



Evaluation of Kinetic Models of Lead Uptake from Wastewater by Activated Carbon Derived from Coconut Leaves

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ABSTRACT

Activated carbon was prepared from coconut leaves by using chemical activation method, using phosphoric acid as dehydrating agent and at slow pyrolysis of 400°C in inert atmosphere. The present study, explored the feasibility of using waste coconut leaves (CL) based carbon as adsorbent for the removal of lead under different temperature conditions from waste solution. BET surface area of CL₃ found 1060.57 m²/g greater than CL₁ and CL₂. The batch sorption study experiments were conducted with respect to solute concentration (2.8-110 mg/L) and solution temperature (40-70°C). The Langmuir Isotherm, Freundlich Isotherm and Temkin Isotherm studies were conducted and applied to the experimental equilibrium data, and isotherm constants are calculated. A comparison of kinetic models was applied to the adsorption of lead ion. Coconut leaves carbon was evaluated for the, Elovich, intraparticle diffusion and Bangham's kinetic models. The experimental data fitted very well for the pseudo first-order and pseudo second-order. The results show that the sorption capacity increases with an increase in solution temperature from 40°C, 50°C, 60°C and 70°C. The results have established good potentiality for the carbon particles to be used as a sorbent for the removal of lead from wastewater.

INTRODUCTION

The most universal problem in environmental pollution is water pollution. The discharge of heavy metals into water-courses is a serious pollution problem which may affect the quality of water supply. Increasing concentrations of these metals in the water constitute a severe health hazard mainly due to their non-degradability and toxicity. Numerous metals such as, copper (Cu), lead (Pb), manganese (Mn), mercury (Hg), etc. are known to be significantly toxic (Bhattacharya & Venkobachar 1984).

Disposal of coconut leaves by open-field, burning frequently, causes serious air pollution. In recent years, attention has been focused on the utilization of local agricultural by-products as sorbent (Bhattacharya & Venkobachar 1984, Gong et al. 2005, Robinson 2002). To improve the sorption capacity of these biomaterials, the agricultural waste was converted to activated carbon. The activated carbons in laboratory scale is manufactured by chemical activation method at 400°C denoted as one-stage process (Molina-Sabio et al. 1991). One-step procedure appears to be preferable because of lower activation temperature used, thereby reducing production costs in term of energy and time saving. This process results in activated carbon with high adsorption capacity (Minkova et al. 1991).

The solid waste can be recycled and the amounts of disposal waste can be reduced significantly by the application of proper decontamination technology. Therefore, it is necessary to treat the secondary waste to increase the decontamination efficiency. One of the efficient methods to treat the secondary waste is the sorption

MATERIALS

The adsorbents were prepared from the coconut leaves. Adsorbate solutions were prepared from lead nitrate (Pb(NO₃)₂), procured from M/s. Thomas Baker, India. Metals removed: Lead (Pb) chemical activation utilises chemicals like phosphoric acid (H₃PO₄) procured from M/s. Thomas Baker, India

PREPARATION OF ACTIVATED CARBON

Raw coconut leaves based carbon was used for adsorption in this work. For the preparation of coconut leaves activated carbon, 50 g at an impregnation ratio of 3:1 and was dried at a heating rate 3°C/10 min in the presence of N₂ flow (3 mL/min). The heating continued up to a final temperature of 400°C, and held at this temperature for 90 min. The carbon was left to cool down and washed with distilled water, dried at 110°C and stored in stoppered bottles. The samples were given the abbreviations, CL₁, CL₂ and CL₃ for

Table 1: Adsorbate used for analysis.

Sr.No.	Chemical Name	Chemical Formula	Molecular Weight(g/mole)	Colour
1	Lead Nitrate	Pb(NO ₃) ₂	331.2	Colourless

Table 2: Adsorbents used, their surface areas (found by Autosorb-1).

Sr.No.	Adsorbents	Surface Area(m ² /g)
1	Coconut Leaves (CL-01)-50gm-1:1	760.54
2	Coconut Leaves (CL-02)-50gm-2:1	1003.90
3	Coconut Leaves (CL-03)-50gm-3:1	1060.57

carbons activated at 400°C respectively.

Coconut leaves, were cleaned using tap water. Washed sample material was then sun dried for 2-5 days and treated with phosphoric acid and heated at 400°C under a controlled atmosphere to obtain the carbon. This was washed repeatedly with distilled water till the filtrate was neutral litmus, to ensure that free acids present in the material were completely removed. Subsequently, the carbon was dried, sieved and particles less than 105 micron were used in the experiments as shown in Fig. 1.

Absorbate: Stock solutions of lead nitrate (Pb(NO₃)₂) (1000 ppm) for adsorption study was prepared from solid powders of pure metal salts. Lead is found frequently in our environment, it has no known purpose in our bodies. When lead gets inside the body, the body confuses it with calcium and other essential nutrients. This confusion can cause permanent damage to the health of both children and adults.

