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Experimental and Statistical Studies on the Adsorption of Lead in Aqueous Solution using Activated Carbon from *Bauhinia Purpurea* Leaves.

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ABSTRACT

Activated carbons prepared from Bauhinia Purpurea Leaves (ACBPL) are used as low cost adsorbents for the complete removal of lead ions from wastewater effluents. Experiments were performed at *pH* : 5.0,C_i : 100 mg/L, *w* = 0.1 g, *T*: 303 K and t : 30 min and the maximum efficiency of lead onto ACBPL as adsorbent was 98.52 %. The results were analyzed statistically and optimum conditions were identified as *pH*: 4.77, C_i: 105.70 mg/L, *w*: 0.123 grams and *T*: 305.31. The predicted value of adsorption efficiency of Pb on ACBPL adsorbent used CCD is 95.55%.The square (*F* = 420.223 and *P* = 0.00) and linear (*F* = 6248.36 and *P* = 0.000) terms were highly significant than interactive (*F* = 28.804 and *P* = 0.4470*)*parameters. Based on high ‘t’ and low ‘P’ value (< 0.05), both the linear and the squared terms, i.e., pH (X_1), C_i(X_2), *w* (X_3) and *T* (X_4), show significant effect; while the interaction effects, X_1X_3,X_1X_4andX_3X_4 are found to be insignificant. The negative values of ΔG^o, ΔH^o and ΔS^o revealed that the adsorption process is exothermic, increase the adsorption efficiency and Pb deposition on the ACBPL surface at lower temperatures.

Keywords: Lead, Bauhinia Purpurea Leaves (ACBPL), Adsorption Isotherms, Kinetics, Central Composite Design (CCD), thermodynamic studies.

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INTRODUCTION

The waste discharges having heavy metals coming from the various sources directly entered into the water to change the physical,chemical and biological properties have become one of the most serious problems that threaten biological community and human life [1]. Lead is one of the most toxic and harmful metals that widely dispersed through mining, textile, tannery, metal-plating, petrochemical, battery and fertilizer production, lead is deposited in soil, aquatic life-forms and tissues, frame part of the human evolved way of life. Thus, the toxicity, bio-accumulation and persistence of this metal are transmitted through the food chain and the environment to cause environmental and human health problems [2]. Too much lead can damage various systems of the body, including the nervous and reproductive systems and the kidneys, and it can cause high blood pressure and anemia. The Environmental Protection Agency (EPA) standards for lead in wastewater and drinking water are 0.5 and 0.05 mg/L respectively [3].

Use activated carbons (AC) as adsorbent materials have rendered the adsorption technology a versatile technique for wastewater remediation [4]. Hence, research of the recent past, mainly focused on utilizing low cost waste materials as alternative's to activated carbon from a Bauhinia Purpurea Leaves(ACBPL) is used as an adsorbent. ACBPL is of high porosity and high surface area material manufactured by carbonization and activation of carbonaceous materials by either physical or chemical activation methods [5]. Appropriate activation conditions of temperature, time, etc. have been found to enhance both surface area and pore volume of activated carbons developed from carbon black [6] and this has resulted in improved adsorption behavior. The objective of the present study was to prepare activate porous carbon from Bauhinia Purpurea Leaves with a combination of physical and chemical treatment in an attempt to develop surface porosity as well as to incorporate desired functional groups on the surface of the resultant activated carbon. The adsorption capacity of the developed carbon was further evaluated for lead ion removal from wastewater.

Research studies commonly used different technique for process Optimization [7]. The CCD (central composite design) was present as the most successful in optimization studies and it has some advantages of the required small number of the performed experiments inthe modeling process, the consumption of chemicals and time was reduced. RSM is one of the relevant multivariate techniques which can deal with multi-variant experimental design strategy, statistical modeling and process optimization [8]. It is used to examine the relationship between one or more response variables and a set of quantitative experimental variables or factors. The process optimization of the lead recovery from ACBPL as the adsorbent using adsorption process has not been reported in literature. Hence the present work intends to assess the effects of variables such as initial lead concentration, weight of the adsorbent, temperature and pH of the solution to identify the optimum conditions using a central composite design (CCD).

MATERIALS AND METHODS

Preparation of activated carbon from Bauhinia Purpurea Leaves

The *Bhuhinia purpurea* leaves were collected from GMR Institute of Technology, Rajam, India. The collected bark and leaves were washed several times with deionized water until the wash water contains no dirt. These washed leaves and bark were completely dried under sunlight for 30 days and were cut into small pieces and powdered using domestic mixer. Then dried in an oven at 100 ◦C for 2 hours. The dried material is now placed in the cooker for carbonization and it is continuously heated continuously for 20min.The obtained carbonized product is now treated with 30% Hydrogen peroxide (H_2O_2) for 10 to 15 min to oxidize adhering organic impurities. Now the obtained product is placed in oven for 24hr at 60 ◦C. The materials were washed with deionized water three times to remove H_2O_2 and dried at 110◦C for 2hours in oven. The dried material was activated to 700 ◦C for 2hr in a covered silica crucible by heating in a muffle furnace. After that, take 100 grams of carbon powder from a muffle furnace and mixing with 100 games $Zncl_2$ dissolved in 500 ml of distilled water containing 22 gms of HCL. The chemically treated material was left overnight and carbonized. Carbonized material was refluxed with 10 % HCL solution for 3 hrs and filtered. This was followed by drying of the material at 100 ◦C for 24 hours. The dried product was sieved to desired particle sizes of 85-100, 100-150 and 150–200 µm. Finally, the Activated carbon Bauhinia Purpurea Leaves (ACBPL) was stored.

Preparation of stock solution

Adsorbate solution was prepared from Lead nitrate (Merck- A.R. Grade). About 1.598 g of lead nitrate was weighed and a standard stock solution of concentration 1000 mg/l was prepared in double distilled water and further working solutions of lower concentrations (100,125,150,175 and 200 ppm) were prepared as and when required.

Adsorption Experimentation

Metal investigation was completed in the batch process. The adsorption studies were completed in the exploratory conditions of various effective process parameters of pH 2-5.5, metal ion concentrations 100-200 mgL^{-1},theweight of the adsorbent 0.025-0.15 g and the particle size of the adsorbent vary from 74 (100 mesh) -177 (200 mesh) µm. Agitation speed of 250 RPM was kept steady in the orbital shaker with the suitable time interims from 5-60 min. The mixed adsorbent solutions were taken out and filtered by Watmann filter paper and analyzed for lead ion concentration in an Atomic Absorption Spectrophotometer (Perkin Elmer model-3100).Batch experiments were conducted varies the temperature of the metal solution utilizing orbital shaker from 303 K-323K with equilibrium adsorption time of 30 min and analyzed by AAS to assess the thermodynamic parameters and study the feasibility of the process with temperature.

Metal deposited on the surface of the adsorbent (q)

In order to estimate the uptake of the lead ions, a whole arrangement experiments were performed at different process variables for the ACBPL adsorbent. The metal uptake of lead onto ACBPL utilizing the accompanying mathematical expression:

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

Where q_t is the amount of metal deposited on the ACBPL adsorbent surface *(mg/g)*,C_i is the initial concentration of solute 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 *(ml)* and *w* is the weight of the ACBPL adsorbent.

RESULTS AND DISCUSSIONS

Equilibrium adsorption process time for ACBPL adsorbent

The efficiency of ACBPL adsorbent is mainly depends on the adsorption process time. The adsorption experiments were conducted for different lead concentrations from 100 mg/L- 200 mg/l with the function of adsorption process time and adsorption efficiency of ACBPL are demonstrated in Fig: 1. The adsorption efficiency of lead ions increases gradually with increasing process time and reaches equilibrium at around 30 min, at which point the maximum amount lead is removed from the solution. This quick uptake of lead can be clarified by the creation of the most active sites on the surface of the ACBPL by the thermal-chemical treatment process during the preparation of ACBPL from *Bhuhinia purpurea* leaves. The outcomes in the Fig:1.depicts that the adsorption efficiency is increased from 90.11 to 98.52% at a contact time of 30 min with 100 mg/L metal concentration. The Fig: 2. shows that the maximum metal doposited on the adsorbent surface at 30 min adsorption process time is 24.27mg/g.

