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Equilibrium sorption isotherms and kinetics for the sorption of lead onto low cost activated sorbents

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ABSTRACT

Studies on the removal of lead (II) ions by adsorption onto acid activated coconut fibres and walnut shells have been carried out. Effect of various parameters like pH, contact time, adsorbent dosage, agitation speed shows 76.1% and 72.6% Pb (II) removal at 2-5, 120 minutes, 8g, 160rpm by coconut and walnut activated carbon (CAC &WAC) respectively. Percentage removal of lead (II) ions increased with the increase in initial concentration. Adsorption data were modeled with Freundlich and Langmuir isotherms, first order kinetic equation proposed by Lagergren. Both the isotherms were found to be applicable except Lagergren first order kinetic equation. Adsorption capacity of CAC is found to be more as compared to WAC.

KEYWORDS

Adsorption isotherms;
Kinetic equations;
Activated carbon;
Adsorption;
Heavy metals;
Equilibrium studies.

INTRODUCTION

Lead is a typical toxic heavy metal with cumulative and non degradative characteristics. The most common cause of lead poisoning is dust and chips from old paint[1]. Human activities like use of leaded gasoline, fuel combustion, industrial processes and solid waste combustion, also contribute to lead accumulation[2]. At present there is an urgent need to develop new cheaper indigenously prepared activated carbons from these wastes. Several attempts have been made to prepare carbons from unconventional raw materials like saw dust, bamboo dust, cow dung, rice husk, waste tea leaves, wood charcoal and rice hulls by activation with chemicals at different temperatures[3]. The reported results revealed that activated carbons prepared from coconut fibres (CAC) and walnut shells (WAC) exhibit a high adsorption capacity, obeyed Freundlich and Langmuir isotherms although not favourable for first order kinetic equations. The present research work is an attempt to prepare activated carbon to study the suitability of low cost sorbents for the removal of lead (II) ions by determining the effect of various process parameters like initial concentration, contact time, adsorbent dose, pH and to model the adsorption data with various isotherms and first order kinetic equations. .

MATERIALS AND METHODS

Batch kinetic studies

The procured biosorbents were dried in ambient temperature and then ground and screened through a set of sieves. Both the sieved materials were soaked in known concentration of formaldehyde and sulphuric acid mixture. After this treatment, these are washed with distilled water and acetone. This mixture is then dried in oven at 50^{0}C for 2-3hrs. The mixture was soaked in 1% sodium carbonate overnight to remove residual acid. Next day, it was washed with distilled water and dried at 105^{0}C for 24 hours. This produced a uniform material for the complete set of sorption tests which were stored in an air tight plastic container for further investigations.

The amount of adsorption at time t, qt (mg g^{-1}), was calculated by:

$$q_t = \frac{(C_0 - C_t)V}{W} \quad (1)$$

Where, C_o and C_t (mg l^{-1}) are the liquid-phase concentrations of lead at initial and any time t, respectively. V is the volume of solution (litre) and W is the mass of dry adsorbent used (g). Adsorption data obtained from the effect of initial concentration, contact time were employed in testing the applicability of isotherms and kinetic equations respectively.

RESULTS AND DISCUSSION

The kinetics of adsorption of lead (II) ions by CAC and WAC has been studied by testing the applicability of various first order kinetic equations proposed[4,5]. The rate constant of adsorption is determined from the pseudo first-order equation[6]:

$$\ln (qe - qt) = \ln qe - k_1 t \quad (2)$$

where, q_e and q_t are the amounts of lead adsorbed (mg g^{-1}) at equilibrium and at time t (min), respectively as shown in TABLE 1 and K_1 is the first order rate constant for adsorption of lead (II) ions (h^{-1}). Values of K_1 were calculated from the plots of ln (q_e -q_t) versus t for CAC and WAC and found to be 0.003 and 0.002 respectively (Figure 1, Figure 2). Applicability of Pseudo first order kinetics was verified through the value of coefficient of determination, r^2 0.698 (CAC) and 0.683(WAC)[7]. The experimental value of qe i.e. 0.60 for CAC and 0.40 for WAC do not agree with the calculated values 3.70 and 3.59 for CAC and WAC respectively (TABLE 1). This shows that the adsorption of lead onto activated carbons produced from both the adsorbents is not applicable to first-order kinetics.

