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Modelling and Optimization of Energy-Efficient Procedures for Removing Lead from Aqueous Solutions Using Activated Carbons Prepared from Waste Tyres and *Bauhinia purpurea* Leaves

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ABSTRACT

The present study provides two naturally available sources for making adsorbents, waste tyres and *Bauhinia purpurea* leaves, for the removal of lead from effluents. Equilibrium isotherms, kinetic models and thermodynamic studies were applied to observe the suitability of these adsorbents. Response surface methodology was adopted to investigate the influence of different process variables in lead adsorption process using both the adsorbents. For all the process parameters, the square and linear model terms were having significant effect than interactive model terms of lead adsorption process for both the adsorbents. The interaction effects of the process variables of X_1X_2, X_1X_3, X_2X_3 and X_2X_4 were highly influenced by the percentage removal of lead by using activated carbons prepared from waste tyres. To study the interaction effects of the process variables of X_1X_2, X_2X_3 and X_2X_4 were highly influenced by the adsorption efficiency of lead by using activated carbons prepared from *Bauhinia purpurea* leaves. All the squared terms, X_1, X_2, X_3 and X_4 show a negative influence on the adsorption of lead on the two adsorbents. The interaction effect between process variables of X_1X_2 (*p: 0.000, t: 9.243*), X_1X_3 *(p: 0.03, t: 2.36)*, X_2X_3 *(p: 0.000, t: 4.75)* and X_2X_4 *(p: 0.02, t: 2.71)*, were found to be statistically significant and have positive effect on adsorption efficiency using *ACWT* as an adsorbent. The interaction effect between process variables of X_1X_2 *(p: 0.000, t: 8.1049)*, X_2X_3 *(t: 5.9657, p: 0.000)* and X_2X_4 *(t: 5.9657, p: 0.000)* was found to be statistically significant and positive effect on adsorption efficiency of lead, whereas other interactions were insignificant and did not influence the adsorption efficiency of lead using activated carbons of *Bauhinia purpurea* leaves adsorbent. Based on the statistical approach, the experimental results were analysed by using *ACWT* and *ACBPL* adsorbents for the removal of lead and the optimum process conditions were as follows: *pH*: 4.98 and 4.77, C_i: 140.01 mg/L and 105.7 mg/L, *w*: 0.12 g and 0.123 g, *T*: 314.46 K and 305.31 K and maximum adsorption efficiency of 95.64% and 95.55%, respectively.

INTRODUCTION

For a sustainable human society clean technology and green chemistry is needed for preserving and/or reducing the adverse effects of pollutants on the environment. To provide comforts and necessities to the unceasing global population, rapid industrialization is inevitable, but the environment is severely affected by this large scale industrialization and human activities in the name of development (Mishra et al. 2009). The environmental contamination of heavy metals has become an issue of great concern worldwide (Chung-Hsin et al. 2016). It is often the result of uncontrolled and unlimited discharges from manufacturing, processing and purifying industries (Fu & Wang 2011) (Table 1). Lead, zinc, cadmium, mercury, arsenic, chromium, copper and nickel are the common trace elements found in the aqueous solutions which are non-biodegradable and high toxic (Akunwa et al. 2014). Once the toxic elements are released into the environment, they are difficult to be treated by natural processes and continue to bio-accumulate in the human body and the food chain (Gercel et al. 2007). Therefore, the government environmental protection agencies have set acceptable limits for the heavy metals in drinking water as well as wastewaters (Momcilovic et al. 2011). These strict regulations and standards encouraged researchers to search for new technologies which are environmentally friendly and can reduce heavy metal concentrations in the discharged wastewaters to be within the maximum allowable limits (Corda & Kini 2020). Sources of heavy metals and their impacts are given in Table 1.

Among all the heavy metals, lead is considered as one of the toxic pollutants is generated from a majority of industrial operations (Table 1) (Karnib et al. 2014). A major use of lead is the production of anti-knock compounds for addition to petrol, particularly tetraethyl lead, $Pb(C_2H_5)_4$. The impacts

Table 1: Heavy metals sources, impacts on the health of mankind and acceptable limits in drinking water (Salam et al. 2011).

Heavy metal	Sources	Impacts on humans	Acceptable limits in drinking water (mg/L) IS 10500:2012
Cd	Mining of metals, Smelting and fossil fuel combustion	Affects renal functions, bone, Pulmonary and cardiovascular tissues, lung cancer, etc.	0.003
Pb	Batteries, Cable Sheathing, Sheets and pipes, Chloro-alkali, Petroleum refinery, Paints and dyes, Fertilizers and Motor vehicles	Damage to nervous system, brain and kidney, loss of appetite, High blood pressure, Digestive issues, Muscle and joint pain.	0.01
Hg	Metal Finishing, Metallurgical Industries	Tremors and Incoordination, manic behaviour, anaemia	0.001
Zn	Car and Aeronautic industries, galvanizing plants, textile, etc.	Nausea, Vomiting, dizziness, diarrhoea, fever	5.0
Cu	Alloys, Catalyst, Anti-fouling Paints, Wood Preservative	Convulsions, Cramps, death	0.05
Ni	Electroplating, Catalyst materials, Arc welding, Batteries, etc.	Sensitization of immune system, pulmonary fibrosis and skin dermatitis	0.02

of lead on humans are given in Table 1. Generally, the current trend of research is focused on the usage of naturally available and waste material for the treatment of wastewater. This area is getting importance throughout the world since it minimizes the cost of operation as naturally available materials can obtain cheaply and it also curtails the waste disposal problems (Chowdhury et al. 2012). Especially in developing countries like India, this technique becomes most attractive since most of the industries discharge effluents directly into water bodies because of their high treatment cost (Gaya et al. 2015). The best choice to mitigate heavy metal contamination in wastewater is to eliminate it at the origin, i.e. before the dispersion of metal contaminant to multifarious ecosystems (Bohli et al. 2013, Caccin et al. 2016). Conventional methods are either less effective or more expensive in treating high volumes; require the use of expensive chemicals and low metal concentration in the aqueous form (Juanqin et al. 2016). Most of these processes suffer from high operating cost and recurring expenses such as chemicals, which are not suitable for the small-scale industries (Salam et al. 2011, Jia & Li 2015). Low cost activated carbons are prepared by thermo-chemical methods of various unused materials and plant biomass used for the removal of heavy metals and dyes, recovery of valuable materials (Juan et al. 2013). The literature also reviewed that the plant biomass as waste materials such as leaves, pods, peel, bark, activated carbon cloth (ACC), etc., had been extensively used as adsorbents for the removal of heavy metals from effluents (Gupta et al. 2014, Ming-sheng et al. 2016). The present study aims to investigate the feasibility of alternative, low cost and novel adsorbents for efficient removal of lead and from an aqueous solution. The two adsorbents chosen for the present study are available plenty in nature. Hence, the present investigation is carried out to remove lead onto activated carbon of waste tyres and *Bauhinia purpurea* leaves using adsorption technique (Joga Rao et al. 2019). The present work is focused to test the equilibrium data using different isotherm models and to estimate kinetic parameters using different kinetic models available in the literature. Thermodynamic studies are used to evaluate the thermodynamic energy parameters and compare the adsorption capacities of different adsorbents used in the literature with activated carbon of waste tyres and *Bauhinia purpurea* leaves (Joga Rao et al. 2018). The literature survey also includes the optimization of process variables by using response surface methodology (Jain et al. 2011).

