Biosorption of copper from wastewater using jatropha seed coat

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Jatropha (*Jatropha curcas* L.) seed coat was investigated for removal of Cu (II) from aqueous solutions. Impact of pH of the solution, sorption time, and initial metal ion concentration on sorption capacity was investigated. Adsorption equilibrium was reached in 80 min and 82-89% of Cu (II) was removed by jatropha seed coat at initial Cu (II) concentrations (20-50 mg l^{-1}). Adsorption data, analyzed using Langmuir, Freundlich and Redlich–Peterson isotherms, showed that adsorption equilibrium followed Langmuir and Freundlich isotherms. Kinetics of adsorption followed Elovichian rate equation at 30°C. The most plausible mechanism of adsorption seemed to be electrostatic attraction of Cu (II) towards lignocellulosic polar groups of jatropha seed coat. The study showed that powdered jatropha seed coat can be used as an adsorbent for removal of Cu (II) from wastewater.

Keywords: Cu (II), Adsorption isotherms, Chemical kinetics, Freundlich isotherm, Jatropha seed coat, Langmuir isotherm, Redlich–Peterson isotherm

Introduction

Discharge of effluents containing copper ions from industries such as metal cleaning and plating, paper and pulp, fertilizers and pesticides causes environmental problems. Permissible limit[1] of copper in effluent for discharge into inland surface water is 3.0 mg l^{-1} and safe limit of copper in drinking water is 0.05 mg l^{-1}. Prolonged oral administration of excessive copper can cause lever damage, hemochromatosis, gastrointestinal catarrh[2], neurotoxicity, commonly known as Wilson's disease[3] and cancer[4]. Treatment processes for copper removal from wastewater include chemical precipitation, coagulation/ flocculation, ion exchange, cementation, complexation/ sequestration, electrochemical operation, biological treatment, and adsorption[5-8]. In adsorption process, besides activated carbon, other adsorbent materials studied, include low-cost carbonaceous materials[9], agricultural products and by-products such as peat, saw dust, palm fiber, rice husk, peanut hull, coir husk, banana pith, tree fern, and leaves[10-12].

Jatropha (*Jatropha curcas* L., Family: *Euphorbiaceae*), or physic nut, is gaining popularity for

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eco-restoration of degraded lands and production of biodiesel. Jatropha can be maximum beneficial if main product (biodiesel) and by-products (seed shell, seed coat, seed cake and glycerin) are fully exploited. Seed cake is used as organic manure. Seed coat is used as mulch[13] and can be used for removal of heavy metals from wastewater. It contains cellulose and lignin, and the surface of cellulose in contact with water is negatively charged that can attract cations such as Cu (II). Lignin has various polar groups (alcohols, carbonyls, acids, amino, phenolic hydroxyls, and ethers) as potential chemical bonding agents for chemisorption.

This study presents jatropha seed coat for adsorption of Cu (II) from aqueous solutions, studies effect of pH, agitation time and initial concentration of Cu (II) on adsorption, and determines sorption kinetics, and isotherm constants of Cu (II) adsorption on seed coat.

Materials and Methods

Adsorbent Material

Seed coat from jatropha seeds, procured from Jatropha Vikas Sansthan, New Delhi, India, was dried at 100°C in an oven for 24 h, ground, sieved (70 mm mesh sieve) and stored in an airtight plastic container. Seed coat has following values: particle density, 2.99 g cm^{-3}; particle

size, 55μ; pH, 7.95; moisture, 8.77%; loss on ignition, 92.95%, N, 0.95%; P, 0.16%; K, 9.15%; cellulose, 34.78%; hemicellulose, 24.32%; and lignin, 11.79%.

Adsorbate Solution

A stock solution (1000 mg dm^{-3}) of Cu (II) was prepared using copper sulphate pentahydrate (CuSO$_4$.5H$_2$O) in distilled water containing 2M HNO$_3$, (20 ml) to prevent hydrolysis. Working solution was prepared by diluting stock solution with distilled water.

Kinetic Studies

Batch sorption experiments were performed at a constant temperature (30°C) on a rotary shaker at 165 rpm using conical flasks (125 ml). Powdered seed coat (1 g) was thoroughly mixed with copper solutions (50 ml). After shaking flasks for predetermined period, reaction mixtures were centrifuged at 8500 rpm. Aliquots of supernatants were withdrawn and analyzed with atomic adsorption spectrophotometer (AAS) for the concentration of Cu (II). Effect of pH and initial concentration of adsorbate on Cu (II) removal was studied using adsorbent (1 g) and Cu (II) varying concentrations (20-50 mg l^{-1}). pH (2-8) of the solution was adjusted with 0.1N NaOH/HNO$_3$.