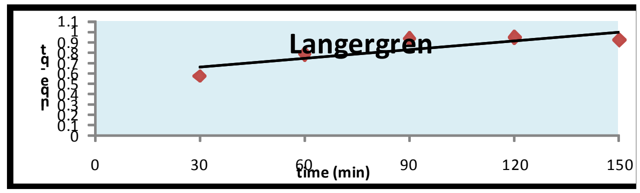

Figure 1 : Langergren adsorption isotherm for lead removal by CAC (*Cocos nucifera*)

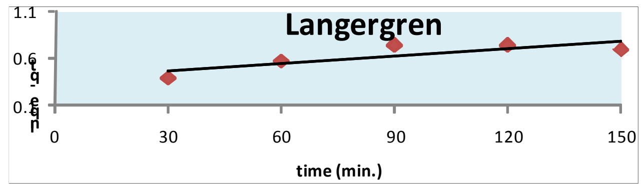

Figure 2 : Langergren adsorption isotherm for lead removal by WAC (*Juglans regia*)

Adsorption isotherms for Pb (II) removal treated with CAC and WAC

The logarithmic form of Freundlich model is given by the following equation:

$$\log q_e = \log K_F + (1/n) \log C_e \quad (3)$$

Linear plot of log Ce vs log qe shows that the adsorption of metal ions onto CAC and WAC follows the Freundlich isotherm model (Figure 3, Figure 4). It also indicates that the average energy adsorption decreases with the increasing adsorption density. The values of K_F and n were calculated from the intercept and slope as given in (TABLE 1). The values of 1/n between 1 and 10 represent good adsorption of the adsorbate onto the adsorbent. It was found that value of 1/n for CAC is 0.5 indicating normal Freundlich isotherm and 1 for WAC depicting cooperative adsorption. The plot of log q_e versus log C_e gives straight lines with slope '1/n' which shows that the adsorption of lead follows the Freundlich isotherm.

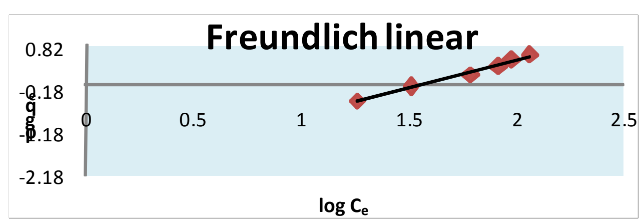

Figure 3 : Linear form of Freundlich adsorption isotherm for CAC (*Cocos nucifera*)

The linear form of Langmuir's isotherm model is given by the following equation:

$$C_e/q_e = 1/Q_o b + (1/Q_o) C_e \quad (4)$$

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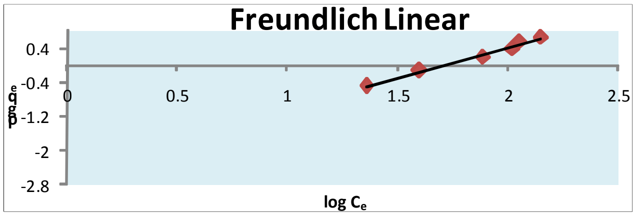

Figure 4 : Linear form of Freundlich adsorption isotherm for WAC (*Juglans regia*)

The Langmuir constants were calculated from these isotherms (TABLE 1). The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless equilibrium parameter (R_L)[8,9]. defined by:

$R_L = 1/(1 + bC_0)$ **(5)**

The value of R_L indicates the type of the isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

