models. Langmuir model was fitted well by its good correlation co-efficient values. Desorption studies and recovery of adsorbent were carried out by using dil. HCl solution. The results suggested that the Annona squamoa bark powder can be used as effective, eco-friendly, low cost adsorbent in the removal of Pb (II) ions from aqueous solution.

Keywords: Biosorbent; Annona squamosa; Isotherms; Kinetics; Desorption

INTRODUCTION

In recent years increasing industries are responsible to release lot of polluted waste in the environment and damaging the ecosystem [1]. Heavy metal pollution has gained much attention worldwide because unlike other toxic pollutants, they are not biodegradable [2]. Among all heavy metals, Pb (II) is one which has more toxic nature when releases into the environment. Greater levels of Pb (II) in the adjacent-normal parts of kidneys with carcinomas are responsible for the individual effect or synergistic effect on enzymatic systems in oncogenic pathway [3]. According to the Environmental Protection Agency (EPA), the safe level of Pb (II) in drinking water is $50\mu g/L$ where as in waste water it is $500\mu g/L$. By the information of World Health Organization (WHO) the safe level of Pb (II) in drinking water is $10\mu g/L$ [4]. Lead can dissociates and exists in Pb (II) ionic form at low pH values and these Pb (II) ions enters into the human body by ingestion, inhalation of contaminated air and by taking contaminated food and water [5]. Lead is a general metabolic poison and behaves as enzyme inhibitor. In young children Pb (II) causes mental retardation, semi permanent damage of brain [6]. There is a growing demand to find relatively efficient, low cost and easily available adsorbents for the adsorption of toxic heavy metals. Heavy metals removal from diluted aqueous solution gaining an interest by the application of biomass from different origin. Sequestering of toxic heavy metals with the help of biomaterials has become an alternative method to economically expensive traditional

methods like coagulation, precipitation, adsorption etc. [7]. Biosorption is a popular technique that utilizes inactive/dead biological materials for the removal of heavy metals. Biosorption of metals is not based on only one mechanism. It consists of several ones that quantitatively and qualitatively differ according to the type of biomass, its origin and its processing. Metal adsorption involves complex mechanisms like ion exchange, chelation, adsorption by physical forces and ion entrapment in inter & intrafibrilar capillaries and spaces of the structural polysaccharide cell wall network [8]. Various biosorbents from different origins were used to remove Pb (II) ions from waste water [9-11]. Among the different biosorbents Custard apple (Annona squamosa) bark powder was used as a novel adsorbent in the present study and it is one of the good adsorbents to sequester Pb (II) ions from aqueous solution. Annona squamosa plants as biological resources mostly available in large quantities across the world. It can be used as medicinal plant in India.

EXPERIMENTAL SECTION

2.1. Biosorbent preparation

The bark of Annona squamosa tree was collected from S.V. University premises, Tirupati, Andhra Pradesh. The bark was peeled off from tree and made into several small pieces. To remove dirt particles the bark was washed with deionised water for several times and dried in sunlight. The dried pieces were ground in a steel mill to get fine powder and it was sieved. This powder was again subjected to washing with deionised water to remove the soluble materials present in it. After washing it was dried at 70°C in hot air oven for 4 hours. The final product was named as Custard apple bark (CAB) powder.

2.2. Chemicals and equipment

All chemicals were Analytical grade. Stock solution of the test reagent was made by dissolving $PbCl_2$ in double distilled water from a Merck Millipore-Q water system. Working standards were prepared by progressive dilution of stock Pb (II) solution using double distilled water. The pH meter was calibrated using standard buffer solutions of pH 4.0, 7.0 and 9.2. The pH measurements were made using an Elico LI120 pH meter. Test solutions pHs were adjusted using HCl (0.1 N) and NaOH (0.1 N). The metal concentrations in the samples were determined using an atomic adsorption spectrophotometer (Shimadzu Model AA-6300). Bruker Alpha FT-IR spectrophotometer between the wave numbers 4000 and 400cm⁻¹. Scanning electron microscope ((Model: EVO ma 15 manufactured by Carl Zeiss) has been used to study the surface morphology of the biosorbent. Wide-angle X-ray diffraction (WAXD) patterns of CAB samples were recorded on an X-ray diffractometer (XRD-6000, Shimadzu) by using Cu K α radiation.