Isotherm Studies

Isotherm studies to determine equilibrium time were carried out at different initial concentrations (20-50 ppm) of Cu (II) at pH 4 and 5. Powdered seed coat (1 g) was thoroughly mixed with copper solution (50 ml) of desired initial concentration. Flasks put in a rotary shaker (165 rpm) at 30°C for 70-80 min. Reaction mixtures were then centrifuged at 8500 rpm. Aliquots of supernatants were withdrawn and analyzed with AAS for Cu (II) concentration.

All experiments were carried out in duplicate and mean values were presented. Sorption capacity (q$_t$) at specified time (t) was calculated as

$$q_t = \frac{C_o V - C_t V}{M} \qquad ...(1)$$

where, C_0 = initial concentration of Cu (II), C_t, =concentration at time t, V= volume of solution, and M =mass of seed coat. Amount (q$_e$) of Cu (II) adsorbed at equilibrium was calculated as

$$q_e = \frac{C_0 - C_e}{M} \qquad ...(2)$$

where, Ce is concentration of Cu (II) in mg l^{-1} at equilibrium in aqueous phase.

Results and Discussion

Removal of Cu (II) by Powdered Jatropha Seed coat

Effect of Initial Concentration

Removal of Cu (II) by jatropha seed coat (pH 4-6 and 8 at 30°C) decreased from 89% to 82% with increased concentration of Cu (II) from 20 ppm to 50 ppm (Fig. 1). But actual amount of copper adsorbed per unit mass of adsorbent increased with increase in chromium concentration in the test solution. As copper concentration in the test solution was increased from 20 to 50 mg l^{-1}, unit adsorption of copper on seed coat increased from 0.89 to 2.06 mg g^{-1}. Maximum amount of Cu (II) was adsorbed within initial 40 min and equilibrium time for adsorption of Cu (II) on seed coat was 80 min. The results are consistent with other studies[14].

Effect of pH

Solution pH affects surface charge of adsorbent and degree of ionization and speciation of adsorbate. Removal of Cu (II) by seed coat increased with pH, attained peak at 4-6, and decreased thereafter (Fig. 2), may be due to precipitation of Cu(OH)$_2$ beyond pH 5.0. Therefore, pH 4 and 5 were chosen for further experimentation to avoid hydrolysis of Cu(II).
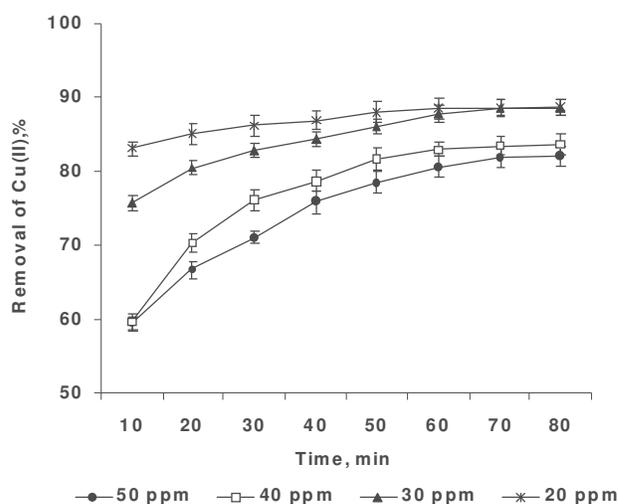