MATERIALS AND METHODS

Chemicals and Instrumentation

The chemicals and instruments used for the experimentation are given in Table 2.

Preparation of Adsorbents

The raw adsorbents, waste tyres and *Bauhinia purpurea* leaves used in the present study were collected in Rajam and Srikakulam. Low cost activated carbons are prepared by carbonization and activation of carbonaceous materials by either physical or chemical activation methods (Joga Rao

Table 2: Chemicals and instrumentation.

Chemicals	Instruments
$Pb(NO_3)_2$ (99%)	Orbital shaker (REMI-CIS-24plus model
NaOH (98%)	pH Meter
HCl (35%)	Filter paper (Whatman-42)
$ZnCl_2$ (70%)	Analytical Balance (Shimadzu, AUX220)
H_2O_2 (30%)	Atomic Absorption Spectrometer (AAS) (Perkin Elmer model 400A)

et al. 2016). The dried products of both the adsorbents were sieved to the desired particle size range of 74-177 μm.

Preparation of Metal Solutions

Adsorbate solution of lead with a concentration of 1000 mg/L was prepared separately by dissolving 1.598 g of 100% $Pb(NO_3)_2$ in 1000 mL of double-distilled water. From the standard stock solutions, working solutions of lower concentrations of lead were prepared (100, 125, 150, 175 and 200 mg/L) for use in batch experiments. After adsorption, the final effluent solution was analysed by atomic absorption spectrophotometer of Perkin Elmer model-3100, a flame type AAS.

Batch Adsorption Experimental Studies

The adsorption studies were conducted for both the adsorbents in the exploratory conditions of various effective process parameters of pH 2-8, contact time 2-120 min, metal ion concentration ranges from 100-200 mg/L, the dosage of the adsorbent 0.025-0.15 g and the particle size of the adsorbent vary from 74 (200 mesh)-177 (85 mesh) μm. Agitation speed of 250 rpm was kept constant in the orbital shaker with a suitable time interval of 2 -120 min. The mixed adsorbent solutions were taken out and filtered by Whatman filter paper and analysed for lead ion concentration. Batch experiments were conducted at various temperatures of the metal solution using orbital shaker from 303-323 K with an optimum contact time of 60 min for the lead at pH value of 5. Samples were analysed by AAS to assess the thermodynamic parameters and study the feasibility of the process with temperature. The amount of lead deposited on the adsorbent surface was determined by using the following equation.

$$q_t = \frac{V(C_o - C_f)}{1000w}$$

Where, q_t is the amount of lead deposited on the adsorbent surface (mg/g), C_o is the initial solute concentration in the solution before adsorption (mg/L), C_f is the final concentration of solute in the solution after adsorption (mg/L), V is the volume of the metal solution (L) and w is the dosage of the adsorbent (g).

Adsorption Isotherms, Thermodynamic and Kinetic Models

The adsorption isotherms indicate the distribution of adsorbed molecules between the liquid phase and solid phase when the adsorption process reaches an equilibrium state. Linear isotherm models, Langmuir, Freundlich, and Dubinin-Radushkevich (D-R) were tested for the equilibrium studies of lead metal ion using both the adsorbents. The fitness of equilibrium data for the pseudo-first-order and pseudo-second-order models were investigated and compared for the two adsorbents. Thermodynamic studies provide information about the feasibility of the adsorption process. It also plays an important role in the study of the nature of the adsorption process. The thermodynamic energy parameters like Enthalpy change (ΔH°), Entropy change (ΔS°), and Gibb's free energy (ΔG°) are used to determine the spontaneity, heat change and affinity of the adsorption process. For isotherm and kinetic analysis, adsorption experiments were conducted by varying the isothermal temperatures of lead solution from 303-323 K with different initial concentrations (100-200 mg/L). 0.1 g of activated carbon of optimum particle size was added to flasks containing 25 mL of lead solution with optimum solution pH. Flasks were shaken at constant mixing speed (250 rpm) at a predetermined temperature in a defined time intervals (equilibrium time constant for isotherm modelling). Then the samples were withdrawn from the shaker, filtered and analysed for metal concentration. The isotherms, kinetic and thermodynamic feasibility modelling equations used for the fitness of the adsorbents of the lead adsorption process are listed in Tables 3 and 4.

The central composite design (CCD) was used to optimize lead removal by activated carbons prepared from waste tyres and *Bauhinia purpurea* leaves in a batch system (Joga Rao et al. 2016). Initial metal ion concentration, pH, temperature and adsorbent dosage are the input variables considered for the optimization of heavy metal removal.

RESULTS AND DISCUSSION

The effect of various process parameters on the removal of lead from aqueous solutions prepared in the laboratory by using activated carbon of waste tyres and *Bauhinia purpurea* leaves were presented. The parameters studied and the range of parameters covered is compiled in Table 5. The experimental data were first analysed graphically and then theoretically to justify the observations made from the graphical analysis. The equilibrium calculations, kinetic models developed, thermodynamic data and optimization of selected variables using response surface methodology are presented here.

Suitability of Two Parameter Adsorption Isotherms

The equilibrium isothermal results were analysed using three of the most commonly used isotherm equations, Langmuir, Freundlich and Dubinin–Radushkevich (D-R). The experimental data were tested for the fitness of Freundlich isotherm model of lead adsorption process by using activated carbons prepared from waste tyres (ACWT) and *Bauhinia purpurea*

Table 3: Linear isotherm model equations.