2.3. Batch biosorption process

Batch adsorption tests were carried out at room temperature and used to investigate the effect of various parameters on Pb (II) adsorption. A series of 250 ml conical flasks are taken for the experiment. Fixed amount of adsorbent was placed in conical flasks contains 50 ml of 50 mg L⁻¹ Pb (II) solution. The pH was adjusted in the range of pH 2-9 by adding little aliquots of dil. HCl and dil. NaOH. Then the conical flask was closed with the help of stopper. The sealed conical flasks were placed on a mechanical shaking incubator and shaken well for about 24 hours at 300 rpm speed and 27°C temperature to get equilibrium. After shaking, the suspension was filtered and then the filtrate was analyzed for residual lead ion concentration. The concentrations of lead were determined by Flame atomic adsorption spectrophotometer. The effect of pH was determined by adjusting the initial pH values ranging from 2-9. Adsorbent dosage was determined by taking different quantities of doses from 100 mg to 1000 mg and keeping the initial concentration and contact time constant. The effect of contact time was determined by varying the contact time form 10 min to 100 min. The adsorption isotherms were evaluated from 10 mg L⁻¹ to 170 mg L⁻¹ by keeping the adsorbent constant (300 mg). Blank test was performed in the same experimental conditions without biosorbent.

From the metal concentrations measured before and after the adsorption (C_0 and C_e , in mg L⁻¹ respectively) and dry weight of biosorbent (W in kg), as well as volume of aqueous solution (V in ml), the uptake capacity of lead ion (q_e , mg g⁻¹) and the removal percentage (E %) were calculated according to Equations (1) and (2) :

$$q_{e} = (C_{0} - C_{e}) \frac{v}{W}$$
(1)
$$E\% = \frac{C_{0} - C_{e}}{C_{0}} X100$$
(2)

2.4. Desorption studies

The reversibility of adsorption was investigated by carrying out desorption experiments. Desorption of Pb (II) from metal loaded CAB was carried out by using dil. HCl with different concentrations. After determination of metal content in the final solutions, the biosorbent was washed with excess of acid solution and distilled water in order to reuse the CAB.

RESULTS AND DISCUSSION

3.1. Characterization of the biosorbent

3.1.1. FT-IR spectra

The FTIR spectra of CAB and CAB with Pb (II) are presented in Fig. 1. The FTIR spectrum of CAB showed a number of absorption peaks, reflecting the presence of complex functional groups on the surface of the biosorbent. In the spectrum, the broad band at around 3300 cm^{-1} is attributed to the presence of free and hydrogen bonded -OH stretching vibration. The band at 2950-2899 cm⁻¹ is due to the C-H stretching vibration and the one at 1440-1410 cm⁻¹ corresponds to CH₂ bending vibration. The peak at 1155-1145 cm-1 relates to C-O-C anti symmetric stretching vibration. The adsorption band at 1200-1000 cm⁻¹ is attributed to cellulose peak at finger print region stretching vibration. These peaks are all the characteristic absorption bands of cellulose [12]. After treatment of CAB with Pb (II) the characteristic adsorption peaks are disturbed and shifted. The reason may be the functional groups present in CAB are bound with metal ions.

3.1.2. X-ray diffraction (XRD)

The crystal phases of CAB were determined by X-ray powder diffraction (Fig. 2). The XRD study revealed that the presence of amorphous regions, which is favorable for biosorption of metal ion onto CAB. The spectrum shows that in raw CAB the peaks at 21° , 28° , 35° indicates the amorphous regions in the adsorbent. No other peaks were observed which explains the crystalline nature.