Variance of hydrogen ion concentration of metal ion binding

The adsorption process, mostly effected by changing the pH of metal solution .This parameter is directly effects the surface charges of the adsorbents as well as the degree of ionization of different metal ions in the aqueous solution. The effect of pH on adsorption of lead at constant temperature (303 K) and the time of adsorption process30 min is shown in Fig:3. It was observed that the adsorption efficiency is very low at strong acidic medium (pH = 1–3). After pH 3, adsorption efficiency, increase sharply up to pH 5 because more metal binding sites could be exposed and carried negative charges, with subsequent attraction of the positively charged metal ions with the adsorbent surface. The Solution pH value is increased 5.5 to 6; leads undergo hydrolysis process forming a lead hydroxide precipitation and dissociate functional groups on the adsorbent surface. This subsequently leads to a shift in reaction kinetics and equilibrium characteristics of adsorption process. These studies concluded that the competition of hydrogen ions on the ACBPL surfaces is not metal specific. As the pH is lowered, the overall surface charge on the cell wall will become positive, which inhibits the approach of positively charged metal cations. With the increase of solution pH, absorbent surface is more negatively charged and the functional groups of the ACBPL were more competent to bind the metal ions at the surface. The maximum removal of efficiency 98.52% is obtained at pH 5.0. From Fig: 4,indicates that the maximum amount of lead deposited on the surface of ACBPL adsorbent is changes from 24.27 mg/g – 43.03 with respective to change in concentration from 100 mg/L – 200 mg/L.

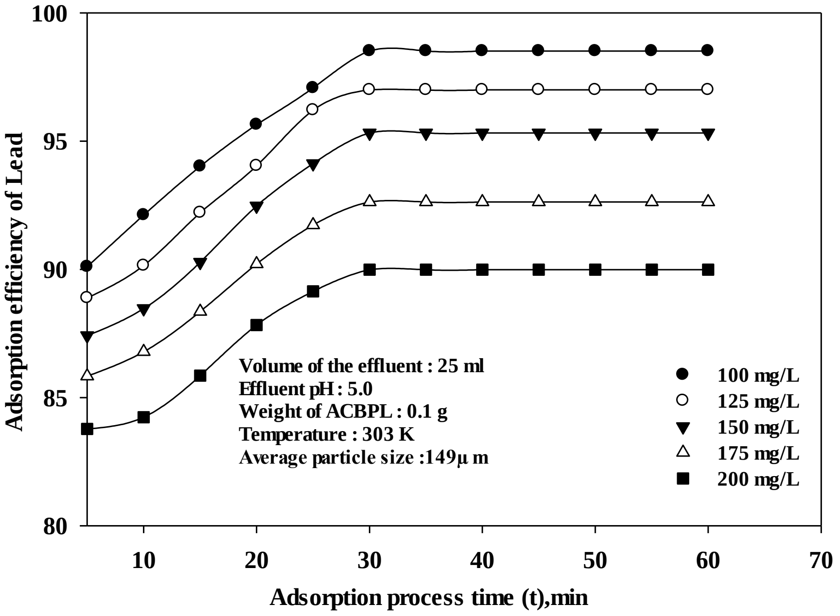

Fig 1: Effect of adsorption process time on the adsorption efficiency of Lead using ACBPL

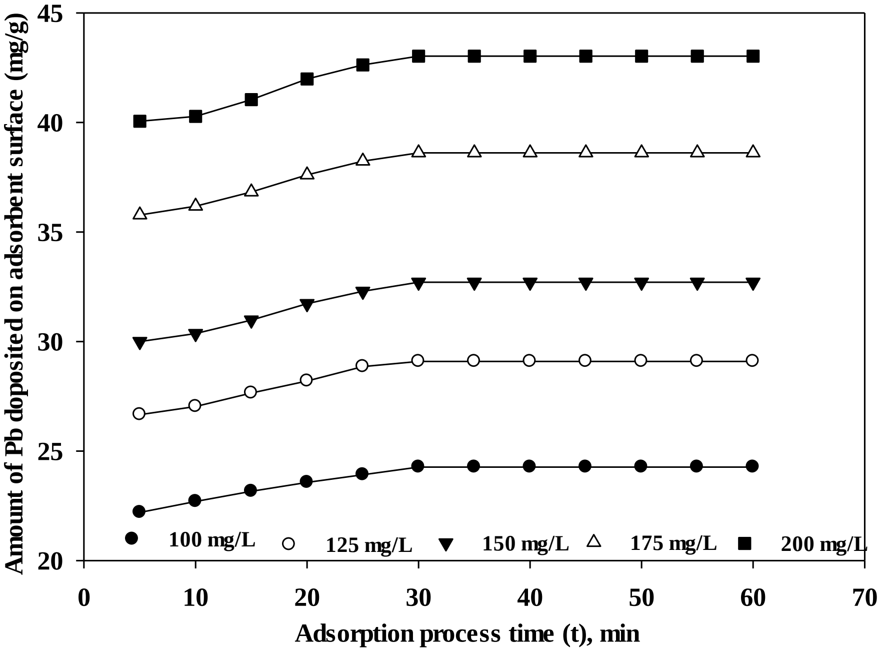

Fig 2: Variance of adsorption process time for deposition of Lead on ACBPL adsorbent

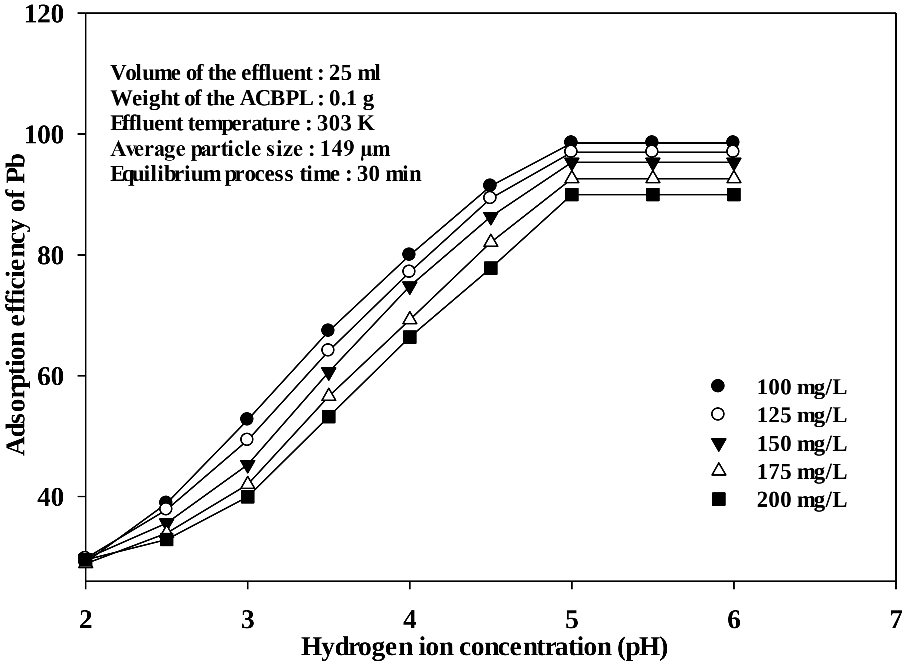

Fig 3: Variance of hydrogen ion concentration on the adsorption efficiency of Pb using ACBPL.

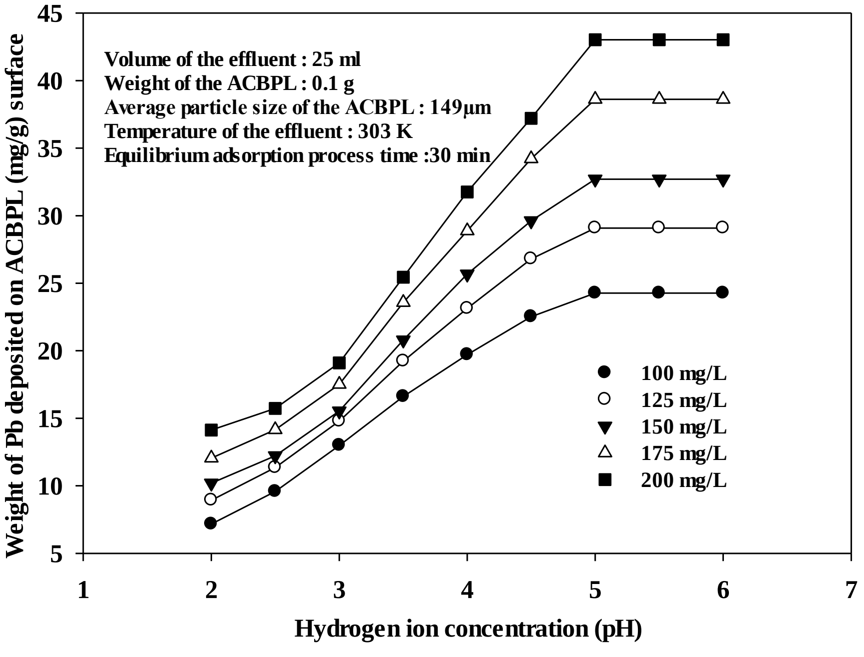

Fig 4: Variance of hydrogen ion concentration for the deposition of Pb on the ACBPL surface

The influence of adsorbent weight on adsorption efficiency and metal deposited on ACBPL

Surface

The Fig: 5. Concluded that the adsorption efficiency has been increased proportionally with increased the weight of adsorbent. The Fig: 6.Shows that the amount of lead deposited on the surface of the ACBPL adsorbent is increased from 19.22 mg/g-24.42 mg/g(C_i: 100 mg/L) with increases weight of the adsorbent.