Isotherm	Modelling equation	Specifications
Freundlich	$\ln q_{eq} = \ln K_f + \frac{1}{n_f} \ln c_{eq}$	q_{eq} is the metal uptake at equilibrium (mg/g); C_{eq} is the equilibrium concentration (mg/L); k_f is the Freundlich constant [$(mg/g)/(L/g)^n$]; is the adsorption intensity constant.
Langmuir	$\frac{1}{q_{eq}} = \frac{1}{q_{max} K_L C_{eq}} + \frac{1}{q_{max}}$ $R_L = \frac{1}{1 + K_L C_i}$	q_{max} is the adsorption binding capacity (*mg/g*) K_L is an affinity of adsorbent (*L/g*); R_L is the separation factor ($0<R_L<1$; *Favourable*).
D-R	$lnq_{eq} = lnq_o - K_d \varepsilon^2$ $\varepsilon = RT \ln(1 + \frac{1}{C_e})$ $E = \frac{1}{\sqrt{2K_d}}$	ε is Polanyi potential; K_d (Mol^2/J^2) is the free energy of adsorption per mole of the adsorbate; q_o (*mg/g*) is the Dubinin-Radushkevich isotherm constant; E (kJ/mol) is the mean adsorption energy (≤8kJ/mol, physical adsorption; >8kJ/mol, chemisorption).

Table 4: Linear kinetic and thermodynamic feasibility model equations.

Model	Modeling equation	Specifications
First order kinetic	$\ln(q_{eq} - q_t) = \ln q_{eq} - k_f t$	q_t (mg/g) is the adsorption intensity at time t; q_{eq} (mg/g) is the adsorption intensity at equilibrium; k_f (1/min) is the rate constant of the first-order adsorption.
Second order kinetic	$\frac{t}{q_t} = \frac{1}{k_s q_{eq}^2} + \frac{1}{q_{eq}}(t)$	k_s is the rate constant of pseudo-second order sorption, (g/mg/min).
Thermodynamic feasibility	$\ln K_e = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT}$ $\Delta G^o = -RT \ln K_e$	K_e is the adsorption equilibrium constant

leaves (ACBPL) and analysed by plotting lnq_e verses lnC_e as shown in Figs.1 (a) and 1(b). The Freundlich isotherm model, gives the straight line relationship with correlation coefficients (0.972 for ACWT and 0.996 for ACBPL at 303K) decreasing with increasing temperature and described that at lower temperatures and concentrations this model was fitted for both the adsorbents as given in Table 6. The values of $1/n_f$ <1 (0.221 for ACWT and 0.223 for ACBPL), and K_f (19.10 for ACWT and 22.03 for ACBPL) obtained indicated the fast uptake capacity of the adsorbent. The K_f value of lead adsorption was decreased with an increase in temperature (303-323 K). At a low isothermal temperature, the adsorption capacity is more than at higher temperatures.

Based on the equilibrium experimental data, the Figs. 2(a) and 2(b) show the Langmuir plot ($1/q_e$ versus C_e) for the adsorption of lead at different isothermal temperatures, yielding multiple straight lines of different Langmuir isothermal parameters as tabulated in Table 6. The values of

Table 5: Range of process parameters covered in the present study for the adsorption of lead.

Process parameter	ACWT		ACBPL	
	Min	Max	Min	Max
Time of contact, *t* (min)	1	90	5	60
Initial metal ion concentration of the solution, C_i (mg/L)	100	200	100	200
pH of the solution	2	8	2	8
Average particle size of the adsorbent, *d* (μm)	74	177	74	177
Adsorbent dosage, *w* (g)	0.025	0.15	0.025	0.15
Temperature, *T*(K)	303	323	303	323

correlation coefficient (R^2) of lead adsorption decreased (0.901 to 0.888) with increasing temperature using activated carbon of waste tyres adsorbent, indicating that the Langmuir model is favourable at lower temperatures. Fig. 2(b) shows the R^2 values (0.9005 to 0.9915) of lead adsorption process increased with increasing temperature using *Bauhinia purpurea* leaves adsorbent, indicating that the Langmuir model is favourable at moderate temperatures. At temperature 303 K, the maximum value of lead adsorption capacity Q_{max} and K_L values (Table 3) were found to be 41.66 mg/g and 0.923 L/mg for ACWT and 40.81 mg/g and 0.935 L/mg, respectively.

The linear plots of D-R isotherm for both the adsorbents of lead adsorption process are shown in Figs 3(a) and 3(b). The values of D-R isotherm parameters were calculated by using equations (Table 3) and given in Table 6. From the plots, at 303 K, the maximum adsorption capacity, q_o value found to be 35.12 mg/g and 37.18 mg/g for ACWT and ACBPL adsorbents respectively. The magnitude of E can be decided by the chemical or physical adsorption by using suitable adsorbents. The mean adsorption energy E values of lead adsorption process were decreased with increasing isothermal temperature (303-323 K) from 1-0.267 KJ/mole and 1.29-0.223 KJ/mole for ACWT and ACBPL adsorbents respectively. These results revealed that the adsorption process of lead on both the adsorbents could be taken place by physisorption mechanism.

Isothermal Models

The equations given in Table 7 were correlated for the removal of lead by using activated carbon prepared from waste tyres and *Bauhinia purpurea* leaves.

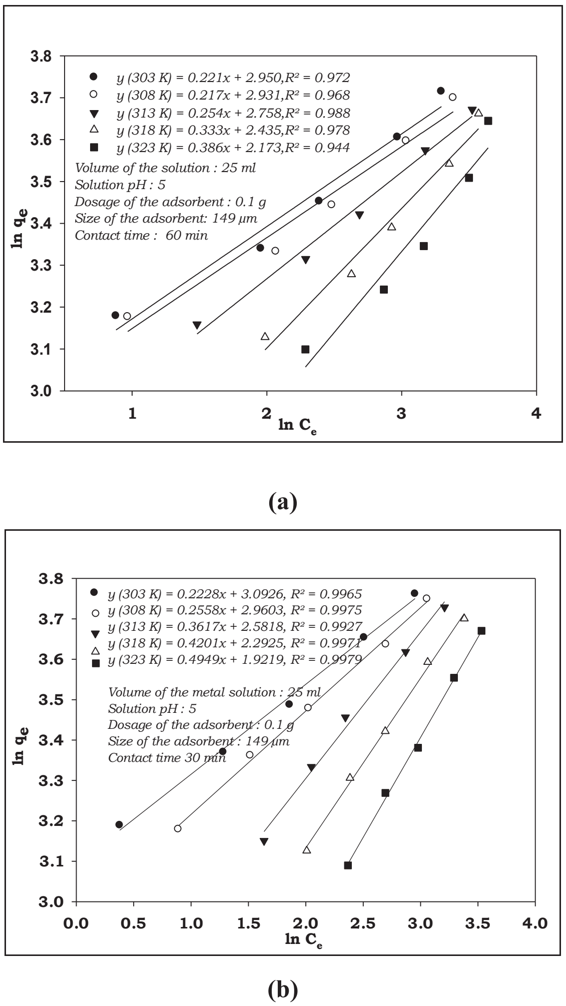


Fig.1: Freundlich isotherm model for adsorption of lead using ACWT (a) and ACBPL (b) adsorbents.