Fig. 1. FTIR spectra of CAB and CAB with Pb (II)



Fig. 2. Powder XRD spectra of Custerd apple bark powder

3.1.3. Scanning Electron Microscopy

The Scanning Electron Microscopic image of CAB was clearly shown in fig.3. The image tells the external morphology of the adsorbent. The image representing in fig.3 consists of the porous, uneven, heterogeneous structures. These characteristics of adsorbent are responsible for biosorption process.



Fig. 3. SEM images of CAB and CAB with Pb (II)

3.2. Effect of pH on removal of Pb (II)

Solution pH is the most important parameter in the biosorption of heavy metals. The speciation of metals in the solution is pH dependent. By changing the pH of the solution, the state of chemically active sites will change. In the present study solution pH was varied in the range from 2 to 9, and adjusted the pH values by using 0.1 N HCl and 0.1 N NaOH. Due to hydrogen ion competition at low solution pH values, the Pb (II) uptake was small. As the pH increases, the amount of Pb (II) uptake increases and the sharpest increase is observed between pH 4.0 and 5.0. The low adsorption of Pb (II) under high acidic conditions is because of the metal binding sties on the biosorbent are closely associated with H^+ and restricted the approach of lead as a result of the repulsive forces [13]. Minimal adsorption quantity of Pb (II) at low pH can be attributed to the competition between H^+ and lead ions. Maximum

removal of lead (II) was achieved at pH 5 ± 0.1 which is the optimum level. At this pH maximum removal of Pb (II) ions was took place.



The adsorption decreases when pH is higher than the optimum level, which may be attributed to the formation of hydroxides of metal ions by the hydrolysis of Pb (II) ions.

3.3. Effect of biosorbent dosage

The removal efficiency and specific uptake of metals depend on type and quantity of the biosorbent. If no information is available for particular type of biomass, it is better to find the optimal dose experimentally. In the present study the quantity of biosorbent was varied from 100mg to 1000 mg. As revealed in Fig. 5, the percentage removal or adsorption capacity increased with increase in biosorbent dose upto the optimum level. The optimum level is the point where the maximum removal of metal ions from aqueous medium. An amount of 300 mg is sufficient for the optimal removal of Pb (II) ions. Moreover, the biosorption capacity was high at low dose rates. The reason for this may be the availability of lesser binding sites and these were fully utilized.



Fig. 5. Effect of dose on the removal of Pb (II) on CAB

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3.4. Effect of contact time and adsorption kinetic study

The contact time profile of the adsorption of Pb (II) on CAB adsorbent has shown in fig 6. A very rapid increasing trend is observed during initial 40 min, and thereafter, the rate of Pb(II) adsorption decreases, after about 50 min, no significant change in Pb (II) removal is obtained. During initial stage of sorption, a large number of vacant surface sites are available for Pb (II) adsorption. After lapse of some time, the remaining vacant surface sites are difficult to be occupied due to repulsive forces from lead ions adsorbed on adsorbents surface. Here, the active external sites get almost saturated. Thereafter, lead ions have to immerse deeper into the active intra-particular sites encountering much larger resistance. This slows down the rate of Pb (II) adsorption during later period of adsorption.

The kinetic parameters are helpful for the prediction of the adsorption rate and give important information for designing and modeling of the adsorption process. Thus, the kinetics of Pb (II) adsorption onto CAB was analyzed using pseudo-first-order [14], pseudo-second-order [15] and intraparticle diffusion kinetic models [16]. The conformity between experimental data and the model-predicted values was expressed by the correlation coefficients ($R^2 \approx 1$). The relatively higher value is the more applicable model to the kinetics of Pb (II) adsorption onto CAB.