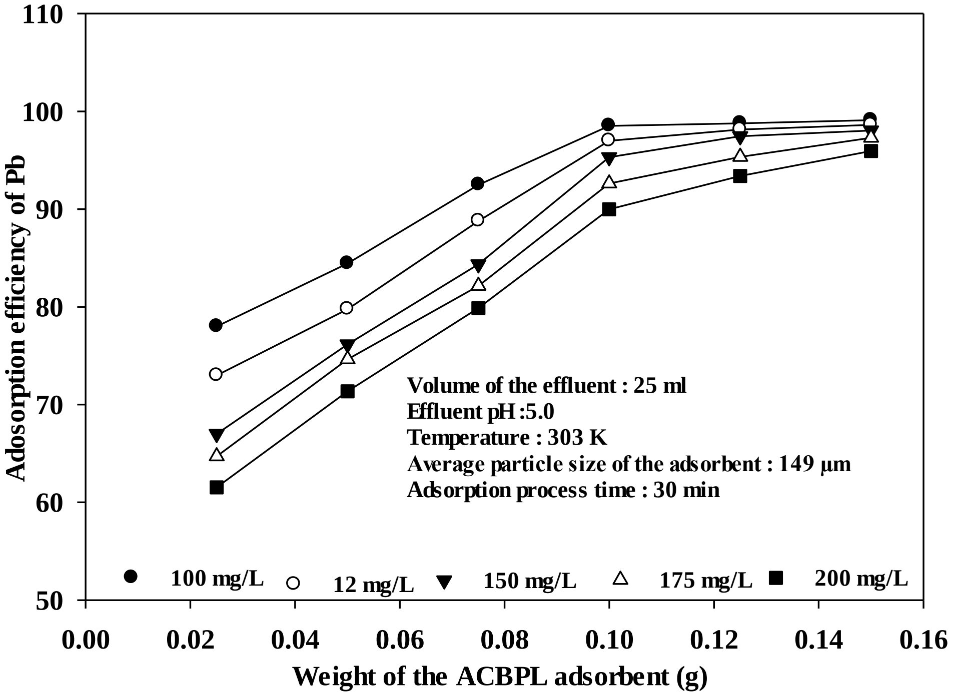

Fig 5: The variance of adsorbent weight on adsorption efficiency, using ACBPL as Adsorbent.

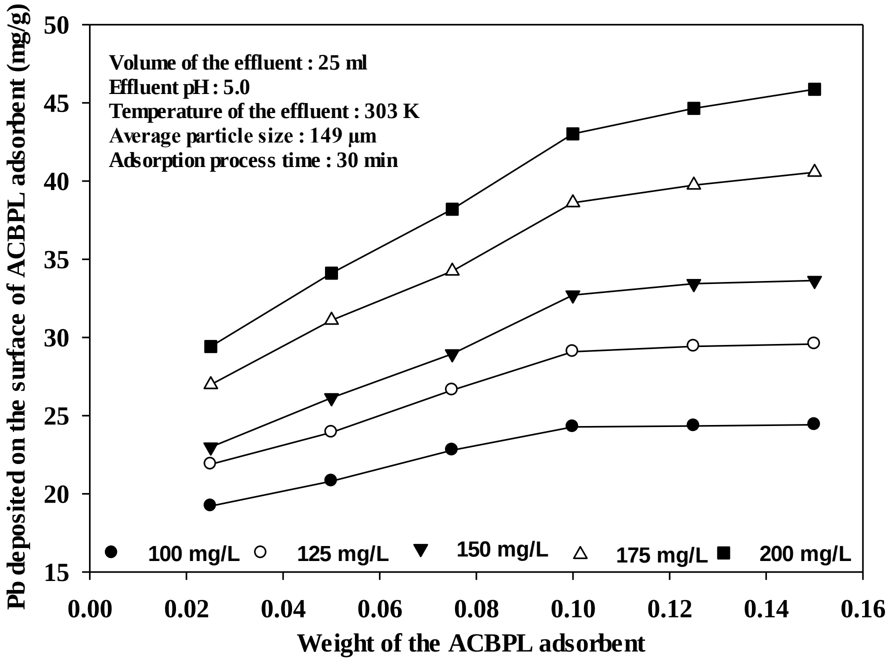

Fig 6: The variance of adsorbent weight on Pb deposited, using ACBPL as Adsorbent.

Variance of average particle size of ACBPL adsorbent

The number of active sites per unit volume of adsorbent for solid - liquid interface highly influences on adsorption efficiency and metal deposited on ACBPL surface. From Fig:7. The particle size increases from74 µm to 177 µm, the rate of adsorption decreases from 99.56% to 97.46 % (C_i : 100 mg/L) and metal uptake is declining from 24.53 mg/l to 24.01 mg/l. The contactness of the solid – liquid is higher for smaller particles to compare with larger particles, which shows that there is more rapid adsorption and high mass transfer to enhance the adsorption process. Fig.8.Shows that the particle size, moderately influenced the metal deposition on ACBPL surface and the maximum amount of Pb deposited on the adsorbent surface at 74 µm is 99.56% .

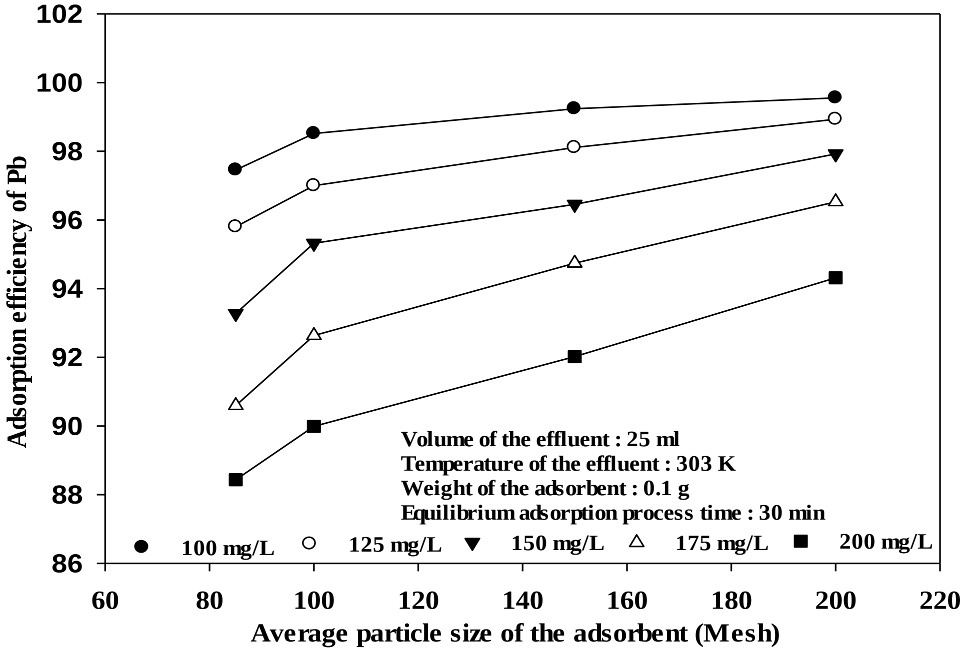

Fig 7: Effect of average particle size on adsorption efficiency of Lead on to ACBPL adsorbent.

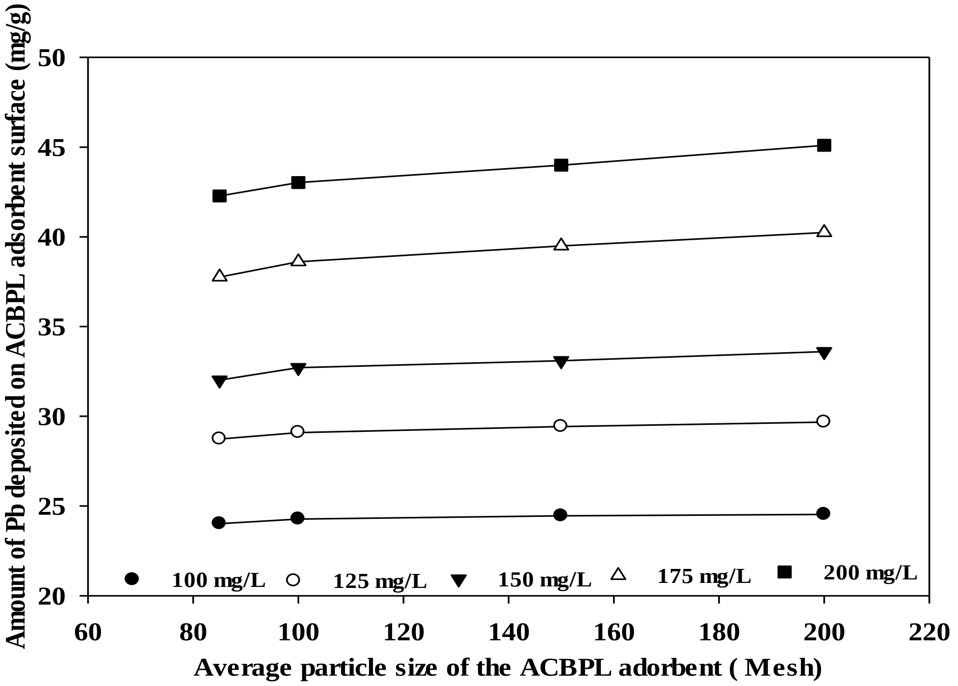

Fig 8: Variance of average particle size on the metal uptake of ACBPL adsorbent.