Batch adsorption: Adsorption was performed in batch, where 2 g of activated carbon was interacted with 40 cm³ of dye wastewater and allowed to stand for 30 minutes. It was then filtered using Whatman filter paper (No. 42). The process was repeated at pre-set times (60, 90, 120 and 150 minutes). The concentration of lead in the dye wastewater was determined before and after interaction with the activated carbon by a bulk scientific atomic absorption spectrophotometer (MODEL 210VGP).

Surface area analysis: The surface area of the activated carbons was measured by BET (Brunauer-Emmett-Teller nitrogen adsorption technique) (Abbas Sabah Thajeel 2013, Robinson et al. 2002). The physicochemical characteristics determined for these activated carbons as well as scanning electron microscopy, H₃PO₄ was the best activating agent (Khalid et al.2000).

Determination of surface area of adsorbent is accomplished by using N₂ adsorption at liquid N₂ temperature in which adsorbed N₂ molecules adhere to surface site as a

monolayer. The surface area of adsorbents is tabulated in Table 2. The Table 2 reveals that CLC has the highest surface area. The surface area of different carbons follows the order: CL₃ > CL₂ > CL₁. CL₃ has the highest surface area among the three adsorbents. The presence of micro-pores may be contributing to the high surface area of CL₃, presented in Table 2. Thus CL₃ is adapted for further study as surface area is high as compared to CL₁ and CL₂.

SEM analysis: As coconut leaves is flex, SEM analysis was performed to get the coconut leaves carbon exhibit morphology; fiber and sheet-like particles are observed in Fig. 2

From Fig. 3, fiber like sand sheet like structure is observed which indicates the adsorption capacity of active carbon and in turn helps to describe the adsorption kinetics.

In order to describe the adsorption kinetics for lead on activated carbon, pseudo first-order, pseudo second-order and Elovich Model were applied to the experimental data.

Kinetic studies: 20 mg of the adsorbent in 25 mL reagent bottles containing 10 mL of lead solution (30 ppm) was mixed and placed in the shaker at constant temperature for different time intervals. The adsorbent was finally removed by filtration, lead nitrate (Pb(NO₃)₂) concentration was determined. The contact time required for complete metal adsorption was determined and utilized in the remaining tests.

Equilibrium studies : Adsorption equilibrium studies were conducted at an initial lead solution pH of 6-6.5. Equilibrium data were obtained by adding 0.05-0.1 g of CL active carbon into a series of conical flasks each filled with 10 mL of lead solution (5 ppm). The conical flasks covered with aluminum foil and were placed in a thermostatic shaker for 4 h at 28°C. The removal efficiency (R_E%) of lead on CL carbon, the sorption capacity, (q) and distribution ratio (C_d) were calculated from equations (1-3).

$$R_E \% = \frac{C_{in} - C_{out}}{C_{in}} \times 100 \quad \dots(1)$$

$$q_e = V \frac{C_{in} - C_{out}}{m} \quad \dots(2)$$

$$C_d = \frac{\text{Amount adsorbate adsorbed} \times V}{\text{Amount of adsorbate in solution}} \quad \dots(3)$$

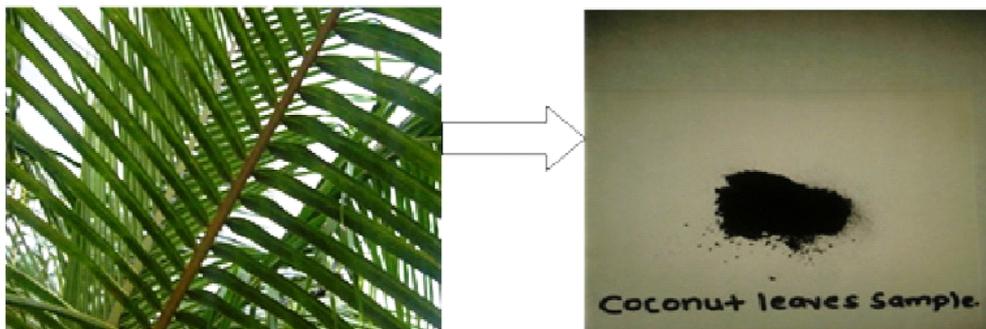


Fig. 1: Coconut leaves derived activated carbon.