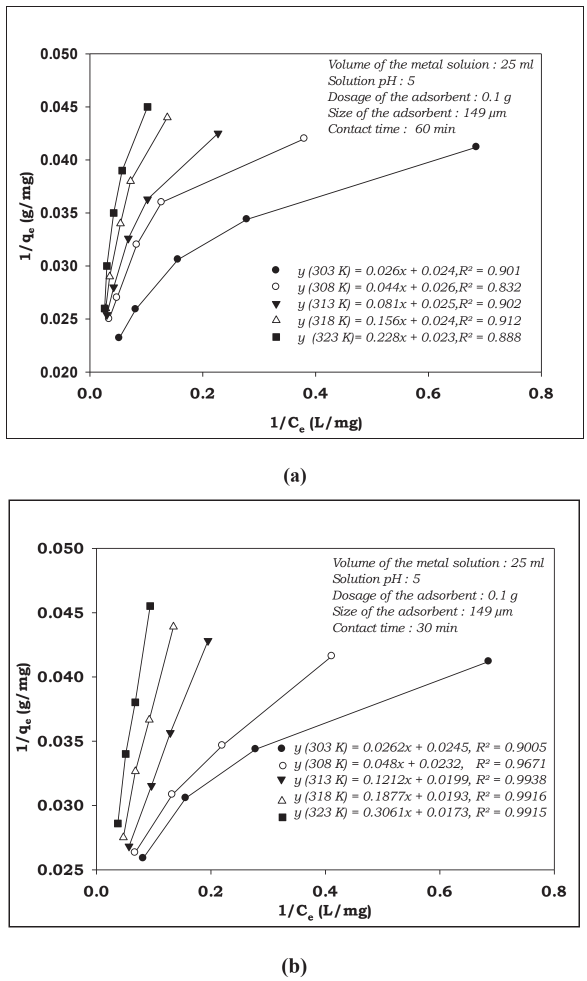
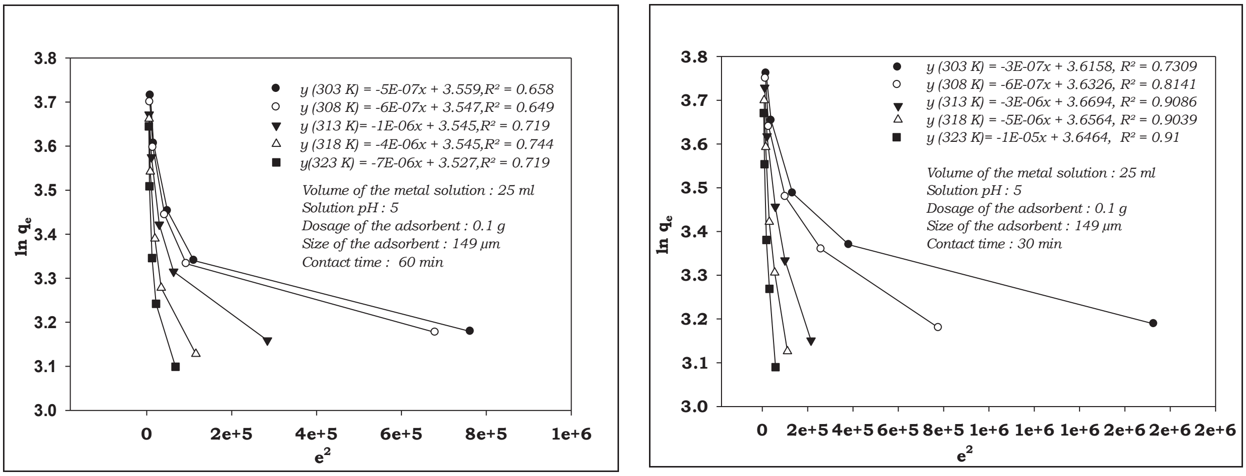


Fig. 2: Langmuir isotherm model for adsorption of lead using ACWT (a) and ACBPL (b) adsorbents.



(a) (b)

Fig. 3: Dubinin-Radushkevich isotherm model for adsorption of using ACWT (a) and ACBPL (b) adsorbents.

Table 6: Isotherm constants for lead adsorption onto activated carbon of waste tyres (t: 60 min) and *Bauhinia purpurea* leaves (t: 30 min).

Activated carbon of waste tyres							*Bauhinia purpurea* leaves				
Temperature (K)		303	308	313	318	323	303	308	313	318	323
Freundlich	K_f	19.1	18.7	15.7	11.4	8.78	22.0	19.3	13.22	9.89	6.83
	n_f	4.52	4.60	3.93	3.0	2.59	4.48	3.90	2.76	2.38	2.02
	R^2	0.97	0.96	0.99	0.97	0.94	0.99	0.99	0.992	0.99	0.99
Langmuir	q_{max}	41.6	38.4	40.0	41.6	43.4	40.8	43.1	50.25	51.8	57.8
	K_L	0.92	0.59	0.30	0 .1	0.1	0.93	0.48	0.164	0.10	0.05
	R^2	0.90	0.83	0.90	0.91	0.88	0.90	0.96	0.993	0.99	0.99
	R_L	0.01	0.01	0.03	0.06	0.09	0.00	0.02	0.057	0.08	0.15
D-R	q_o	35.1	34.7	34.6	4.63	34.0	37.1	37.8	39.22	38.7	38.3
	E	1	0.91	0.70	0.35	0.26	1.29	0.91	0.408	0.31	0.22
	R^2	0.65	0.64	0.64	0.90	0.71	0.73	0.81	0.908	0.90	0.91

Kinetic Modelling

The kinetics of adsorption studies describes the metal deposition rate and residence time of sorption reaction. The kinetic data provide the necessary information required for optimizing the operating conditions in full scale batch or continuous adsorption process. The kinetic data also help in determining the rate limiting step involved in the adsorption process. The experimental results were analysed to test the kinetic model and the linear plots of $ln\ (q_{eq} - q_t)$ versus t (Table 4) are shown in Figs. 4 (a) and 4(b) for ACWT and ACBPL adsorbents, respectively. The calculated first-order rate constants (k_f) and their corresponding linear regression correlation coefficient values are compiled in Table 8. The linear regression correlation coefficient values R^2 were found in the range of 0.949 to 0.974 and 0.966 to 0.891 for ACWT and ACBPL adsorbents respectively. The results show that the correlation coefficients were very high, the experimental q_{eq} values did not agree with the calculated q_{eq} values. This implies that the adsorption of the lead for both the adsorbents did not follow the first-order kinetics. The validity of the pseudo-second-order kinetic model for the adsorption of lead using activated carbons prepared from waste tyres and *Bauhinia purpurea* leaves adsorbents were evaluated separately with the help of the linear plots of t/q_t versus t (Table 4). The value of the constant k_s and q_{eq} can be calculated from the slope and intercept of Figs.5 (a) and 5(b). The pseudo-second-order rate constant k_s, the calculated q_{eq} value and the corresponding linear regression correlation coefficient values R^2 are given in