Fig. 6. Effect of contact time on the removal of Pb (II) on CAB

3.4.1Pseudo-first-order equation

The adsorption kinetic data were described by the Lagergren pseudofirst-order model [14], which is the earliest known equation describing the adsorption rate based on the adsorption capacity. The differential equation is generally expressed a follows:

$$\frac{dq_t}{dt} = K_1(q_e - q_t) \tag{3}$$

where q_e and q_t are the adsorption capacity at equilibrium and time t respectively (mg g⁻¹). K₁ is the rate constant of the pseudo first order adsorption (min⁻¹). Integrating Equation (3) for the boundary conditions t=0-t and qt=0-qt gives:

$$\log\left(\frac{q_e}{q_e - q_t}\right) = \frac{K_1}{2.303}t$$
(4)

Equation (4) can be rearranged to obtain the following linear form:

$$\log(q_e - q_t) = \log(q_e) - \frac{\kappa_1}{2.303}t$$
(5)

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3.4.2 Pseudo-second-order equation

The adsorption kinetic may be described by the pseudo-second-order model [15]. The differential equation is generally given as follows:

$$\frac{dq_t}{dt} = K_1 (q_e - q_t)^2 \tag{6}$$

where k_2 (g (mg min)⁻¹) is the second-order rate constant of adsorption. Integrating Equation (6) for the boundary conditions $q_t=0-q_t$ at t=0-t is simplified as can be rearranged and linearized to obtain:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e}(t)$$
(7)

The second-order rate constants were used to calculate the initial sorption rate, given by the following equation:

$$h = K_2 q_e^2 \tag{8}$$

If the second-order kinetics is applicable, then the plot of t/q_t versus t should show a linear relationship. The values of K_2 and the equilibrium adsorption capacity q_e were calculated from the intercept and slope of the plots of t/q_t versus t (Fig. 7). The linear plots of t/q_t versus t show good agreement between experimental and calculated q_e values at different initial Pb (II) concentrations (Table. 1). The correlation coefficients for the second-order kinetic model are >0.98, which led to the conclusion that the kinetics followed a pseudo-second-order kinetic model.

		Pseudo first order		Pseudo second order			
Initial concentration(mg L ⁻¹)	$q_e \exp{(mg \ g^{-1})}$	$q_e \ cal \ (mg \ g^{-1})$	K ₁ x 10 ⁻² (min ⁻¹)	\mathbb{R}^2	qe cal (mg g ⁻¹)	$K_2 \ge 10^{-2}$ (g mg ⁻¹ min ⁻¹)	\mathbb{R}^2
10	1.5275	1.3726	0.0782	0.95209	2.599969	0.11358	0.9995
30	4.595	2.4797	0.0543	0.98595	4.90076	0.03751	0.9995
50	7.71	4.3848	0.0647	0.99318	8.145312	0.027342	0.9996

3.4.3The intraparticle diffusion model

The adsorbate species are most probably transported from the bulk of the solution into the solid phase through the intraparticle diffusion/transport process, which is often the rate-limiting step in many adsorption processes, especially in a rapidly stirred batch reactor [16]. Since the Pb (II) ions are probably transported from its aqueous solution to the adsorbent by intraparticle diffusion. The intraparticle diffusion is another kinetic model which should be used to study the rate of Pb (II) adsorption onto CAB. The possibility of intraparticular diffusion was explored by using the intraparticle diffusion model, which is commonly expressed by the following equation:

$$q_t = K_{dif} t^{1/2} + C (9)$$

where C (mg g⁻¹) is intercept and K_{dif} is intraparticle diffusion rate constant (mg g⁻¹ min^{-1/2}). The values of q_t were found to be linearly correlated with the values of $t_{1/2}$ (Fig. 8) and the rate constant K_{dif} can be directly evaluated from the slope of the regression line (Tab. 2). The values of the intercept C provide information about the thickness of the boundary layer, the resistance to the external mass transfer increases as the intercept increases. The constant C was found to increase with an increase of Pb (II) concentration from 10 to 50mg L⁻¹, indicating the increase of the thickness of the boundary layer and the decrease of the chance of the external mass transfer and hence, the increase of the chance of internal mass transfer. The R² values given in Tab. 2 are close to unity indicating the application of this model. This may confirm that the rate-limiting step is the intraparticle diffusion process. The linearity of the plots demonstrated that the intraparticle diffusion played a significant role in the uptake of the adsorbate by adsorbent. However, as there is no still sufficient indication about it, it was shown that if the intraparticle diffusion is the sole rate-limiting step, it is essential for the q_t versus $t_{1/2}$ plots to pass through the origin, which is not the case [17]. So it may be concluded that the surface adsorption and the intraparticle diffusion were concurrently operating during the Pb (II) and CAB interactions.



Fig. 8. Intraparticle diffusion kinetics for adsorption of Pb (II) onto CAB

Table 2 Intra-particle diffusion model parameters for the removal of Pb (II) by CAB

Initial concentration (mg L^{-1})	$K_{id} (mg g^{-1} min^{-1/2})$	$C (mg g^{-1})$	R^2
10	0.07161	0.91936	0.90528
30	0.20094	2.86652	0.92886
50	0.3098	5.0783	0.90399

3.5 Analysis of adsorption isotherms

Adsorption isotherm provides a relationship between concentration of metal ion in solution and the amount of the same adsorbed on the adsorbent when both the phases are in equilibrium. In the present study, the Pb (II) uptake capacity of CAB was evaluated using the Langmuir, Freundlich and Dubinin–Radushkevich (D–R) adsorption isotherm models and the plots are shown in Fig. 9.

The Langmuir isotherm model assumes that the biosorption takes place at specific homogeneous sites on the surface of the biosorbent, it means once a metal ion occupies a binding site, no further adsorption can occur at that site where the first metal ion binds [18]. The non linear form of the Langmuir equation can be written as followed in the equation (10):

$$q_e = \frac{q_{max}K_d C_e}{(1+K_d C_e)} \tag{10}$$

where q_e is the biosorption capacity at equilibrium (mg g⁻¹), q_{max} is the maximum Pb (II) specific uptake (mg g⁻¹), and K_d represents the equilibrium constant of the biosorption reaction. The essential features of the Langmuir isotherm may be expressed in terms of equilibrium parameter R_L, which is a dimensionless constant referred to as separation factor or equilibrium parameter [19].

$$R_L = \frac{1}{1 + (1 + K_d C_0)} \tag{11}$$

Where:

 C_0 = initial concentration

 K_L = the constant related to the energy of adsorption (Langmuir Constant). R_L value indicates the adsorption nature to be either unfavorable if RL>1), linear if RL =1, favorable if 0< RL<1 and irreversible if R_L =0 [20]. From the data, the R_L is greater than 0 but less than 1 indicating that Langmuir isotherm is favorable. From this research work, the maximum monolayer coverage capacity (Q_o) from Langmuir Isotherm model was determined to be 32.27 mg g⁻¹, R_L (the separation factor) is 0.2243 indicating that the equilibrium sorption was favourable and the R^2 value is 0.99 proving that the sorption data fitted well to Langmuir Isotherm model.

The Freundlich equilibrium isotherm equation is an empirical equation used for the description of multilayer adsorption with interaction between adsorbed molecules representing the heterogenous surface properties [21]. The Freundlich equation can be written as:

$$q_e = K_f C_e^{1/n} \tag{12}$$

where K_f is the Freundlich isotherm constant, 'n' represents the adsorption intensity, C_e indicates the equilibrium concentration of adsorbate (mg L⁻¹), q_e is the amount of adsorbate adsorbed per gram of the adsorbent at equilibrium (mg g⁻¹).