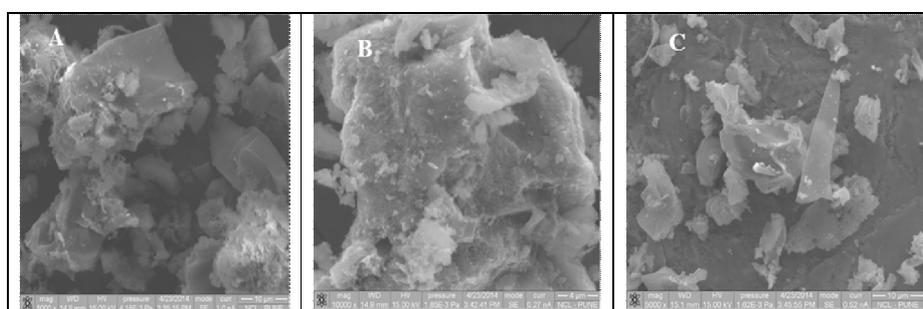


Fig. 2: SEM images A, B, C at 5000x magnification, of synthesized adsorbents with phosphoric acid, for varying {acid: adsorbent} ratio. (A)Coconut leaves $CL_1(1:1)$, (B) Coconut leaves $CL_2(2:1)$, (C) Coconut leaves $CL_3(3:1)$.

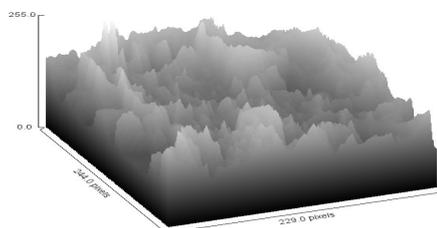


Fig. 3: SEM 3D surface plot of coconut leaves active carbon.

Where C_{in} and C_{out} are the initial and final concentrations of lead (mg/L) in aqueous solution, respectively. V is the volume of the solution (mL) and m represents the weight of the adsorbent (mg).

RESULTS AND DISCUSSION

Preliminary experiments show that coconut leaves (CL_3) derived activated carbon gives the highest methylene blue number compared to the other carbon adsorbents (CL_1 , CL_2 and CL_4). Therefore, CL_3 carbon was selected for further detailed experimental investigations. The aim was to find out the effect of various parameters on its affinity towards the uptake of lead nitrate ($Pb(NO_3)_2$).

Determination of adsorption kinetics: The kinetic data of

experiments conducted with an initial metal concentration of lead nitrate (122.8 ppm) on adsorbent (CL_3) are presented in Fig. 4. The kinetics data were fitted to the pseudo first order model and pseudo second order kinetic model.

Kinetics plot: The kinetics data were fitted into the pseudo first order rate equation, and the pseudo second order rate equation. This was confirmed by plotting graphs and comparing the linearized form of rate equation with the equation $y = mx + c$. Thus by plotting $\log(q_e - q_t)$ vs. t for pseudo first order and t/q_t vs. t for pseudo second order rate equation, the rate constants for the respective equations were found at four different temperatures. The pseudo first order kinetics plot and pseudo second order kinetics plot for lead metal with adsorbates lead nitrate ($Pb(NO_3)_2$) using an adsorbent (CL_3) are presented in Figs. 5 and 6.

Determination of kinetics constants: Table 3 shows pseudo first order and pseudo second order kinetic constants for adsorption of lead metal with adsorbate lead nitrate using adsorbent (CL_3) at temperatures 40°C, 50°C, 60°C, 70°C.

Effect of pH: It is known that pH is an important factor for the adsorption of metal ions on the adsorbents. The dependency of adsorption of lead ion on the CL_3 carbon was also analyzed by plotting adsorption uptake of $Pb(II)$ ions as a

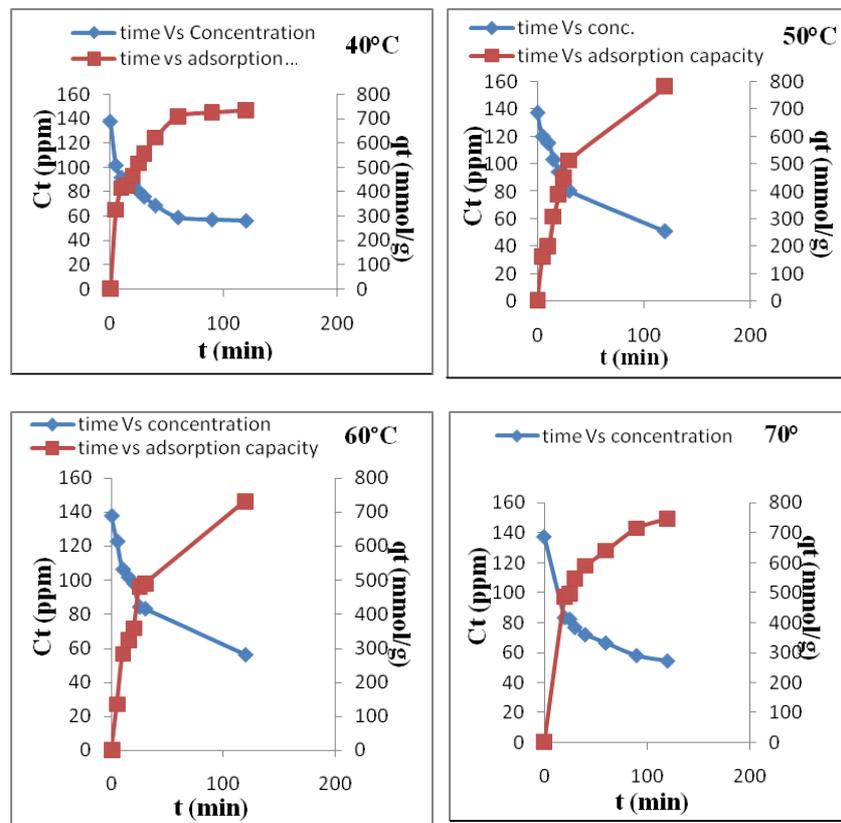
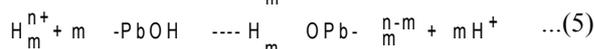
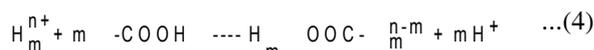