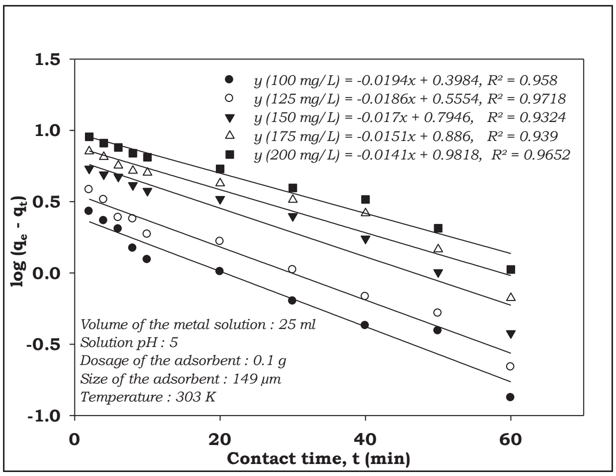
Table 9. The results indicate that the experimental q_e, and calculated q_e values are very close to each other and also R^2 value is closer to unity for both the adsorbents. The high R^2 values indicate that the experimental data are well correlated to the second-order kinetic equation.

Kinetic Models

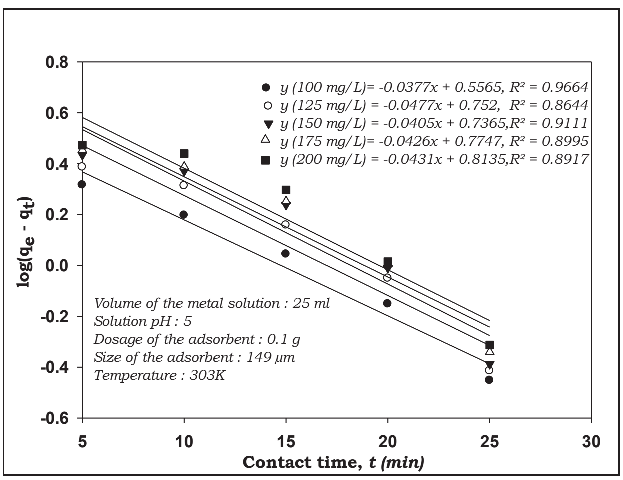
The following equations in Table 10 were correlated for the removal of lead by using activated carbon prepared from waste tyres and *Bauhinia purpurea* leaves.

Table 7: Isothermal Modeling for the removal of lead using activated carbons.

Isotherm	ACWT		ACBPL	
	Modelling	R^2	Modelling	R^2
Langmuir	$q_e = \frac{38.45C_e}{1 + 0.923C_e}$	0.901	$q_e = \frac{38.15C_e}{1 + 0.935C_e}$	0.900
Freundlich	$q_e = 19.1C_e^{0.22}$	0.972	$q_e = 22.03C_e^{0.22}$	0.996
R-D	$q_e = 35.12e^{(-5*10^{-7})\varepsilon^2}$	0.659	$q_e = 37.18e^{(-3*10^{-7})\varepsilon^2}$	0.731

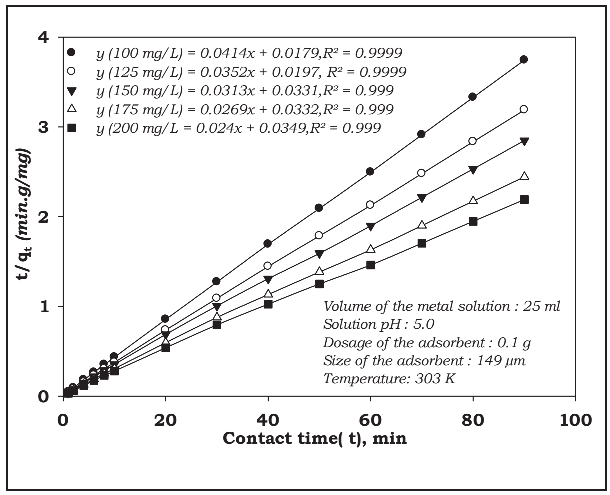


(a)

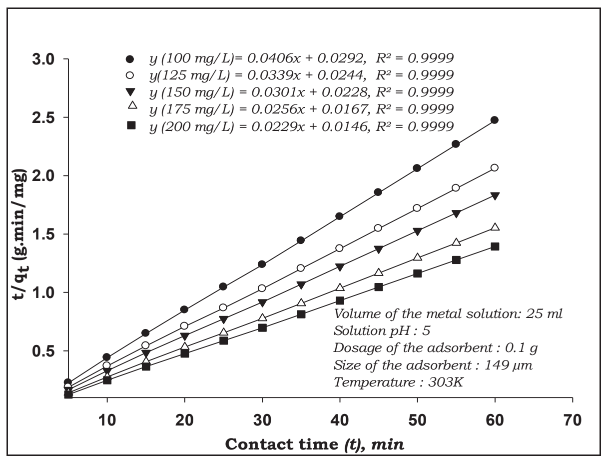


(b)

Fig. 4: First-order Kinetic model for adsorption of lead using ACWT (a) and ACBPL (b) adsorbents.



(a)



(b)

Fig. 5: Second-order kinetic model for adsorption of lead using ACWT (a) and ACBPL (b) adsorbents.

Table 8: First-order kinetic constants for the adsorption of lead using ACWT and ACBPL adsorbents.

C_i	$q_{e,\ exp}$	ACWT			$q_{e,\ exp}$	ACBPL		
		k_f	q_{eq} cal	R^2		k_f	q_{eq} cal	R^2
100	24.034	0.023	1.42	0.949	24.27	0.037	1.74	0.966
125	28.221	0.022	1.66	0.974	29.09	0.047	2.12	0.864
150	31.59	0.025	2.22	0.895	32.71	0.040	2.08	0.911
175	36.81	0.018	2.34	0.966	38.62	0.042	2.16	0.899
200	41.06	0.017	2.58	0.974	43.03	0.0431	2.25	0.891

Table 9: Second-order kinetic constants for the adsorption of lead using ACWT and ACBPL adsorbents.