Dubinin and his co-workers conceived this equation for subcritical vapors in micro pore solids where the adsorption process follows a pore filling mechanism onto energetically non uniform surface [22]. The Dubinin-Radushkevich (D-R) model, which does not assume a homogeneous surface or a constant sorption potential as the Langmuir model, was also used to test the experimental data.

$$q_e = Q_m \exp\left(-K \left[RT \ln\left(1 + \frac{1}{C_e}\right)\right]^2\right)$$
(13)

$$q_e = Q_m \exp(-K\varepsilon^2) \tag{14}$$

where Q_m is the maximum amount of the metal ion that could be sorbed onto unit weight of sorbent (mg g⁻¹), ϵ is the Polanyi potential which is equal to RT ln (1+1/C_e), where R and T are the universal gas constant (kJ mol⁻¹ K⁻¹) and the absolute temperature (K), respectively. The K in equations (13) and (14) is related to the mean free energy of sorption per mole of the sorbate when it is transferred to the surface of the solid from infinity in the solution and this energy can be computed using the following relationship.

$$E = \frac{1}{\sqrt{2K}} \tag{15}$$



Fig. 9. Biosorption isotherms of Pb (II) onto CAB

The results (correlation coefficient values, χ (Chi) values) concluded that the Langmuir adsorption isotherm model exhibit a better fit to the equilibrium data than Freundlich, Dubinin–Radushkevich adsorption isotherms. The R² values of four adsorption models shown in Table 3. Therefore, the biosorption process of Pb (II) by CAB can be interpreted as monolayer adsorption.

Table 3 Isotherm parameters of Pb (II) biosorption on CAB at various initial concentrations

Isotherm model	Values	
Langmuir		
$Q_{max} (mg g^{-1})$	32.27477	
b (L mg ⁻¹)	0.06914	
\mathbf{R}^2	0.99488	
χ^2	0.36731	
Freundlich		
$K_f(mg g^{-1})$	3.23785	
Ν	1.77407	
\mathbb{R}^2	0.96098	
χ^2	2.79906	
Dubinin-Radushkevich		
$Q_m(mg g^{-1})$	20.14736	
К	0.02056	
\mathbb{R}^2	0.93618	
χ^2	4.57846	
E	5.491522	

3.6. Comparision with other adsorbents

The maximum adsorption capacity (Q_{max}) of different adsorbents [23-26] was shown in Table 4. This can explain the adsorption capacities of different adsorbents. The results indicate that CAB is a potential adsorbent in the removal of Pb (II) from the waste water.

3.6. Desorption of Pb (II) from sorbent

Desorption studies were useful to identify the nature of biosorption process and to recover the metal from sorbent. Moreover, it also will help to regenerate the sorbents reuse to adsorb metal ions, and to develop the successful sorption process. In present study HCl was used as desorbing agent with various concentration and found that desorption of metal from the sorbent using 0.15 N HCl was quantitative (Fig. 10)



Fig. 10. Effect of HCl concentration on the desorption of Pb (II) from CAB

Table 4 Comparision of Q_{max} values of different adsorbents in the removal of Pb (II) metal ions

Adsorbent	Q _{max}	References
Oryza sativa husk	8.6	[23]
barley straws	23.2	[24]
Banana peel	2.18	[25]
Ceiba pentandra hulls	25.5	[26]
CAB	32.27	Present study

CONCLUSION

From the findings of this research, it can be concluded that Custard apple bark (CAB) powder is a versatile, novel and eco friendly adsorbent which can be used successfully for the removal of Pb (II) ions from aqueous medium. The results obtained from the above studies showed that the removal of maximum lead ions by CAB was observed at pH 5.0. Equilibrium adsorption showed that the biosorption process followed Langmuir adsorption isotherm model better than Freundlich, and D-R isotherm models, which indicates that monolayer adsorption exists under the experimental conditions employed. The kinetics studies indicated that lead removal followed pseudo-second-order rate equation. This study demonstrated that CAB could be used as an effective biosorbent for removal of lead ions from wastewater.

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