Fig. 4: Variation in concentration of lead metal and adsorption capacity of activated carbon from coconut leaf with time, Batch Conditions: Wt. of adsorbent: 0.02g, vol. of adsorbate: 180cm³, adsorption time: 2hrs, adsorption temperature: 40°C, 50°C, 60°C, 70°C.

functional pH at a constant initial concentration (18 mg/L) in Fig. 2. It is clear that a marked influence with a gradual rise in the uptake with increase in pH from 2 to 10. According to pH results, we can assume that Pb (II) ion in solution is able to bind chemically with carboxyl groups in the carbon. This means that an ion-exchange reaction takes place in the adsorption of Pb (II) ion. CL₃ based carbon contain lead dioxide (PbO₂) and the hydrolysis of lead dioxide produces hydrous oxide surface group - PbOH. The ion-exchange reaction is accomplished through the substitution of protons of the surface carboxyl group by lead ion, according to the following reactions as shown in Fig. 7.



Where H_mⁿ⁺ = heavy metal ion with n⁺ charge, -COOH = carboxyl group, -PbOH = PbOH group, and mH⁺ = number of protons released.

In such a system, at low pH, because of the high concentration of H⁺, equation (4 and 5) lies to the left. The ion exchange sites are mainly protonated and are less available

for ion exchange. Equations (4 and 5) proceed further to the right and metal ion removal is increased by increased pH. Within this pH range, the ion exchange process is the major mechanism for removal of metal ion from solution. In the subsequent studies, experiments were performed in the solution pH value of 6 to avoid any possible hydroxide precipitation

From Table 4, it is observed that % removal of lead adsorption on coconut leaves activated carbon decreases as weight of adsorbent decreases from 0.1-0.01gm. It is further proposed to study to apply adsorption isotherm analysis.

Analysis of Adsorption Isotherm

Adsorption isotherms for lead metal with two adsorbates (lead nitrate and lead chloride) on adsorbent activated carbon obtained from coconut leaves having acid : solid ratio as 3:1, were fitted to different isotherm models viz. Langmuir, Freundlich and Temkin.

Langmuir isotherm: The Langmuir isotherm model suggests that adsorption takes place as a monolayer coverage on homogeneous surface containing a finite number of va-

Table 3: Pseudo First order and pseudo second order kinetic constants for adsorption of lead.

Temperature	Adsorbate= ((PbNO ₃) ₂)				
	Pseudo first order(log(q _e -q _t)=log(q _e -k ₂ t))		Pseudo second order((t/q _t = 1/K ₃ q _e + t/q _e))		
	K ₂	R ²	q _e	K ₃	R ²
40°C	0.0226	0.9867	769.23	0.0000502	0.9093
50°C	0.0247	0.9889	769.23	0.0000976	0.9508
60°C	0.0243	0.9911	833.33	0.0000036	0.8023
70°C	0.0211	0.9035	666.66	0.0000885	0.9345

Table 4: Removal of lead using coconut leaves derived active carbon.

Sample	CL-01	CL-02	CL-03
Weight of adsorbent	% Removal	% Removal	% Removal
0.1 gm	80.84	90.353	90.907
0.05 gm	78.704	80.647	84.449
0.02 gm	76.317	79.72	76.596
0.01 gm	76.682	78	74.048

cant sites energetically equivalent to each other in respect of adsorption phenomenon and with negligible interaction between adsorbed molecules. The energy of adsorption is constant and does not depend on the degree of occupation of the adsorbent active centers. The empirical non linear Langmuir equation is given by the following equation

$$q_e = \frac{q_m K_L C_e}{(1 + K_L C_e)} \quad \dots(6)$$

q_e is the equilibrium metal concentration on the adsorbent (mg g⁻¹).