C_i	$q_{e,\ exp}$	ACWT			$q_{e,exp}$	ACBPL		
		k_s	q_{eq} cal	R^2		k_s	q_{eq} cal	R^2
100	24.03	0.098	24.3	0.999	0.419	0.180	0.489	0.996
125	28.22	0.064	28.57	0.999	0.694	0.055	0.870	0.990
150	31.59	0.029	32.25	0.999	1.033	0.052	0.990	0.991
175	36.81	0.021	37.17	0.999	1.299	0.050	1.142	0.992
200	41.06	0.016	41.67	0.999	1.507	0.041	1.306	0.991

Thermodynamic Modeling

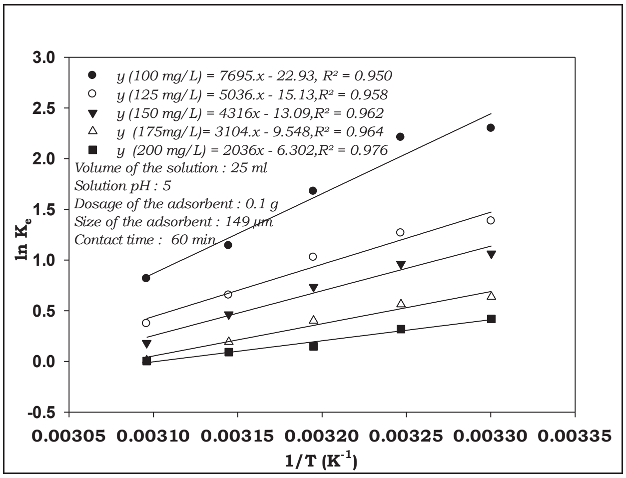
Thermodynamic energy parameters (ΔH°, ΔS°, and ΔG°) give evidence of the direction of the adsorption process. The experiments were conducted for lead using activated carbon prepared from waste tyres and *Bauhinia purpurea* leaves at different initial concentrations (100-200 mg/L) of metal solutions with the solution temperature varied in the range of 303 to 323 K. The equilibrium constants (K_e) obtained from the equation given in Table 4 were used to evaluate the thermodynamic energy parameters. The values of ΔH°, ΔS° and ΔG° were calculated from the slope and intercept of the linear Vant-Hoff's plot, i.e. $lnK_e \;\; vs \;\; \left(\frac{1}{T}\right)$. These plots are shown in Figs. 6(a) and 6(b) for ACWT and ACBPL adsorbents, respectively. The estimated thermodynamic energy parameter values of ΔH°, ΔS° and ΔG° are given in Table 11. The variation of thermodynamic energy parameters (ΔG°, ΔH° and ΔS°) with solution temperature of the adsorbents were described that the adsorption process is exothermic, increased the adsorption efficiency and lead deposition on both the adsorbent surfaces and spontaneous at lower temperatures. The negative value of ΔS° indicates the decreased randomness at the solid-solute interface during the adsorption process.

Optimization of Adsorption Process Parameters Using RSM

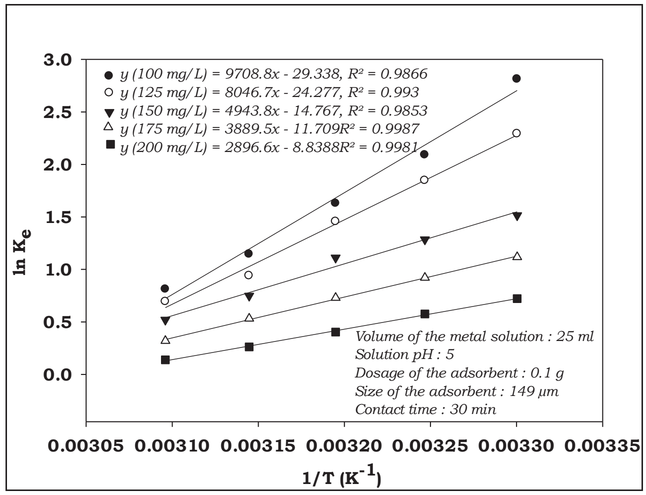
In the present study, response surface methodology was adopted to investigate the influence of different process variables in the adsorption process using activated carbons prepared from waste tyres and *Bauhinia purpurea* leaves. The effect of various parameters such as pH (X_1), initial metal concentration (X_2), dosage of the adsorbent (X_3) and temperature (X_4) of lead onto activated carbon of waste tyres and *Bauhinia purpurea* leaves were studied using full factorial central composite design (CCD). The response was expressed as the adsorption efficiency (%) of lead on both the adsorbents. The levels of independent process variables used in a CCD are shown in Table12.

Table 10: Kinetic models for the removal of lead using activated carbons.

Model	ACWT		ACBPL	
	Kinetic model	R^2	Kinetic model	R^2
1st First order	$q_t = 24.034\,(1 - e^{-0.023t})$	0.949	$q_t = 24.27\,(1 - e^{-0.037t})$	0.966
2nd order	$\frac{dq_t}{dt} = 0.098(24.03 - q_t)^2$	0.999	$\frac{dq_t}{dt} = 0.056(24.27 - q_t)^2$	0.999



(a)



(b)

Fig. 6: Van't-Hoff relation for the determination of thermodynamic properties.

Table 11: Variation of thermodynamic parameters for the adsorption of lead using ACWT and ACBPL adsorbents.

C_i (mg/L)	*ACWT*		*ACBPL*		*-ΔG° (kJ/mol)*		
	-ΔH° (kJ/mol)	*-ΔS° (kJ/mol.K)*	*-ΔH° (kJ/mol)*	*-ΔS° (kJ/mol.K)*	*T (K)*	*ACWT*	*ACBPL*
100	63.976	0.196	80.78	0.243	303	5.78	7.08
125	41.869	0.125	66.9	0.201	308	5.65	5.87
150	35.883	0.108	41.10	0.122	313	4.36	4.68
175	25.806	0.079	32.33	0.097	318	3.01	3.44
200	16.927	0.052	24.08	0.073	323	2.18	2.22

RSM was used to develop a mathematical model to represent all the correlations among independent variables and responses of interest, i.e. adsorption efficiency of metals. The experimental data with multiple regression analysis were obtained from the following second-order polynomial equations found to represent the adsorption efficiencies of lead (Y_1%) for ACWT and (Y_2%) for ACBPL adsorbents, respectively.