Fig. 1—Effect of agitation time on removal of Cu (II) (%) from aqueous solution by jatropha seed coat
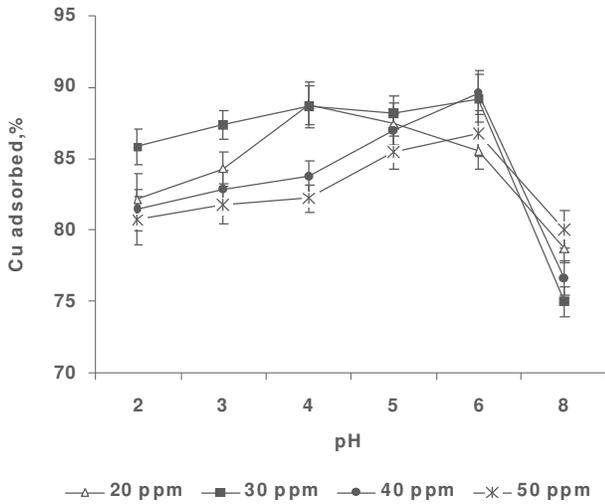
Fig. 2—Effect of pH on removal of Cu (II) (%) from aqueous solution by jatropha seed coat
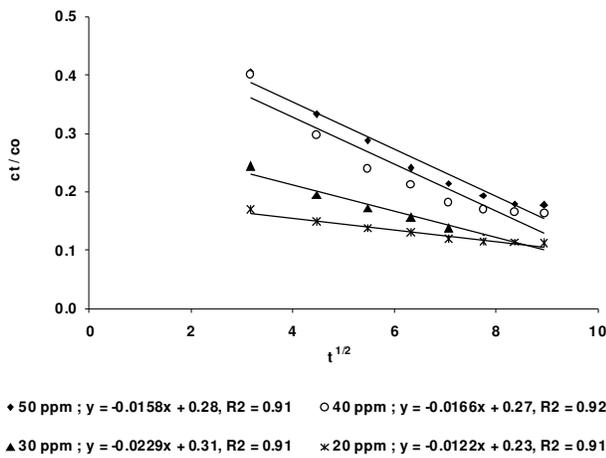

♦ 50 ppm ; y = -0.0158x + 0.28, R2 = 0.91   ○ 40 ppm ; y = -0.0166x + 0.27, R2 = 0.92

▲ 30 ppm ; y = -0.0229x + 0.31, R2 = 0.91   ✕ 20 ppm ; y = -0.0122x + 0.23, R2 = 0.91

Fig. 3—Pore diffusion of Cu (II) on jatropha seed coat at 30°C and pH 4

Adsorption Kinetics

Adsorption of metal ions could be a reaction kinetic-controlled process, a diffusion controlled process or a combination of the two processes. To find out the rate determining step of reaction, three reaction kinetic models (pseudo first-order, pseudo second-order, and Elovich) were used to identify best equation in terms of correlation coefficient (R^2) and sum of error squares (SSE) for correlation between the predicted and observed data. Rate constants of adsorption of Cu (II) at 30°C were determined using Lagergren[15], pseudo second-order[16], Elovich[17], and pore diffusion using Weber and Morris equations[18].
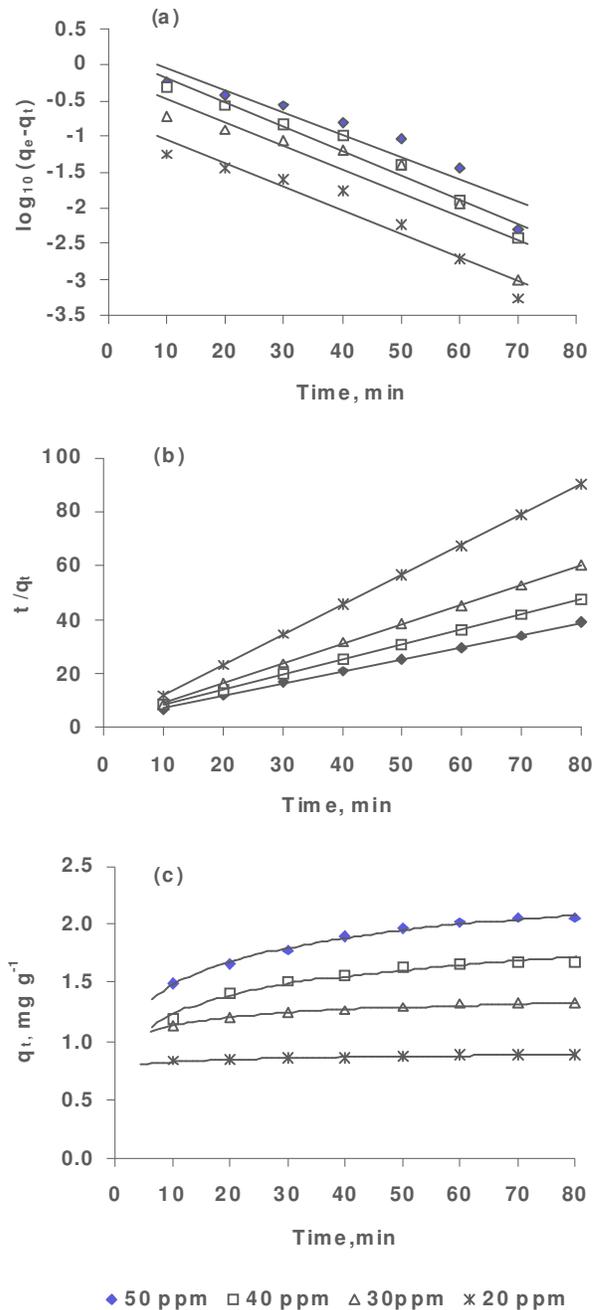