C_e, the equilibrium metal concentration in solution (mg L⁻¹)

q_m, the monolayer capacity of the adsorbent (mg g⁻¹)

K_L, the Langmuir constant (L mg⁻¹) related to energy of adsorption

And, the linear form of the equation can be written as:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \quad \dots(7)$$

The values of K_L and q_m were determined from the slope and intercept of the representation 1/q_e versus 1/C_e respectively. To determine if adsorption process is favorable or unfavorable for Langmuir type adsorption process, Langmuir isotherm is then classified using a dimensionless constant separation factor (R_L), which can be defined as:

$$RL = \frac{1}{1 + K_L C_m} \quad \dots(8)$$

Where, C_m is the maximum initial metal concentration (mg L⁻¹). The values of this parameter indicated the shape of the isotherm: for which R_L>1 is unfavorable, R_L=1 is linear,

0<R_L<1 is favorable, and R_L=0 is irreversible (Fig. 8) (Reza Ansari & Babak Seyghal 2013).

Freundlich isotherm: The Freundlich adsorption isotherm can be applied for non-ideal adsorption on heterogeneous surfaces and multilayer adsorption. This model earlier known as empirical equation and is shown to be consistent with exponential distribution of active centers, characteristic of heterogeneous surfaces. It is expressed by the following equation (Khalid et al. 2000).

$$q_e = K_F C_e^{1/n} \quad \dots(9)$$

Where q_e is the amount of metal adsorbed per unit of adsorbent (mg g⁻¹), C_e is the concentration of non-retained dye at equilibrium (mg L⁻¹), K_F (mg^(1-1/n)/g L^{1/n}) and 1/n are Freundlich empirical parameters relating to multilayer adsorption capacity and adsorption intensity, respectively.

For a suitable adsorption system 1/n value varies between 0 and 1. Linear form of the Freundlich isotherm model is given by Eq.10. The values of K_F and 1/n can be obtained from the linear plot of ln q_e versus ln C_e (Bhatnagar et al. 2005, Tutem et al. 1998).

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad \dots(10)$$

The constant K_F is an approximate indicator of adsorption capacity, while 1/n is a function of the strength of adsorption in the adsorption process. If n = 1 then the partition between the two phases are independent of the concentration. If value of 1/n is below one, it indicates a normal adsorption. On the other hand, 1/n being above one, indicates cooperative adsorption. The function has an asymptotic maximum as pressure increases without bound.

From Fig. 9, as the temperature increases, the constants k and n change to reflect the empirical observation that the quantity adsorbed rises more slowly and higher pressures are required to saturate the surface. However, K_f and n are parameters characteristic of the sorbent-sorbate system, which must be determined by data fitting, whereas, linear regression is generally used to determine the parameters of kinetic and isotherm models. Specifically, the linear least-

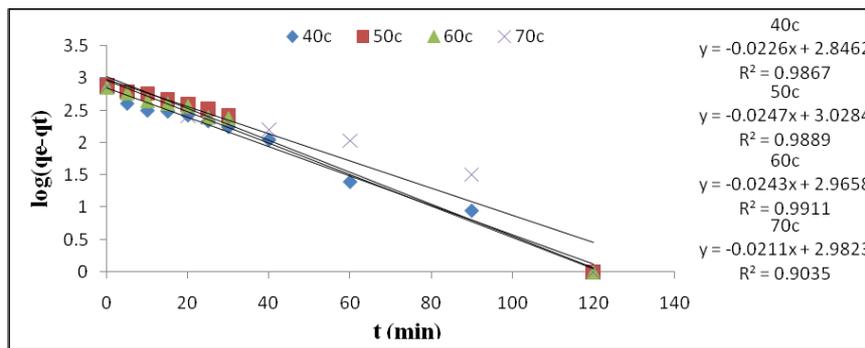


Fig. 5: Kinetic plots for the pseudo first order ($\log(q_e - q_t) = \log(q_e - k_1 t)$) adsorption of lead (Pb) metal on activated carbon from coconut leaves with lead nitrate as adsorbate. (Adsorption Temperatures = 40°C, 50°C, 60°C, 70°C).

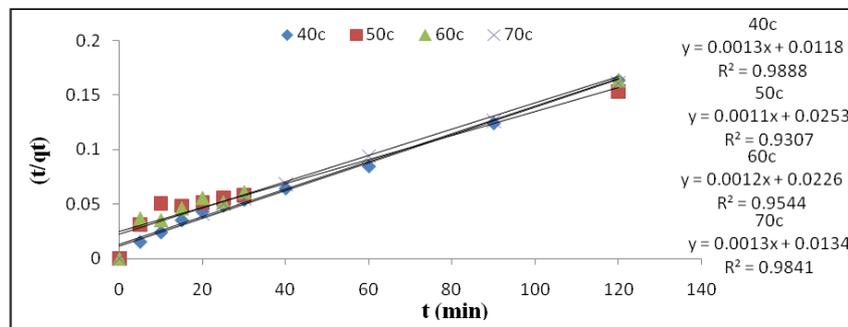


Fig. 6: Kinetic plot for the pseudo second order ($(t/q_t = 1/K_2 q_e + t/q_e)$) adsorption of lead (Pb) metal on activated carbon from coconut leaves with lead nitrate as adsorbate. (Adsorption Temperatures = 40°C, 50°C, 60°C, 70°C).

squares method and the linearly transformed equations have been widely applied to correlate sorption data, where $1/n$ is a heterogeneity parameter; the smaller $1/n$, the greater the expected heterogeneity. This expression reduces to a linear adsorption isotherm when $1/n = 1$. If n lies between one and ten, this indicates a favourable sorption process.