$$(Y_1\%) = -7779.95 + 86.38\,X_1 - 1.71\,X_2 - 375.23\,X_3 + 49.62\,X_4 - 9.35X_1^2 - 653X_3^2 - 0.08X_4^2 + 0.18\,X_1X_2 + 45.40\,X_1X_3 - 0.07X_1X_4 + 1.83X_2X_3 + 0.01X_2X_4 + 2.4X_3X_4$$

$$(Y_2\%) = -1729.67 + 39.37X_1 - 0.6X_2 + 258.18X_3 + 11.45X_4 - 4.49X_1^2 - 1333.33X_3^2 - 0.02\,X_4^2 + 0.03X_1X_2 + 2.90X_1X_3 + 0.4X_2X_3 + 0.05X_3X_4$$

The influence of linear, square and interaction effects of process variables on the adsorption efficiency of lead by using activated carbons prepared from waste tyres and *Bauhinia purpurea* leaves are given in Tables 14, 15, 16 and 17. These results were demonstrated by means of Fisher's *F*-test and Student *t*-test and *p*-value. For all the parameters (Tables 14 and 15), the square ($F = 378.03$ and $P = 0.000006$ for *ACWT*; $F = 420.223$ and $P = 0.00$ for ACBPL) and linear ($F = 4032.26$ and $P = 0.000006$ for ACWT; $F = 6248.36$ and $P = 0.000$ for ACBPL) model terms were having significant effect than interactive ($F = 122.54$ and $P = 1.248$ for ACWT;

Table 12: Experimental variables and levels investigated by central composite design for the adsorption of lead.

Variable	Process parameter	Level of Process parameters				
		-2	-1	0	1	2
X_1	Solution pH	3	3.5	4	4.5	5
X_2	Initial metal concentration, C_i (mg/L)	100	125	150	175	200
X_3	Dosage of the adsorbent, w (g)	0.05	0.075	0.1	0.125	0.15
X_4	Temperature (K)	303	308	313	318	323

Table 13: The optimal values of the process variables and responses (adsorption efficiency) by using RSM.

Process Variable	ACWT		ACBPL	
	Opt.	Expt.	Opt.	Expt.
pH	4.98	5	4.77	5
C_i (mg/L)	140.01	150	105.7	125
w (g)	0.12	0.125	0.123	0.125
T (K)	314.46	313	305.31	303
(% Y)	95.64	94.26	95.55	98.14

F = 28.804 and *P* = 0.447 for ACBPL) model terms of lead adsorption process for both the adsorbents. Because of their p-values being less than 0.05; the interaction effects of the process variables of X_1X_2, X_1X_3, X_2X_3 and X_2X_4 were highly influenced on the percentage removal of lead, whereas combinations of X_1X_4 and X_3X_4 were insignificant effect on the percentage removal of lead by using activated carbons prepared from waste tyres (Table 14). To study the interaction effects of the process variables of X_1X_2, X_2X_3 and X_2X_4 were highly influenced on the percentage removal of lead, whereas combinations of X_1X_3, X_1X_4 and X_3X_4 were insignificant effect on the percentage removal of lead by using activated carbons prepared from *Bauhinia purpurea* leaves (Table 15). The magnitude of *t*-value gives the positive or negative influence of the independent or process variables on % removal, whereas p-value indicates the significant or insignificant effect of process variables on % removal of metals. The coefficients of X_1 and X_4 showed the greatest significant negative effect and the positive effect by the other variable X_4 (Table 16) on the lead adsorption process by using ACWT adsorbent. Whereas, the coefficients of X_1, X_3 and X_4 showed the greatest linear positive effect and the negative effect by the other variable X_2 (Table 17) on lead removal by using ACBPL adsorbent. All the squared terms, X_1, X_2, X_3 and X_4 shows a negative influence on the adsorption of lead on both the adsorbents. The interaction effect between process variables of X_1X_2 (p = 0.000, t = 9.243), X_1X_3 (p = 0.03, t = 2.36), X_2X_3 (p = 0.000, t = 4.75) and X_2X_4 (p = 0.02, t = 2.71), were found to be statistically significant and having positive effect on % removal using *ACWT* as an adsorbent, whereas the combination of X_1X_4 were insignificant effect on the adsorption efficiency of lead. The interaction effect between process variables of X_1X_2 (p = 0.000, t = 8.1049), X_2X_3 (t = 5.9657, p = 0.000) and X_2X_4 (t = 5.9657, p = 0.000) was found to be statistically significant and positive effect on adsorption efficiency of lead, whereas other interactions are insignificant and not influenced on the adsorption efficiency of lead using activated carbon of *Bauhinia purpurea* leaves

Table 14: Analysis of variance (ANOVA) for response surface quadratic model for the adsorption of lead using *ACWT* as an adsorbent.

Source	SS	DF	MS	F	P (Prob>F)
Linear	3721.305	4	3721.305	4032.266	0.000006
X_1	2263.207	1	2263.207	2452.326	0.000000
X_2	1245.889	1	1245.889	1349.998	0.000000
X_3	152.611	1	152.611	165.364	0.000000
X_4	59.598	1	59.598	64.578	0.000006
Square	348.88	4	348.88	378.033	0.000006
X_1^2	95.421	1	95.421	103.395	0.000001
X_2^2	92.787	1	92.787	100.540	0.000001
X_3^2	90.985	1	90.985	98.587	0.000001
X_4^2	69.687	1	69.687	75.511	0.000003
Interaction	113.0981	5	113.0981	122.549	1.248837
X_1X_2	78.854	1	78.854	85.444	0.000002
X_1X_3	5.153	1	5.153	5.583	0.037618
X_1X_4	0.0001	1	0.0001	0.00	0.953030
X_2X_3	20.839	1	20.839	22.581	0.000598
X_2X_4	6.812	1	6.812	7.381	0.020044
X_3X_4	1.440	1	1.440	1.560	0.237545
Error	10.152	11	0.923		
Total SS	3994.534	25	R^2 = .9974	R^2 (Adj) = .9942	

DF: degree of freedom; SS: sum of squares; F: factor; P: probability.

Table 15: Analysis of variance (ANOVA) for response surface quadratic model for removal of lead using *ACBPL* as an adsorbent.

Source	SS	DF	MS	F	P (Prob>F)
Linear	688.303	4	172.075	6248.36	0.000000
X_1	389.7816	1	389.7816	14153.60	0.000000
X_2	182.7120	1	182.7120	6634.57	0.000000
X_3	91.6504	1	91.6504	3327.98	0.000000
X_4	24.1603	1	24.1603	877.30	0.000000
Square	46.291	1	11.573	420.223	0.000000
X_1^2	22.0255	1	22.0255	799.78	0.000000
X_2^2	8.1503	1	8.1503	295.95	0.000000
X_3^2	12.1212	1	12.1212	440.14	0.000000
X_4^2	3.9936	1	3.9936	145.02	0.000000
Interaction	3.966	1	0.793	28.804	0.447000
X_1X_2	1.8090	1	1.8090	65.69	0.000006
X_1X_3	0.0210	1	0.0210	0.76	0.400924
X_1X_4	0.0001	1	0.0001	0.00	0.953030
X_2X_3	0.9801	1	0.9801	35.59	0.000094
X_2X_4	1.1556	1	1.1556	41.96	0.000046
X_3X_4	0.0006	1	0.0006	0.02	0.882981
Error	0.3029	11	0.0275		
Total SS	717.5999	25	R^2=.9995	R^2 (Adj) = .99904	

DF: degree of freedom; SS: sum of squares; F: factor F; P: probability.