Fig. 4—Reaction kinetics of Cu (II) sorbed on jatropha seed coat at 30°C and pH 4: (a) Lagergreen model; (b) Pseudo second order model; and (c) Elovich model

Plot of Ct/Co against $t^{0.5}$ is linear only for a short range of contact period (Fig. 3) and does not pass through the origin, indicating that pore diffusion is not the rate-controlling step. Rate constants of pore diffusion (pH 4) were 0.041, 0.04, 0.022 and 0.01 $min^{1/2}$ for 50, 40, 30 and 20 ppm initial concentration of Cu (II), respectively. Plot of log (qe-qt) against t, for pseudo first-order or

Table 1—Kinetic and correlation coefficients for the kinetic reaction models for Cu (II) sorption on Jatropha seed coat at 30°C at pH 4.0

Coefficients	Concentration			
	50	40	30	20
(a) Pseudo first-order model				
k_1	0.0714	0.0783	0.0765	0.0755
q_e	1.8629	1.427	0.7299	0.1892
R^2	0.892	0.963	0.832	0.936
SSE	0.255	0.156	0.352	0.203
(b) Pseudo-second-order model				
k_2	0.073	0.108	0.262	1.021
q_e	2.22	1.79	1.37	0.9
R^2	0.999	0.999	0.999	0.999
SSE	0.361	0.202	0.356	0.213
(c) Elovich equation				
a	4.78	4.48	1.46E+04	1.75E+10
b	3.447	4.264	10.373	35.088
t_0	0.061	0.223	6.80E-05	5.70E-11
R^2	0.996	0.969	0.994	0.987
SSE	0.019	0.031	0.006	0.003

Table 2—Correlation coefficients of the sensitivity analysis plots for different kinetic models for Cu (II) sorption on jatropha seed coat at 30°C

Initial Cu (II) concentration	R^2		
	Pseudo-first order	Pseudo-second order	Elovich
50	0.71	1.00	1.00
40	0.68	0.99	1.00
30	0.69	0.99	1.00
20	0.69	0.98	1.00

Lagergren model (Fig. 4a) and corresponding R^2 and SSE (Table 1) do not provide a good fit (SSE values are above 0.2 to experimental data for the sorption of copper on jatropha seed coat). For pseudo second-order model, the coefficients were determined from qt/t vs t plot (Fig. 4b). The linearity is good (R^2=0.99) but SSE values are above 0.20 at higher concentrations representing a low level of correlation between predicted and observed values. Elovich model had R^2 between 0.97 and 0.99 and SSE values below 0.10 representing a high level of correlation between predicted and observed values (Table 1).

Increasing initial concentrations (C_0) of Cu(II) had no effects on kinetic rate constants in pseudo first-order model and negative effects in pseudo second-order model, and constant a and b for Elovich equation. However, R^2 values in three kinetic models were quite similar and identification of best kinetic reaction was difficult based on above analysis. Therefore, a sensitivity analysis, plotting reciprocal of the rate $Z = (dq/dt)^{-1}$ against t, was used to identify the best kinetic model. The following equations[19] were used to calculate Z_L:

Pseudo-first order equation,

$$Z_L = \frac{1}{q_e \cdot k_1 e^{-k_1 t}} \qquad \text{...(3)}$$

Pseudo-second-order equation,

$$Z_L = \frac{(1 + 2q_e t)^2}{q_e^2 k^2} \qquad \text{...(4)}$$

Elovich equation, $Z_L = b(t + t_0)$ ...(5)

From Eqs 3-5, Z_L–t plot can be obtained and used for a visual sensitivity analysis. Elovich equation provides best correlation of the experimental kinetic data (Table 2).