Temkin isotherm: The isotherm shown in Fig. 10 contains a factor that is explicitly taking into the account of adsorbent-adsorbate interactions. By ignoring the extremely low and large value of concentrations, the model assumes that heat of adsorption (function of temperature) of all molecules in the layer would decrease linearly rather than logarithmic with coverage. As implied in the equation, its derivation, characterized by a uniform distribution of binding energies (up to some maximum binding energy), was carried out by plotting the quantity sorbed q_e against $\ln C_e$ and the constants were determined from the slope and intercept. The model is given by the following equation.

$$q_e = \frac{RT}{b} \ln(A_T C_e) \quad \dots(11)$$

Linearized form can be written as,

$$q_e = \frac{RT}{b} \ln A_T + \left(\frac{RT}{b}\right) \ln C_e \quad \dots(12)$$

Where, $B = \frac{RT}{b}$

$$q_e = B \ln A_T + B \ln C_e$$

A_T = Temkin isotherm equilibrium binding constant (L/g)

b_T = Temkin isotherm constant

R = universal gas constant (8.314 J/mol/K)

T = Temperature at 298 K.

B = Constant related to heat of sorption (J/mol)

Determination of Adsorption Isotherm Constants

Constants of Langmuir, Freundlich and Temkin adsorption isotherm for the adsorption of lead (Pb) on activated carbon from coconut leaves (CL_3) with adsorbate lead nitrate at various temperatures 35°C, 40°C, 50°C, 60°C, 70°C, were determined as shown in Table 5.

Table 5 shows that the correlation coefficients (R^2) of Langmuir isotherm for activated carbon obtained from coconut leaves is unity or close to unity, hence Langmuir

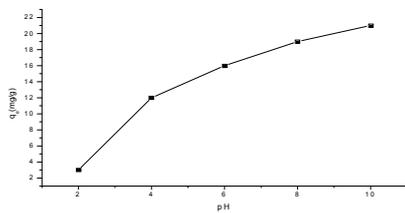


Fig. 7: Effect of lead adsorption onto CL₃ carbon.

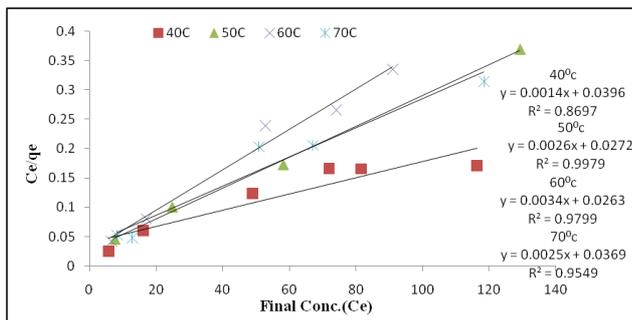


Fig. 8: Plots of the adsorption of lead (Pb) on activated carbon from coconut leaves [CL-01] at 35°C, 40°C, 50°C, 60°C, 70°C.

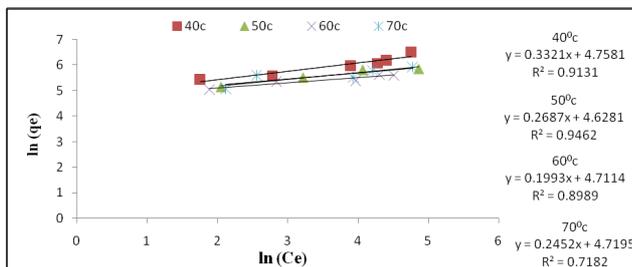


Fig. 9: Plot of $\ln(q_e)$ vs. $\ln(C_e)$ for the adsorption of lead (Pb) on activated carbon from coconut leaves [CL₃] at 40°C, 50°C, 60°C, 70°C.