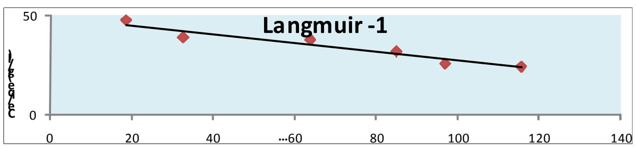

Figure 5 : Linear form of Langmuir-1 adsorption isotherm for CAC (*Cocos nucifera*)

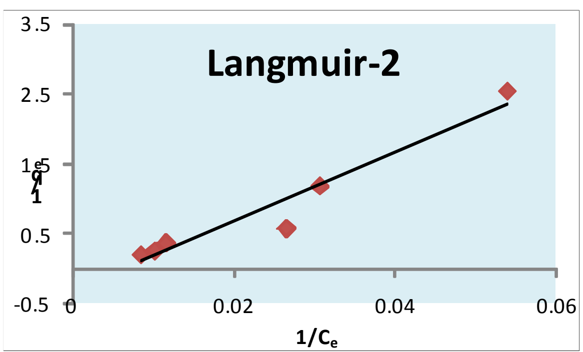

Figure 6 : Linear form of Langmuir-2 adsorption isotherm for CAC (*Cocos nucifera*)

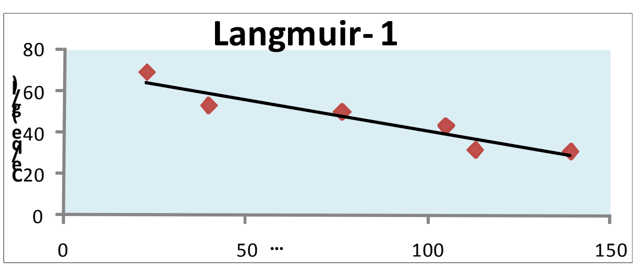

Figure 7 : Linear form of Langmuir- 1 adsorption isotherm for WAC (*Juglans regia*)

CONCLUSIONS

The observed linear relationships are statistically

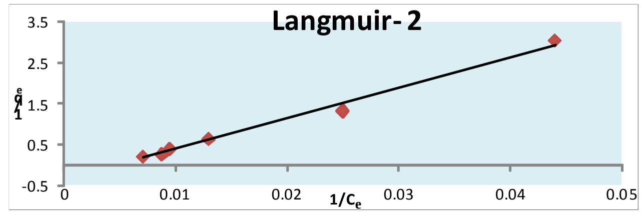

Figure 8 : Linear form of Langmuir- 2 adsorption isotherm for WAC (*Juglans regia*)

TABLE 1 : Isotherm parameters obtained using linear method of Langmuir adsorption

Isotherms	Parameters	CAC	WAC
Freundlich	1/n	0.5	1.0
	K_F	-2.2	-2.1
	r^2	0.992	0.985
Langmuir- 1	q_m (mg/g)	2.22	5.0
	K_a (dm^3/mg)	0.009	0.028
	R_L	0.217	0.454
	r^2	0.925	0.892
Langmuir- 2	q_m (mg/g)	-3.33	-2.5
	K_a (dm^3/mg)	-0.0060	-0.008
	R_L	-0.714	-0.454
	r^2	0.941	0.921

significant as evidenced from correlation coefficient (r) close to unity which indicates applicability of these two adsorption isotherms and the monolayer coverage of lead species on the carbon surface. The monolayer adsorption capacity, q_m value indicates that WAC is a better adsorbent for lead (II) ions. The coefficient of determination r^2 was used to test the best fitting isotherm to the experimental data. The values of q_m, k_a, R_L and r^2 are calculated from Linear plots of Langmuir isotherm (TABLE 1). Freundlich isotherm seems to be more favourable as compared to Langmuir isotherm. Langmuir 1 is more favourable as the coefficient of determination r^2 is more close to unity. The R_L values for the Linear forms of Langmuir isotherms for Langmuir-1 comes out to be in the range of $0 < R_L < 1$ confirming that CAC and WAC are favourale for Langmuir adsorption of Lead (II) removal

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