Suitability of two parameter adsorption Isotherms

In general Frendluich isotherm is widely applied in heterogeneous systems, especially for organic compounds or highly interactive species on activated carbon and molecular sieves[9].The linear form of the Frendluich isotherm model is given by

$$\ln q_{eq} = \ln K_f + \frac{1}{n_f} \ln c_{eq}$$

From the Frendluich isotherm model, from Table.1,the slope (*$1/n_f$*) value is increased with temperature is close to 1, indicates that the adsorption efficiency less and prefer chemisorption only. Fig: 9.The $K_f$declined from 22.03 (mg/g)/ (L/g)^n to 6.83 (mg/g)/(L/g)^n with increased temperature (303K - 323K). In this perspective, at low temperature the adsorption efficiency is more than that higher temperatures. The linearized Langmuir equation was applied to analyze the equilibrium experimental data. The equation is given as:

$$\frac{1}{q_{eq}} = \frac{1}{q_{max} K_L C_{eq}} + \frac{1}{q_{max}}$$

Fig:10. The separation factor (R_L) is evaluated (Table 1) from Langmuir constant (K_L, L/g) is increased with increasing solution temperatures, reflects that the adsorption is more favorable with lower temperature.

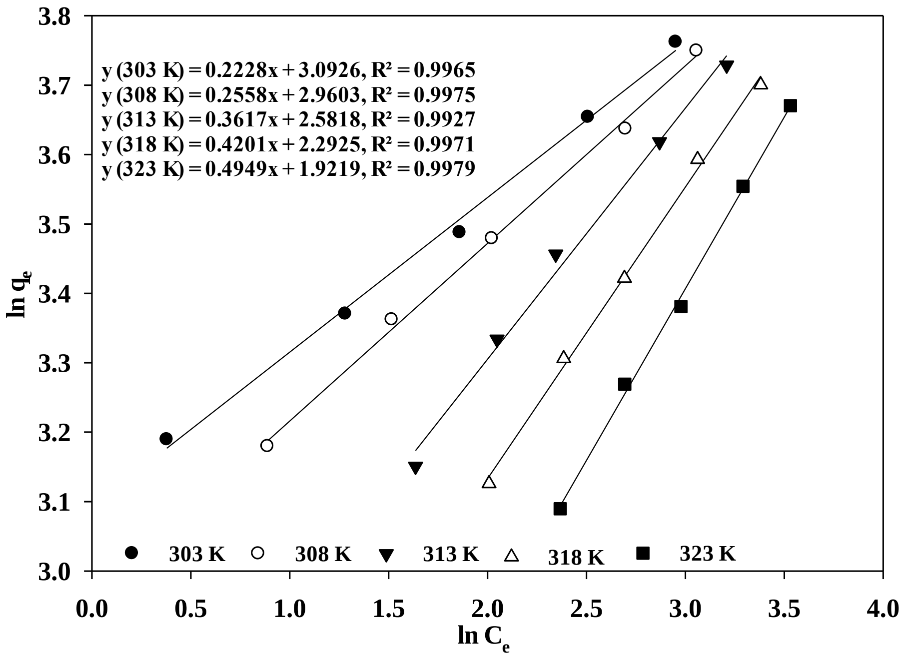

Fig 9: Frendluich isotherms at four different temperatures for adsorption of Lead.

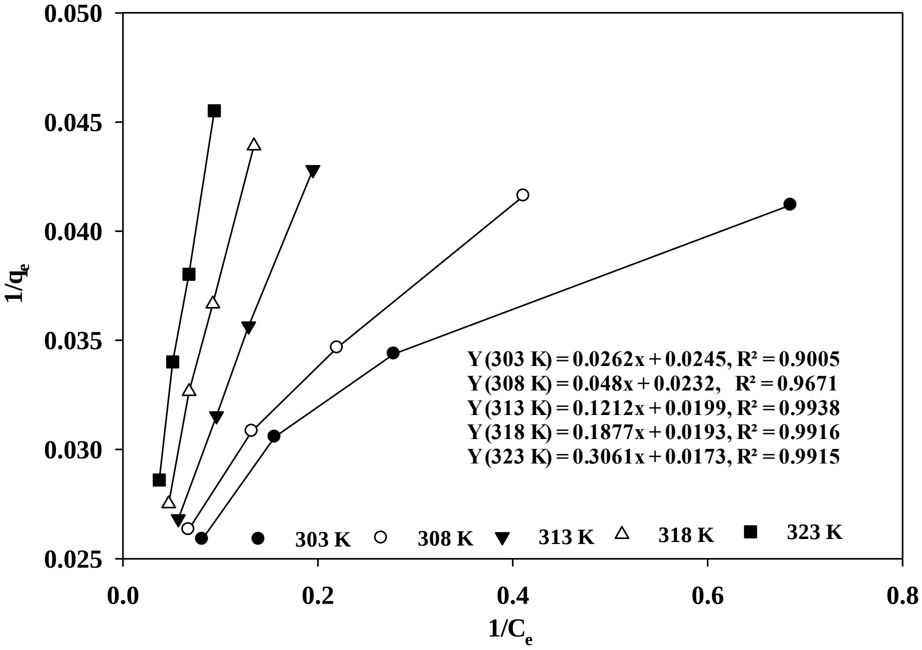

Fig 10: Langmuir isotherms at four different temperatures for the adsorption of Lead.

One of the unique features of the D-R isotherm model lies on the fact that it is temperature dependent has frequently effectively fitted high solute affinity and the intermediate range of concentrations. The D–R equation has been computed by [10]

$$lnq_e = lnq_o - k_d \varepsilon^2$$

Where, K_d is related to the free energy of adsorption per mole of the adsorbate, and q_o is the Dubinin-Radushkevich isotherm constant related to the degree of adsorbate adsorption by the adsorbent surface. The mean free energy of adsorption process was evaluated by the following equation

$$E = \frac{1}{\sqrt{2K_d}}$$

The magnitude of E can be decided chemical or physical adsorption by using ACBPL adsorbent. The mean adsorption energy to lead was exhibited in Table 1. E values declined with increasing temperature from 1.29KJ/mole – 0.223 KJ/mole. It was observed that the scope of an ordinary free energy credited to physical adsorption and the force of attraction between the adsorbate and adsorbent are very weak, therefore this type of adsorption can be easily reversed by heating or by decreasing the pressure.Fig:11.Indicates that the linear behavior of R-D isotherm with respective variation of temperatures of solution. From the Table1, for 100 mg/l of metal solution, it was observed that the adsorption data were very well represented by Freundlich, isotherm for the lead with an average higher correlation coefficient of 0.996, followed by Langmuir and Dubinin – Radushkevich isotherms and with a correlation coefficient of 0.9005, and 0.730 respectively.

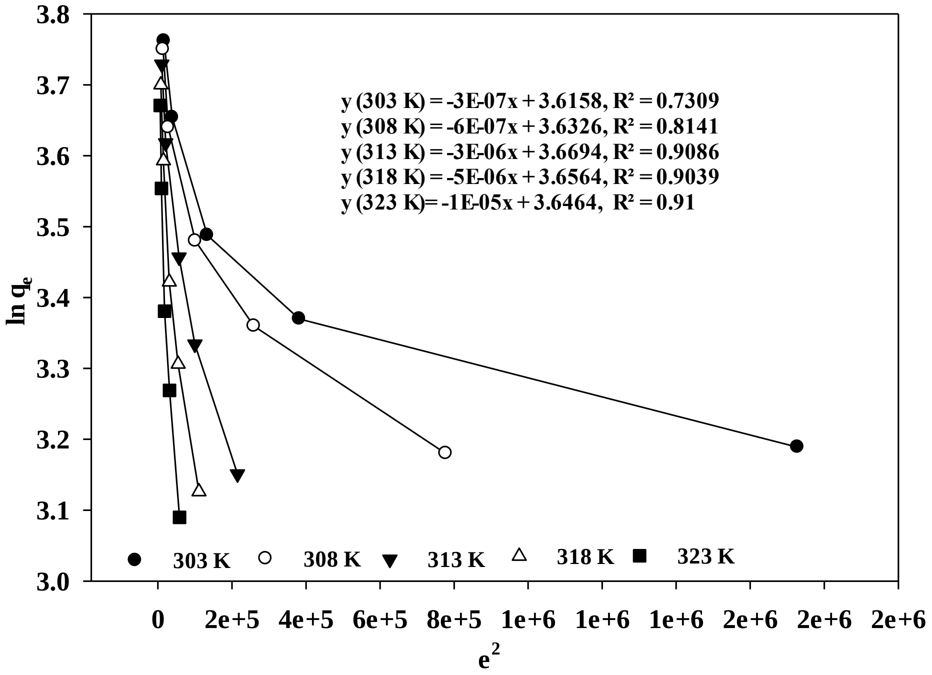

Fig 11: Dubinin - Radushkevich isotherms for adsorption of lead onto ACBPL as an adsorbent.