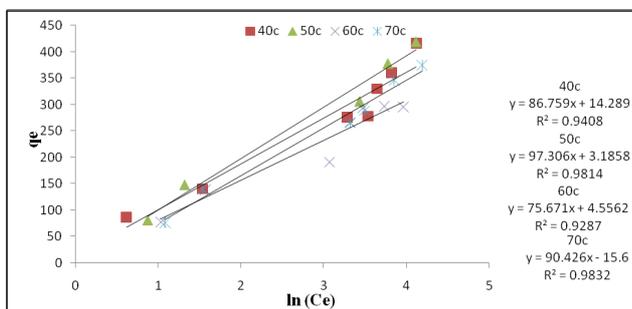


Fig. 10: Plots of q_e vs. $\ln(C_e)$ for the adsorption of lead (Pb) on activated carbon from coconut leaves [CL-01] at 35°C, 40°C, 50°C, 60°C, 70°C.

isotherm gives the best fit for the adsorption data. It simply means that the adsorption is restricted to monolayer capacity and metals are physically adsorbed. Higher value of “b” exhibits the amount of binding energy and adsorption capacity of adsorbent. The fit on Langmuir isotherm indicates the homogenous nature of adsorbent surfaces. Freundlich isotherm shows reasonably good fit. The Freundlich constant “n” represents the adsorption intensity. The values of “n” are greater than unity, indicating that adsorption of the metals is feasible on all the adsorbents synthesized. Temkin isotherm also shows good results for R² value to unity.

KINETIC MODELS

Further to study, the adsorption equilibrium, effectiveness of adsorption is determined, and the types of adsorption mechanism in a given system are identified. Thus, different models are used to predict the adsorption kinetic of lead on CL₃ carbon (Elovich, intra-particle diffusion and Bangham models).

Elovich model: Elovich equation is also used successfully to describe second order kinetic assuming that the actual solid surfaces are energetically heterogeneous, but the equation does not propose any definite mechanism for adsorbate-adsorbent (Ansari Khalkhali & Omidvari 2005). It has extensively been accepted that the chemisorption process can be described by this semi-empirical equation (Ademiluyi & David-West 2012). The linear form of t equation is given by

$$q_t = 1/\beta \ln(\alpha \beta) + 1/\beta \ln(t) \quad \dots(13)$$

α = The initial adsorption rate (mg/g min), and the parameter.

β = The extent of surface coverage and activation energy for chemisorption (g/mg).

The Elovich coefficients were computed from the plots of q_t versus $\ln(t)$. The initial adsorption rate, α , and the desorption constant, β , were calculated from the intercept and slope of the straight-line plots of q_t against $\ln(t)$. Table 2 lists the kinetic constants obtained from the Elovich equation. It is seen that applicability of the simple Elovich equation for the present kinetic data indicates that the Elovich equation was able to describe properly the kinetics of lead adsorption on CL₃ carbon. The value of α and β varied as a function of the solution temperature. Thus, on increasing the solution temperature from 40 to 70°C, the value of β decreased from 0.9 to 0.28 g/mg due to the less available surface for lead ions. On the other hand, an increase in the solution temperature from 40 to 70°C leads to an increase in the value of α from 4.5 to 8.2 mg/g min. This means that adsorption increased while desorption decreased while in-

Table 5: Adsorption isotherm constant of Langmuir, Freundlich and Temkin.

Temp.	Adsorbate (Pb(NO ₃) ₂)								
	Langmuir $C_e/q_e = 1/bV_m + C_e/V_m$			Freundlich $q_e = k \cdot C_e^{1/n}$			Temkin $q_e = RT \ln A + RT \ln C_e$		
	b	V _m	R ²	n	K	R ²	A	B	R ²
40°C	0.035	714.28	0.8697	3.011	116.52	0.9131	0.695	127.12	0.801
50°C	0.095	384.61	0.9979	3.721	102.31	0.9462	1.688	67.794	0.9544
60°C	0.129	294.11	0.9799	5.0175	111.207	0.8989	6.7	42.221	0.885
70°C	0.06777	400	0.9549	4.0783	112.11	0.7182	2.496	62.366	0.7409

Table 6: Comparison of the Elovich, Intra-particle diffusion and Bangham’s adsorption rate constants and the calculated and experimental q_e values at 40°C, 50°C and 60°C and 70°C.

Model	Parameter	Temperature			
		40°C	50°C	60°C	70°C
Elovich model	α (mg/g min)	4.5	7.6	7.9	8.2
	β (g/mg)	0.9	0.86	0.4	0.28
	R ²	0.95	0.89	0.80	0.75
Intra-particle diffusion model	K _{id} (mg/g min ^{1/2})	9.71	14.05	28.51	2.72
	C	0.16	0.039	0.091	0.095
	R ²	0.99	0.89	0.74	0.65
Bangham’s model	D _i (cm ² /s)	0.9×10 ⁻¹¹	1×10 ⁻¹¹	1.3×10 ⁻¹¹	1.38×10 ⁻¹¹
	K _b (mL/g/L)	0.87	1.58	3.9	4.5
	α	0.09	0.038	0.03	0.025
	r ²	0.99	0.95	0.81	0.75

creasing the solution temperature. However, the experimental data did not give a good correlation for these results at high solution temperature.