Table 3—Sorption isotherm constants and their correlation coefficients for Cu (II) sorption on
Jatropha seed coat at 30°C

Langmuir

pH	K_L	a_L	Q_o, µg/g	R^2
4	0.57	0.17	3.33	0.96
5	0.42	0.06	7.50	0.78

Freundlich

pH	b_F	n	K_F	R^2
4.0	0.56	1.76	0.60	0.96
5.0	0.82	1.22	0.42	0.97

Redlich–Peterson

pH	β	K_R	a_R	R^2
4.0	0.46	6.40	9.78	0.93
5.0	0.22	1.70	3.01	0. 80

Adsorption Isotherms

Analyses of the isotherm data is important in order to develop an equation that accurately represents the results and which could be used for design purposes. In this study, equilibrium isotherm for sorption of Cu (II) ions was measured experimentally. The data was analyzed using Langmuir[20], Freundlich[21] and Redlich-Peterson equation[22], the three main equilibrium correlations for q_e and C_e. Jossens et al[23] incorporated features of Langmuir and Freundlich isotherms into a single equation to give a general isotherm equation in agreement with that of Redlich and Peterson as follows:

$$\ln(K_R . \frac{C_e}{q_e} - 1) = \beta \ln C_e + \ln a_R \qquad ...(6)$$

Three isotherm constants, K_R, a_R and β were evaluated from linear plot represented by Eq. (6) using a trial and error optimization method (Table 3). A general trial and error procedure was used to determine R^2 for a series of values of K_R for linear regression of $\ln (C_e)$ on $\ln [K_R (C_e/q_e) - 1]$ and to obtain best value of K_R, which yields a maximum 'optimized' value of R^2.

Langmuir Isotherm

Saturated monolayer sorption capacities, Q_o, for Cu (II) at pH 4 and 5, are 149.25 and 67.11 µg g⁻¹ seed coat, respectively. Linear plots of C_e/q_e versus C_e, show that adsorption obeys Langmuir isotherm model (Fig. 5a). Essential characteristics of Langmuir isotherm can be expressed in terms of equilibrium parameter, R_L [R_L = l/(l+$a_L C_o$), where b is Langmuir constant and C_o is initial concentration of Cu (II)]. According to

McKay[24] and Ho[12], R_L indicates isotherm shape. If R_L >1, isotherm is unfavorable, R_L =1, isotherm is linear, 0<R_L<1, isotherm is favorable and R_L= 0, then isotherm is irreversible. In present experiment, R_L was found between 0 and 1 at all concentrations of Cu (II), indicating seed coat as a good sorbent for copper (Fig. 6). Specific surface area, S, of seed coat was calculated as

$$S = \frac{Q_o NA}{M} \qquad ...(7)$$

where S is specific surface area, m² g⁻¹; Q_o is monolayer sorption capacity, g metal per g seed coat; N is Avogadro number, 6.02 x/10²³; A is cross sectional area of metal ion, m²; and M is molecular weight of metal. For Cu^{2+} molecular weights are 63.5 and cross sectional areas to be 1.58 Å² (Cu^{2+} radius is 0.71 A°) in a close packed monolayer. Therefore, maximum specific surface area of seed coat towards Cu^{2+} binding is 1.123 m²g⁻¹ at pH 4 and 0.499 m² g⁻¹ at pH 5.