Table 1: Isotherms constants for lead adsorption on to ACBPL adsorbentat C_i =100 – 200 *mg/L*, *w* = 0.1g, d: 149 *µm*, *T*: 303-323 K , *pH*: 5.0 and *t* : 30 *min*.

Isotherm model	*Parameter*	*Adsorbate temperature (K)*				
		303	***308***	***313***	***318***	***323***
Freundlich	K_f*(mg/g)/(L/g)*^{n}	*22.03*	*19.30*	*13.22*	*9.89*	*6.83*
	n_f *(L/g)*	*4.48*	*3.90*	*2.76*	*2.38*	*2.02*
	R^2	*0.9965*	*0.9975*	*0.9927*	*0.9971*	*0.997*
Langmuir	q_{max}*(mg/g)*	*40.816*	*43.10*	*50.25*	*51.81*	*57.80*
	K_L *(L/g)*	*0.935*	*0.483*	*0.164*	*0.103*	*0.056*
	R^2	*0.9005*	*0.9**67***	*0.99**3***	*0.99**1***	*0.99**1***
	$R_L=1/(1+K_LC_o)$	*0.0093*	*0.020*	*0.057*	*0.088*	*0.151*
R-D	q_o *(mg/g)*	*37.18*	*37.81*	*39.22*	*38.72*	*38.33*
	K_d (Mol^2kJ^{-2})	$3*10^{-7}$	$6*10^{-7}$	$3*10^{-6}$	$5*10^{-6}$	10^{-5}
	E (kJ/Mole)	*1.290*	*0.912*	*0.408*	*0.316*	*0.223*
	R^2	*0.730*	*0.814*	*0.908*	*0.903*	*0.910*

Feasibility of adsorption process based on thermodynamic studies

Thermodynamic energy parameters (ΔH^o, ΔS^o, and ΔG^o) only to give the evidence of the direction of the adsorption process.Fig:12& 13 shows that the adsorption efficiency and deposition rate of lead on ACBPL surface are decreasing with increasing temperature. The Van't Hoff equation is described the thermodynamic parameters is given by using the following linear equation[11],

$$\ln K = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT}$$

The relationship between ΔG^o and K is given by the following equation,

$$\Delta G^o = -RT \ln K$$

The Van't Hoff plot is drawn in Fig:14from the present data. The values of ΔH^o, ΔS^o and ΔG^o for various initial concentrations of lead at different temperatures are appearing in table-2. The thermodynamic feasibility of adsorption process described that the negative sign values of ΔG^o,ΔH^o and ΔS^o revealed that the adsorption process is exothermic, increase the adsorption efficiency and Pb deposition on the ACBPL surface at lower temperatures. The ACBPL adsorbent used in this study has higher affinity at lower temperatures.

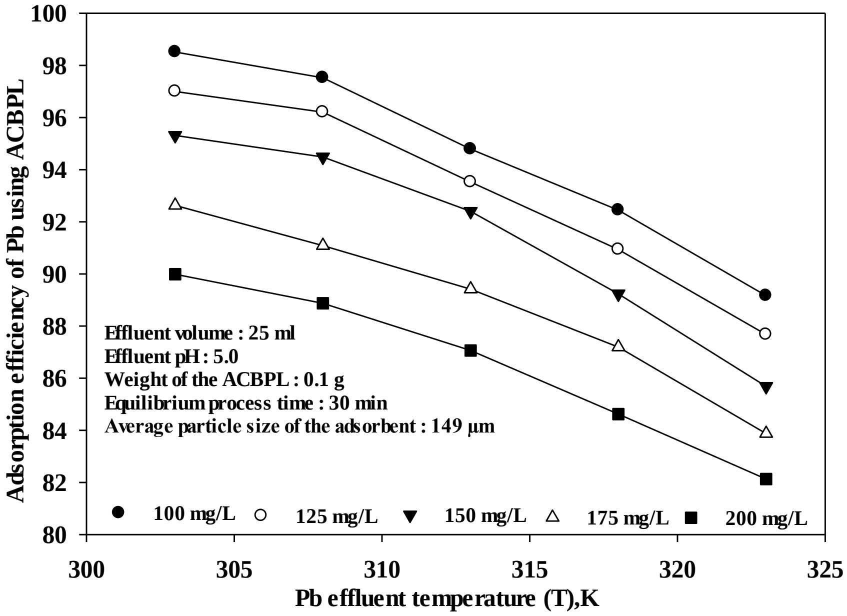

Fig 12: Effect of temperature on adsorption efficiency of Pbon theACBPLas an adsorbent.

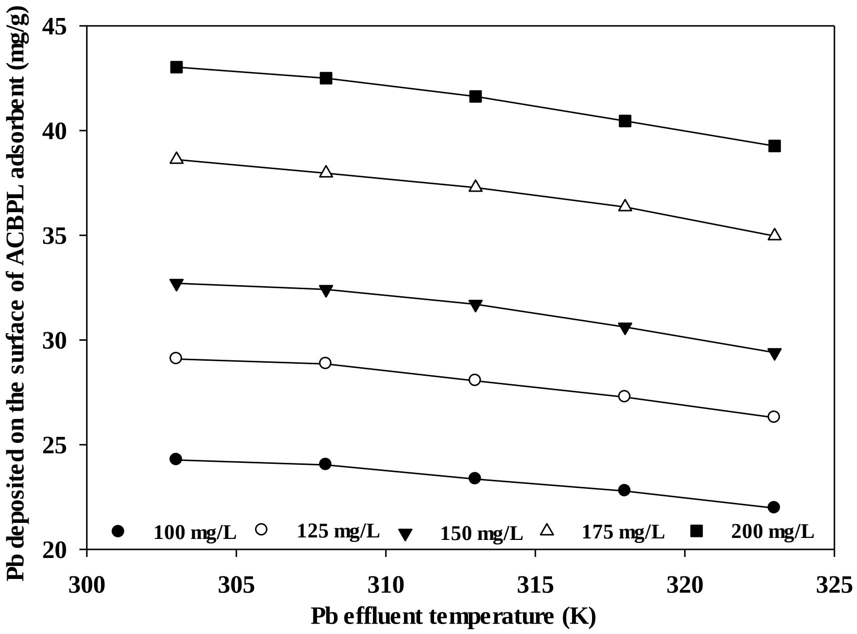

Fig 13: Effect of temperature on Pb deposited on the ACBPL adsorbent surface.

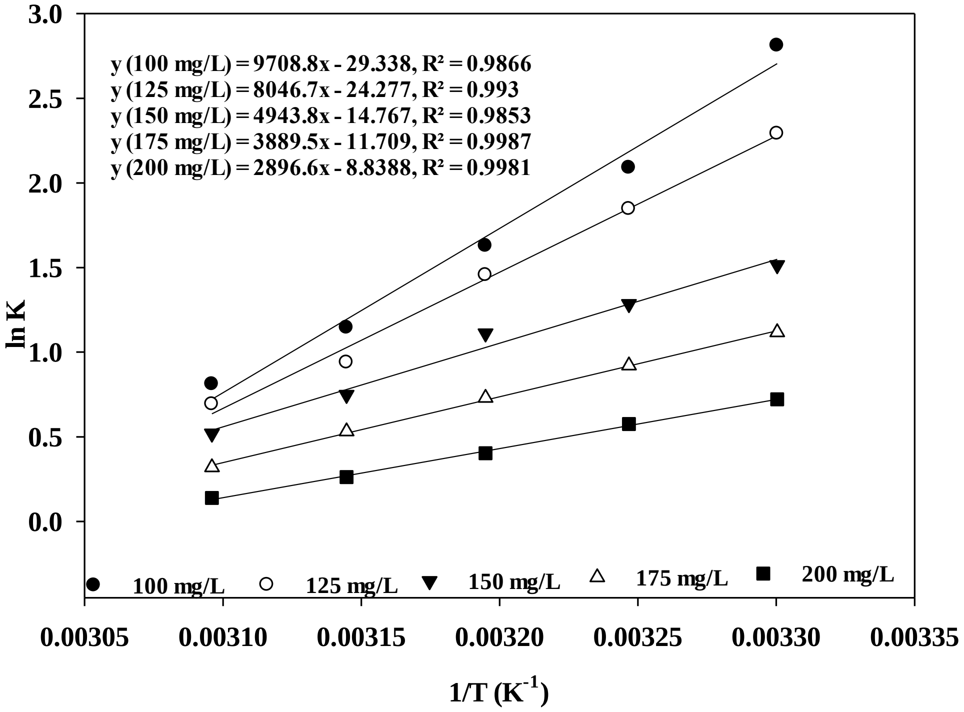

Fig 14: Estimation of thermodynamic energy parameters using Van't- Hoff relation.