Table 16: Estimated regression coefficients and corresponding *t* and *p* values for the adsorption of lead using activated carbon of waste tyres.

Adsorption process Parameter (Mean value)	Regression Coefficient	Standard Error	*t*-Value	p-Value
Constant	-7779.95	927.3439	-8.3895	0.000004
X_1	86.38	31.1518	2.7729	0.018133
X_2	-1.71	0.6175	-2.7667	0.018336
X_3	-375.23	613.4817	-0.6116	0.553203**
X_4	49.62	5.7811	8.5837	0.000003
X_1^2	-9.35	0.9198	-10.1683	0.000001
X_2^2	-0.00	0.0004	-10.0270	0.000001
X_3^2	-3653.00	367.9076	-9.9291	0.000001
X_4^2	-0.08	0.0092	-8.6897	0.000003
X_1X_2	0.18	0.0192	9.2436	0.000002
X_1X_3	45.40	19.2133	2.3629	0.037618
X_1X_4	-0.07	0.0961	-0.7755	0.454392**
X_2X_3	1.83	0.3843	4.7519	0.000598
X_2X_4	0.01	0.0019	2.7169	0.020044
X_3X_4	2.40	1.9213	1.2491	0.237545**

**insignificant ($p \geq 0.05$)

adsorbent. To maximize the adsorption efficiency of lead, regression model equations developed by using response surface methodology for the prediction of the effect of process variables % removal of lead were optimized separately with ACWT and ACBPL adsorbents. The optimal values of the process variables and responses (adsorption efficiency) are provided in Table 13.

The data indicated that the adsorption capacity of the

Table 17: Estimated regression coefficients and corresponding *t* and *p*-values for the adsorption lead (ACBPL).

Adsorption parameter (Mean value)	Regression Coefficient	Standard Error	*t*-Value	p-Value
Constant	-1729.67	160.1935	-10.7974	0.000000
X_1	39.37	5.3813	7.3158	0.000015
X_2	-0.60	0.1067	-5.6486	0.000149
X_3	258.18	105.9756	2.4363	0.033041
X_4	11.45	0.9986	11.4608	0.000000
X_1^2	-4.49	0.1589	-28.2804	0.000000
X_2^2	-0.00	0.0001	-17.2032	0.000000
X_3^2	-1333.33	63.5540	-20.9795	0.000000
X_4^2	-0.02	0.0016	-12.0423	0.000000
X_1X_2	0.03	0.0033	8.1049	0.000006
X_1X_3	2.90	3.3190	0.8738	0.400924**
X_1X_4	0.00	0.0166	0.0603	0.953030**
X_2X_3	0.40	0.0664	5.9657	0.000094
X_2X_4	0.00	0.0003	6.4779	0.000046
X_3X_4	0.05	0.3319	0.1506	0.882981**

**insignificant ($P \geq 0.05$)

activated carbons prepared from waste tyres and *Bauhinia purpurea* leaves adsorbents were higher than most of the adsorbents/biosorbents reported in the literature for the removal of lead from effluents. The results also showed that the adsorption capacity of activated carbon of *Bauhinia purpurea* leaves is high when compared with activated carbon of waste tyres adsorbent for the removal of lead under similar experimental conditions studied.

CONCLUSIONS

The following conclusions could be drawn from the present study on the removal of lead from aqueous solutions using adsorption technique:

- The equilibrium contact time for the adsorption of lead onto activated carbons prepared from waste tyres and *Bauhinia purpurea* leaves were 60 and 30 min, respectively. The maximum rate adsorption was obtained at pH of 5 for both the adsorbents.
- It was found that the experimental data were fitted very well with the Freundlich and Langmuir isothermal models for both the adsorbents, suggesting the involvement of both physisorption and chemisorption.
- Kinetic studies indicated that the adsorption process followed well with the pseudo-second-order kinetic model for the adsorption of lead using activated carbons of waste tyres and *Bauhinia purpurea* leaves for the range of initial metal concentrations studied for the entire adsorption period.
- The thermodynamic feasibility of lead adsorption process with both the adsorbents were described the negative significance values of $\Delta G°$, $\Delta H°$ and $\Delta S°$ revealed that the adsorption process is exothermic, feasible and spontaneous, and increased the adsorption efficiency and lead deposition on the adsorbent surfaces at lower temperatures.
- For all the process parameters, the square (F: 378.03 and P: 0.000006 for ACWT; F: 420.223 and P: 0.00 for ACBPL) and linear (F: 4032.26 and P: 0.000006 for ACWT; F: 6248.36 and P: 0.000 for ACBPL) model terms were having significant effect than interactive (F: 122.54 and P: 1.248 for ACWT; F: 28.804 and P: 0.447 for ACBPL) model terms of lead adsorption process for both the adsorbents.
- The interaction effects of the process variables of X_1X_2, X_1X_3, X_2X_3 and X_2X_4 were highly influenced on the percentage removal of lead, whereas combinations of X_1X_4 and X_3X_4 were insignificant effect on the percentage removal of lead by using activated carbons prepared from waste tyres.
- To study the interaction effects of the process variables of X_1X_2, X_2X_3 and X_2X_4 were highly influenced on the percentage removal of lead, whereas combinations of

X_1X_3, X_1X_4 and X_3X_4 were insignificant effects on the percentage removal of lead by using activated carbons prepared from *Bauhinia purpurea* leaves.

- The coefficients of X_1, and X_4 showed the greatest significant negative effect and the positive effect by the other variable X_4 on the lead adsorption process by using ACWT adsorbent, whereas, the coefficients of X_1, X_3 and X_4 showed the greatest linear positive effect and the negative effect by the other variable X_2 on lead removal by using ACBPL adsorbent.
- Based on the statistical approach the experimental results were analysed by using ACWT and ACBPL adsorbents for the removal of lead and the optimum process conditions were identified as pH: 4.98 and 4.77, Ci: 140.01 mg/L and 105.7 mg/L, w: 0.12 g and 0.123 g, T: 314.46 K and 305.31 K and maximum adsorption efficiency of 95.64% and 95.55%, respectively.

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