Freundlich Isotherm

The values of correlation coefficients indicate that experimental data is in good agreement with Freundlich isotherm (Fig. 5b). Main characteristic of Freundlich equation is based on the assumption that all sites vary in their adsorption energies and most active energetic sites are occupied first and the surface is continually occupied until the lowest energy sites are filled. The b_F (1/n) is indicative of energy or intensity of the reaction and gives an indication of favorability and capacity of the adsorbent/adsorbate system. Values of n>l represents favorable adsorption conditions according to the
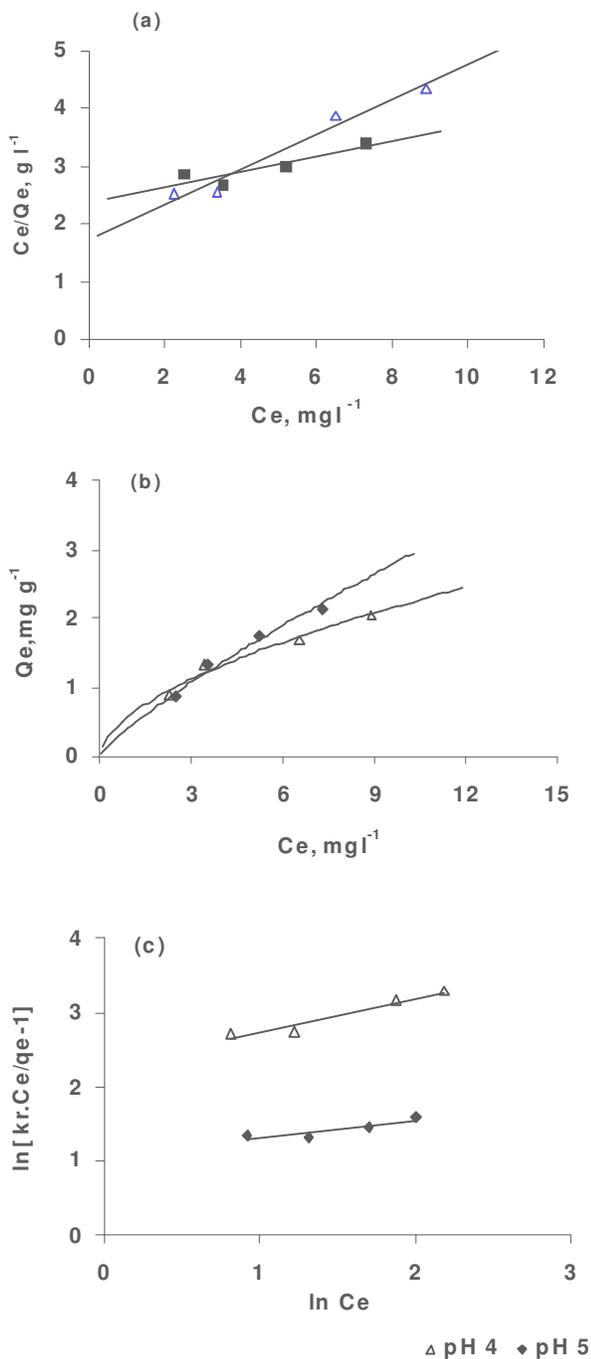
Fig. 6—Plot of separation factor R_L of Langmuir model against initial Cu (II) concentration on jatropha seed coat

Redlich-/Peterson Isotherm

Redlich-/Peterson isotherm is an appropriate description of the data for Cu (II) sorption over the concentration ranges studied (Fig. 5c). Redlich–Peterson equation is a combination of Langmuir and Freundlich equations. In the limits, as exponent β tends to zero, equation becomes more Freundlich, or heterogeneous, and as exponent $\beta \rightarrow 1$, equation approaches the ideal Langmuir condition. The β values are all less than 0.5 but not zero in Redlich–Peterson approach, confirming both Freundlich-type as well as Langmuir mechanism providing considerably better fits to the experimental data.

Conclusions

Jatropha seed coat can be used as an effective adsorbent for removal of metal ions from wastewater. It provides a reasonable adsorption capacity for Cu (II). Adsorption was influenced by solution pH, metal ion concentrations and agitation time. Elovich equation can be used to describe the kinetics of copper-seed coat sorption system at a pH of 4 and sensitivity analysis can be used to identify a true kinetic model. Metal/seed coat isotherms have been developed and analyzed according to three isotherm equations. Freundlich and Langmuir models were found significantly better than Redlich-Peterson model. The most plausible mechanism of adsorption seems to be electrostatic attraction of Cu (II) towards lignocellulosic polar groups in powdered jatropha seed coat.

Fig. 5—Adsorption isotherms of Cu (II) sorbed on jatropha seed coat at 30°C: (a) Langmuir isotherm; (b) Freundlich isotherm; and (c) Redlich-Peterson isotherm

theories. Since all n constants are >1, it is indicative of gradual decrease in sites available for sorption as concentration of copper in solution increases, that is, sorption of new molecules would occur with greater difficulty. This signifies that the surface of jatropha seed coat is heterogeneous.
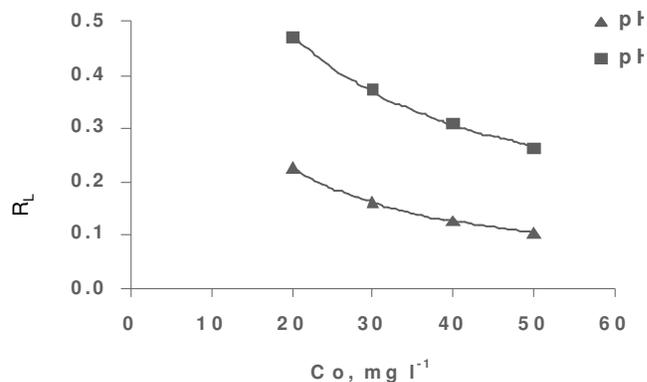
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