Table 2: Thermodynamic energy parameters for the adsorption of Pbusing ACBPL as an adsorbent.

C_i (mg/L)	$-\Delta H^o$ (kJ/mol)	$-\Delta S^o$ (kJ/mol.K)	$-\Delta G^o$(kJ/mol)				
			30°C	35°C	40°C	45°C	50°C
100	80.78	0.243	7.08	5.87	4.68	3.44	2.22
125	66.9	0.201					
150	41.10	0.122					
175	32.33	0.097					
200	24.08	0.073					

Kinetic Modeling for Pb adsorption onto ACBPL adsorbent

In order to investigate the controlling mechanism of adsorption process such as mass transfer and chemical reaction, the pseudo-first-order, pseudo-second-order kinetic and the Elovich models were used to test the experimental data of lead adsorption by treated *ACBPL.* Due to the presence of a greater number of metal ions in industrial wastewater, the adsorption equilibrium was reached much faster due to faster occupancy of adsorption sites by metal ions. Most commonly used pseudo-first-order Lagergren model is generally expressed as

$$\ln(q_e - q_t) = -k_f t + \ln q_e$$

Where q_t(mg/g) is the weight of Pb deposited on adsorbent surface at time *t,* and k_f(min^{-1}) is the first-order adsorption process rate constant. The validity of pseudo – first order kinetic model for the adsorption of lead using ACBPL as adsorbent was evaluated separately using the plot of $ln\ (q_e - q_t)$ verses *t* at different initial concentration (100 – 200 mg/L) of lead at optimum solution pH 5 and temperature is 303 K.Fig:15 show the linear plot of pseudo-first-order kinetic model. Second-order kinetic model is expressed as

$$\frac{t}{q_t} = \frac{1}{q_e} t + \frac{1}{k_s q_e^2}$$

Where k_s (g mg^{-1} min^{-1}) is the second-order adsorption process rate constant. A plot of t/q_tagainst t should give a linear relationship for the applicability of the second-order kinetic model is shown in Fig:16. The validity of the kinetic models is checked and shown in table3.The high R^2 indicates that the experimental data are well correlated to the second-order kinetic equation. So, the rate-limiting step may be chemical adsorption and the adsorption behavior may involve valence forces through the sharing of electrons between metal cations and adsorbent.

The Elovich model gives the information about the type of adsorption mechanism (Physical or Chemical). It is expressed as

$$q = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t$$

Where α initial rate and β representing activation energy required for conception (g/mg).

The constants are obtained from the slope and intercept of a straight line plot of q verses lnt shown in Fig:17. The correlation coefficients summarized in table 3,indicates that the Elovich model is not suitable for higher concentration for removal of lead using ACBPL from a given experimental data.

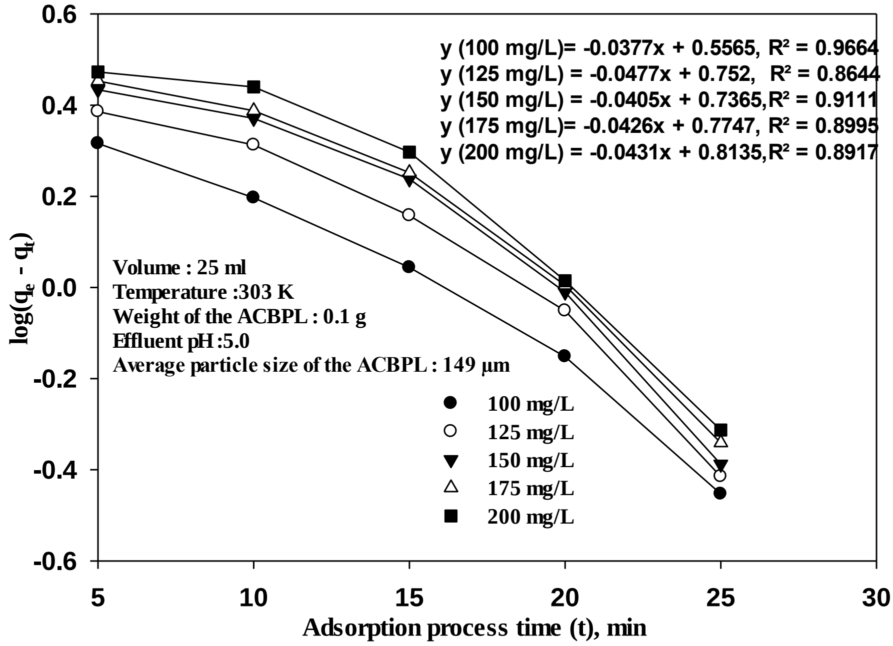

Fig 15: First order Kinetic model for adsorption of lead on to ACBPL as an adsorbent.

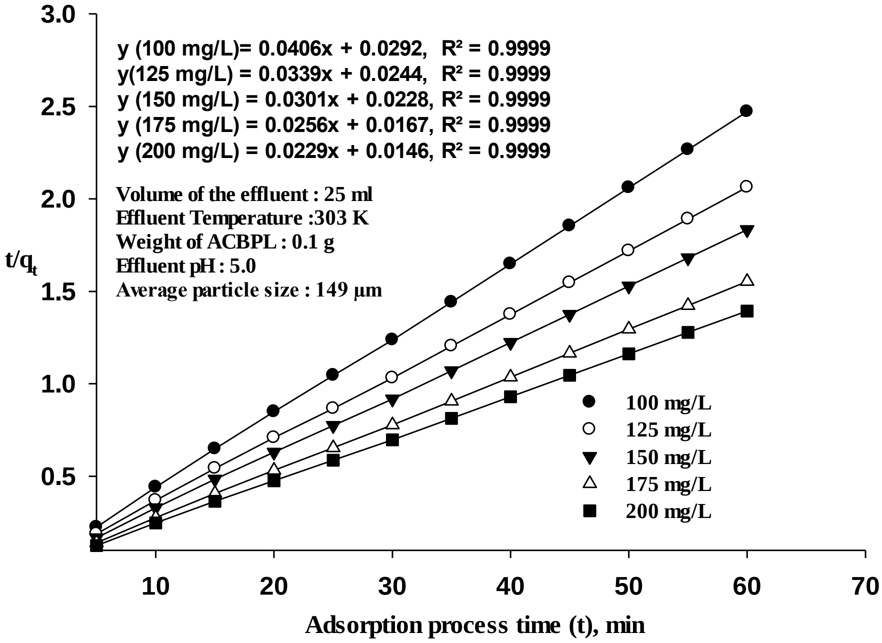

Fig 16: Second order Kinetic model for adsorption of lead on to ACBPLas an adsorbent.

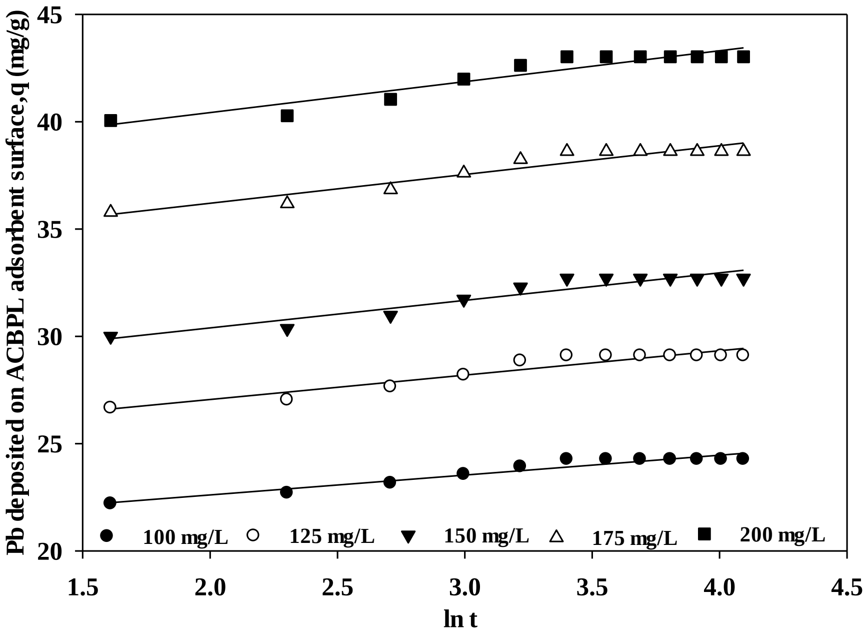

Fig 17: Elovich kinetic model for the adsorption of lead on to ACBPLas an adsorbent.