Intra-particle diffusion model: The pseudo-second-order and Elovich kinetic models could not identify the diffusion mechanism and the kinetic results were then analyzed by using the intra-particle diffusion model. In the model developed by Weber & Morris, McKay & Poots, the initial rate of intra-particle diffusion is calculated by linearization of eq. (12) :

$$q_t = k_{id} t^{(1/2)} + C \quad \dots(14)$$

Where C is the intercept and K_{id} is the intra-particle diffusion rate constant (mg/g min^{1/2}).

According to this model, the plot of uptake, q_t, versus the square root of time (t^{1/2}) should be linear if intra-particle diffusion is involved in the adsorption process and if these lines pass through the origin then intra-particle diffusion is the rate-controlling step (Jr. Weber & Morris 1963). When the plots do not pass through the origin, this is indicative of some degree of boundary layer control and this further show that the intra-particle diffusion is not the only rate-limiting step, but also other kinetic models may control the rate of adsorption, all of which may be operating simultaneously.

The intra-particle diffusion, K_{id}, values were obtained from the slope of the straight-line portions of the plot of q_t

versus t^{1/2} for various solutions temperature. The correlation coefficients (R²) for the intraparticle diffusion model are between 0.99 at 40°C and decreases by increasing the temperature. It was observed that intra-particle rate constant values (K_{id}) increased with solution temperature. Increasing the temperature promoted the pore diffusion in sorbent particles and resulted in an enhancement in the intra-particle diffusion rate. It is likely that a large number of ions diffuse into the pore before being adsorbed. It was observed that the straight lines did not pass through the origin and this further indicates that the intra-particle diffusion is not the only rate-controlling step.

Also, the diffusion coefficients for the intra-particle transport of lead ion within the pores of carbon particles have been calculated by employing the equation (13) (Weber et al. 1963).

$$D_i = \frac{0.03}{t^{1/2}} r^2 \quad \dots(15)$$

Where, D_i is the diffusion coefficient with the unit cm²/s; t_{1/2} is the time (s) for half-adsorption of lead species and r is the average radius of the adsorbent particle in cm. The value of r (atomic radius) was calculated as 175 pm. In these calculations, it has been assumed that the solid phase consists of spherical particles.

The diffusion coefficients varied from 0.9×10⁻¹¹ to 1.38

$\times 10^{-11}$ cm²/s with an increase of solution temperature from 40 to 70°C. At higher temperatures the attraction between the functional groups of CL₃ carbon species gets stronger. The values of the internal diffusion coefficient, D_i , shown in Table 2, fell well within the magnitudes reported in literature (Molina-Sabio et al. 1991). Further, Bangham's equation is used to investigate whether the pore diffusion is rate-controlling step or not.

Bangham's model : Bangham's model (Khalid et al. 2000) equation is generally expressed as

$$\log \frac{c_i}{c_i - c_s} = \log \left[\frac{k_b c_s}{2.303} \right] + \alpha \log t \quad \dots(16)$$

Where, C_s the weight of adsorbent used per liter of solution (g/L), α (<1) and k_b are constants. $\log[C_i/C_i - C_s q_t]$ was plotted against $\log t$. The lead adsorption fits the Bangham's model. α and k_b constants were calculated from the intercept and slope of the straight line plots of $\log[C_i/C_i - C_s q_t]$ against $\log t$. The experimental data are represented by this equation thus the adsorption kinetics is limited by the pore diffusion (Bhatnagar & Jain 2005, Tutem et al. 1998, Reza Ansari & Babak Seyghal 2013).

Table 6 lists the kinetic constants obtained from the Bangham's equation. It will be seen that the value of α and k_b varied as a function of the solution temperature. Thus, on increasing the temperature, the value of α decreased and the value of k_b increased. The experimental data did not give a good correlation at 70°C ($r^2 = 0.75$). In addition, it was found that the correlation coefficients for the Elovich model are higher than those obtained for Bangham's model. This result confirmed that the pore diffusion is not the rate-controlling step. Result is as shown in Table 3.

CONCLUSIONS

This study investigated the equilibrium and the dynamics of the adsorption of lead onto activated carbon prepared by one stage steam pyrolysis of coconut leaves. The adsorption was found to be strongly dependent on pH, contact time and temperature. The adsorption of lead was endothermic in nature with the metal removal capacity increasing with increasing temperature. The Langmuir, Freundlich and Temkin adsorption isotherm predicted the mathematical description of the adsorption equilibrium of lead ions by coconut leaves carbon. The experimental data fitted well to the Langmuir adsorption isotherm. The kinetics of adsorption of Pb (II) on coconut leaves carbon was studied by using kinetic models. The adsorption proceeds according

to the pseudo second order which provides the best correlation of the data in all cases and the experimental $q_e(\text{exp})$ values agree with the calculated ones. Also, it was observed that the intra-particle diffusion was not the only rate-controlling step. Elovich and Bangham model results show that the rate could be enhanced by increasing the adsorption temperature. Lead ions have good affinity towards the sorbent and the increasing randomness at the solid solution interface during the adsorption process.

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