Table 3: Kinetic rate constants for lead adsorption onto ACBPL at*C*$_i$= 100 – 200 mg/L, *w* = 0.1g ,*d* :149 µm, *T*: 303 K, *pH*: 5.0 and *t* : 30 min.

C$_i$ (mg/L)	Pseudo-first-order			Pseudo-Second-order			Elovich Model		
	K$_f$(min^{-1})	q$_e$(mg/g)	R^2	k$_s$(g/mg.min)	q$_e$(mg/g)	R^2	β(g/mg)	α(mg/g.min)	R^2
100	0.037	1.74	0.966	0.056	24.63	0.999	1.079	5.01* 10^9	0.930

125	0.047	2.12	0.864	0.047	29.49	0.999	0.881	$3.49*10^{9}$	0.906
150	0.040	2.08	0.911	0.039	33.22	0.999	0.778	$3.23*10^{9}$	0.909
175	0.042	2.16	0.899	0.039	39.06	0.999	0.746	$9.82*10^{10}$	0.908
200	0.0431	2.25	0.891	0.035	43.66	0.999	0.693	$2.97*10^{11}$	0.895

Optimization of adsorption process parameters using Factorial experimental design

Based on the independent and dependent variables in the adsorption process, RSM consists of design and experiments, response surface modeling through regression and optimization. The application of statistical experimental design techniques adopted in the adsorption process to attaining a high degree of metal removal, closer confirmation of the output response to nominal and target requirements and reduced development time and overall costs[12]. Among the varieties of factorial designs available, Central Composite Design (CCD) is the more viable design. It is held by adding two experimental points along each coordinate axis at opposite sides of the origin and at a length equal to the semi -diagonal of the hyper cube of the factorial design. The new acute values (low and high) for each parameter are summed in this model[13]. For a full factorial

$$\alpha = \left[2^{\frac{m}{4}} \right]$$

In this study four parameters: pH of the solution, initial Pb concentration in the solution (C_o), the weight of the adsorbent (w) and temperature of the solution are considered and thus m= 4 and α = 2 from the above equation. Moreover, the total number of test points (N) in a CCD is ascertained from the accompanying mathematical statement:

$$N = 2^{m} + 2m + m_{o}$$

$m_o$is the number of central points. Thus, total number of experimental runs, N= 26 are considered and accordingly (m= 4;m_o = 2 and α= 2) from the above equation .The response (Y) is the adsorption efficiency of Pb. Information from CCD are subjected to a second-order multiple regression analysis to clarify the behavior of the system using the least squares regression methodology for obtaining the parameter reckoners of the numerical model[14].

$$Y = \alpha_{o} + \sum_{i=1}^{k} \alpha_{i} x_{i} + \sum_{i=1}^{k} \alpha_{ii} x^{2}{}_{i} + \sum \sum_{i<j}^{k} \alpha_{ij} x_{i} x_{j} + \in$$

Where Y is the response, α_o is the constant, α_i is the incline or straight impact of the data element x_i, α_{ii} is the quadratic effect of input factor x_i, α_{ij} is the linear by linear interaction effect between the input factor x_i and ϵ is the residual term. STATISTICA 6.0 is used for regression analysis of the data and to assess the coefficient of the regression equation. Analysis of variance (ANOVA) is utilized to test the significance of each term in the equation and the goodness of fit of the regression model. This RSM is applied to gauge the result by contour plots in order to examine the individual and cumulative effects of the variables and the mutual interactions between the variables on the dependent variable.

Development of regression model equation for Pb adsorption process

Central Composite Design (CCD) was used to develop a correlation between the adsorption efficiency and Process variables affecting the adsorption of Pb from aqueous solution onto ACBPL adsorbent. The complete experimental range and levels of independent variables are given in Table 4. CCD is applied to obtain a correlation between the adsorption of Pb from the aqueous solution and the process variables investigated. The quadratic model suggested by the software was selected. Experiments were planning to obtain a quadratic model consisting of 26 trials and 1 replicate at the center point. The output data given by CCD (Based on the range of variables chosen) are shown in Table 4.Regression analysis is performed to fit the response function of Pb adsorption. The coded values of variables in the equation represent adsorption efficiency (Y) as a function of pH (X_1), concentration (X_2), Weight (X_3) and temperature (X_4). The maximum adsorption of Pb was found to be 95.55% and at the optimal conditions suggested by the design. The information acquired was fitted to a second-order polynomial equation. Regression analyses, ANOVA and response surfaces were executed using the Design Expert Software (Version 8.0.7.1) subsequently. The experimental data with multiple regression analysis was obtained from the following regression equation for the adsorption of Pb:

$$\text{Adsorption efficiency } (Y) = -1729.67 + 39.37 X_1 - 0.6X_2 + 258.18 X_3 + 11.45 X_4 - 4.49X_1^2 - 1333.33X_3^2 - 0.02 X_4^2 + 0.03 X_1X_2 + 2.90 X_1X_3 + 0.4 X_2X_3 + 0.05 X_3X_4$$

Where X_1, X_2, X_3 *and* X_4 are the code values for the independent variables, X_1X_2, X_1X_3, X_1X_4, X_2X_3, X_2X_4, X_3X_4, X_1^2, X_2^2, X_3^2 and X_4^2 are the significant model terms for the adsorption of Pb. The coefficients of the regression models calculated are listed in Table 7. The efficiency of the model in predicting the adsorption efficiency was evaluated by the coefficient of determination (R^2), standard error, t-values, p-values and Fisher's 'F' test value. The R^2 value provides a measure of variability in the observed response that can be explained by the experimental process variables and their interactions. The probability value of greater than 0.0001, indicates the inaccuracy of any model are shown in Table 6. The model has probability values less than 0.0001 means that the experimental data obtained can be experimentally explained with 99% accuracy by the model generated by RSM [15] whereas a low *p*-value (<0.05) indicates that the model is considered to be statistically significant. The interrelationship of the free variables and response can be clarified by the regression model as shown in Table 7. The model is best suited by determination of correlation R^2, 99.9% (0.999) value which is close to 1[16]. The actual and the predicted percentage adsorption of Pb are shown in Fig: 18.

Effect of process variables on adsorption efficiency using RSM

In order to study the combined effect of the factors, experiments were performed for different combinations of the process parameters using statistically designed experiments (Table 7). Apart from the linear effect of the parameters on the adsorption efficiency of Pb, the RSM also gives insight into the squared and interaction effects of the parameters. These analyses were performed by means of Fisher's *F*test and Student *t*-test. For all the parameters (Table 7), The square model ($F = 420.223$ and $P = 0.00$) and Linear ($F = 6248.36$ and $P = 0.000$) model terms highly significant effect than interactive ($F = 28.804$ and $P = 0.447$) model terms of %Pb removal. The Student *t*-test was used to determine the significance of the regression coefficients of the parameters. In general, the larger the magnitude of 't' and smaller the value of '*P*'; the more significant is the corresponding Coefficient term[17]. From the Table.7, it is evident from the results that the squared effects of X_1^2, X_2^2, X_3^2 and X_4^2 variables for Pb were also highly significant, because of their P-values were less than 0.05; the P values of all process independent variables are less than 0.05 are significant and are able to influence the adsorption efficiency of Pb[18]. The magnitude of t-value gives the positive or negative influence on the dependent variable. 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 7) on Pb removal. All the squared terms, X_1, X_2, X_3 and X_4 shows a negative influence on the adsorption of Pb. 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 ($t = 5.9657$, $p = 0.000$) were found to be statistically significant and positive effect on % removal of Pb, whereas other interactions are insignificant and not influenced on the adsorption efficiency of Pb.

The contour plots are used to show the pictorial representation of the influence of independent variables and their interaction on the dependent variable. It represents the interactive effect of any two variables on the response variable, when the remaining variables kept constant. The shape of the surface plots indicates an interaction between the variables. The elliptical shape of the response surface curve indicates good interaction of two variables. Fig:19 (a-f) are plotted between X_1 and X_4, X_3 and X_4, X_2 and X_4, X_1 and X_3, X_1 and X_2 respectively. The response surface plot (Fig:19 (a) to 19(f)) had a clear peak, which indicated that the optimum conditions falls inside the design boundary. The maximum adsorption efficiency of Pb is indicated by the surface confined to the smallest curve of the plot with the other variable maintained at hold value[19].

The projection of the surface and contour plots (Fig: 19(a)) indicates that the adsorption efficiency decreases with increasing temperature and attaining maximum efficiency is 90 % at pH:5.0 and T: 306 K. Similarly, Fig. 19 (b) & 19 (c) indicates that the adsorption efficiency is highly influenced by the initial concentration (92 % at 80 mg/L) and moderately with weight of adsorbent (88 % at 0.14 g of ACBPL) with increasing temperature. From the Fig. *19(d) to19(e*) that the adsorption efficiency increases with the increase in pH from 3 to 5.2; the less removal observed at low pH may be due to the availability of H^+ ion activity is more comparable to Pb^{+2}in the solution. Besides, it was explained that at lower pH value, the surface of the adsorbent is surrounded by H^+ ions, thereby preventing the metal ions from approaching the binding sites of the adsorbent [20]. This means that at the higher H^+ concentration, the repulsion is taking place between the metal and adsorbent and decline adsorption efficiency. In contrast, as the pH increases, the adsorbent surface converted as more negatively charged surface and capture the Pb ions to increase the adsorption efficiency. However, when the pH was greater than 5.2, there was a decrease in the adsorption capacity. This may be due to the occurrence of Pb precipitation. At this stage there are three species present in solution, Pb^{2+} in very small quantities, $Pb(OH)^+$ and $Pb(OH)_2$ in large quantities[21].The adsorption efficiency of Pb increased when the initial concentration was increased from 80 to 100 mg/L (Fig: 19(d), 19(f)). Besides, higher initial concentrations lead to an increase in the affinity of the lead ions towards the active sites. However, a further increase in the initial concentration (>100mg/L) resulted in a decrease in adsorption efficiency of Pb. This indicates that the initial Pb concentration is an effective parameter to maximize the adsorption efficiency. The adsorption efficiency of Pb increased when the adsorbent weight was increased from 0.05 to 0.15g (Fig: 19(d), 19(f)). This was due to the limited availability of the number of adsorbing species for a relatively larger number of surface sites on the adsorbent at a higher weight. However, a further increase in adsorbent dosage (> 0.14g) resulted in a decrease in %removal of Pb. These results may be due to the overlapping of the adsorption sites as a result of overcrowding of adsorbent particles.

Prediction of the responses at the optimum set of conditions

The optimum adsorption conditions determined using RSM for the adsorbent ACBPL batch studies are *pH*:4.77, C_o : 105.7 mg/L, *w*: 0.123g and *T*: 305.31. The model approval has been characterized at optimum levels of the process variables, anticipated by the model to accomplish the maximum adsorption efficiency is95.55%. The experiment has been conducted with optimum process parameters to obtain adsorption efficiency is 94.04%.

Table 4: Experimental variables and levels investigated by central composite design.

Variable	Process parameter	Range of Process parameters				
		-2	**-1**	**0**	**1**	**2**
X_1	Effluent pH	3	3.5	4	4.5	5
X_2	Initial effluent concentration (mg/L)	100	125	150	175	200
X_3	Weight of ACBPL (g)	0.05	0.075	0.1	0.125	0.15
X_4	Temperature (K)	303	308	313	318	323

Table 5: Experimental design matrix and results for adsorption of lead onto ACBPL adsorbent.

Experiment runs	Independent variables				Observed value of adsorption efficiency of Pb	Predicted value of adsorption efficiency of Pb
	x_1	x_2	x_3	x_4		
1	-1	-1	-1	1	92.07	91.88
2	-1	1	1	1	88.65	88.63
3	-1	-1	1	1	85.24	85.30
4	0	2	0	0	75.52	75.76
5	-1	1	1	-1	79.7	79.51
6	0	0	0	2	89.84	89.77
7	2	0	0	0	91.09	91.10
8	0	0	0	-2	88.49	88.41
9	0	0	2	0	92.21	92.13
10	-1	1	-1	-1	81.27	81.31
11	0	0	0	0	88.77	88.89
12	1	-1	-1	-1	76.6	76.65
13	1	-1	1	1	88.32	88.32

14	1	1	-1	-1	75.3	75.16
15	0	-2	0	0	83.81	83.83
16	-1	-1	-1	-1	94.57	94.66
17	-2	0	0	0	81	80.97
18	-1	-1	1	-1	91.02	91.18
19	1	-1	-1	1	84.78	84.66
20	1	-1	1	-1	84.03	83.87
21	0	0	-2	0	80.02	80.06
22	1	1	1	-1	84.26	84.4
23	1	1	1	1	88.21	88.32
24	0	0	0	0	81.14	81.07
25	-1	1	-1	1	88.32	88.32
26	1	1	-1	1	87.25	87.20

Table 6: Analysis of variance (ANOVA) for response surface quadratic model for removal of Lead was used 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 7: Estimated regression coefficients and corresponding *t*- and *P*- values of the models.

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 ($P \geq 0.05$)

Table 8: Optimized process parameters for adsorption of Lead on to ACBPL adsorbent

Process parameters	Initial observed the limits of process parameters	Critical values of process parameters	Final observed the limits of process parameters
Effluent pH	3.0	**4.77**	5.0
Initial effluent concentration (mg/L)	100.00	**105.70**	200.00
Weight of ACBPL (g)	0.050	**0.123**	0.150
Temperature (K)	303.00	**305.31**	323.00

The predicted value of adsorption efficiency of Pb on ACBPL adsorbent used CCD is: **95.55%**

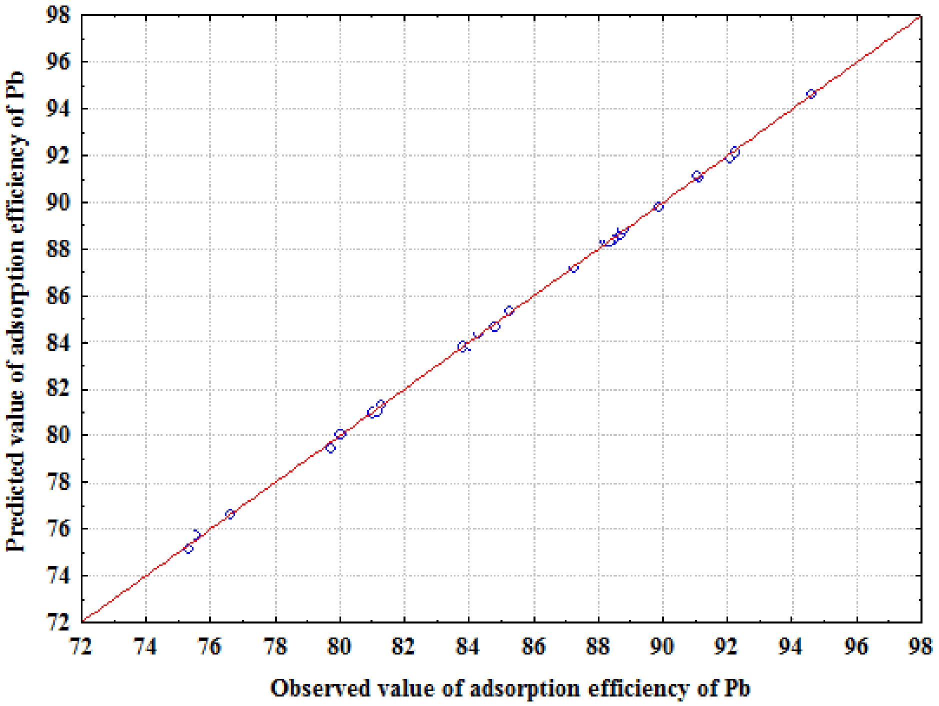

Fig 18: Correlation plot of experimental values Vs predicted values for the adsorption of Lead.

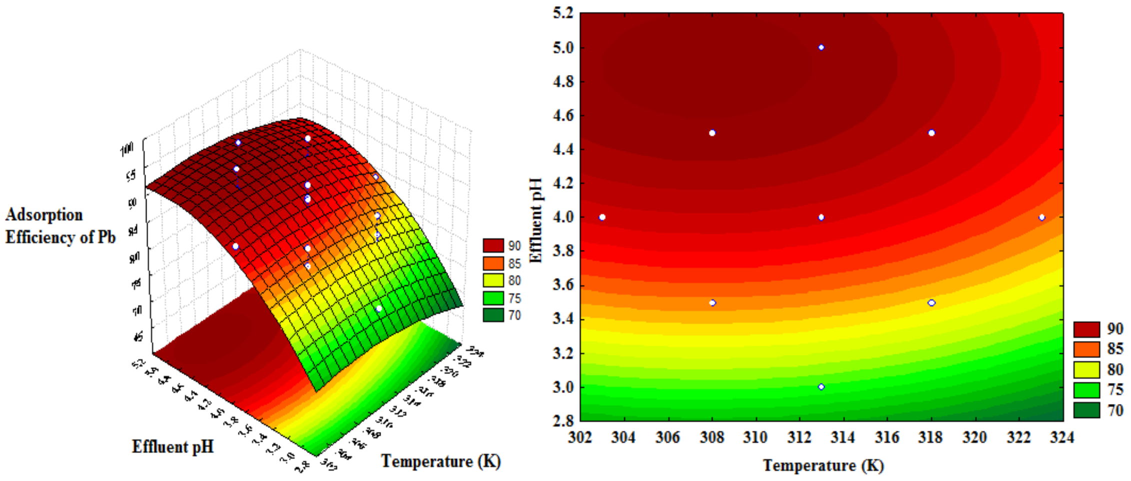

Fig 19 (*a*): Surface and contour plots of Temperature Vs Solution pH for the adsorption of Lead onto ACBPL adsorbent.

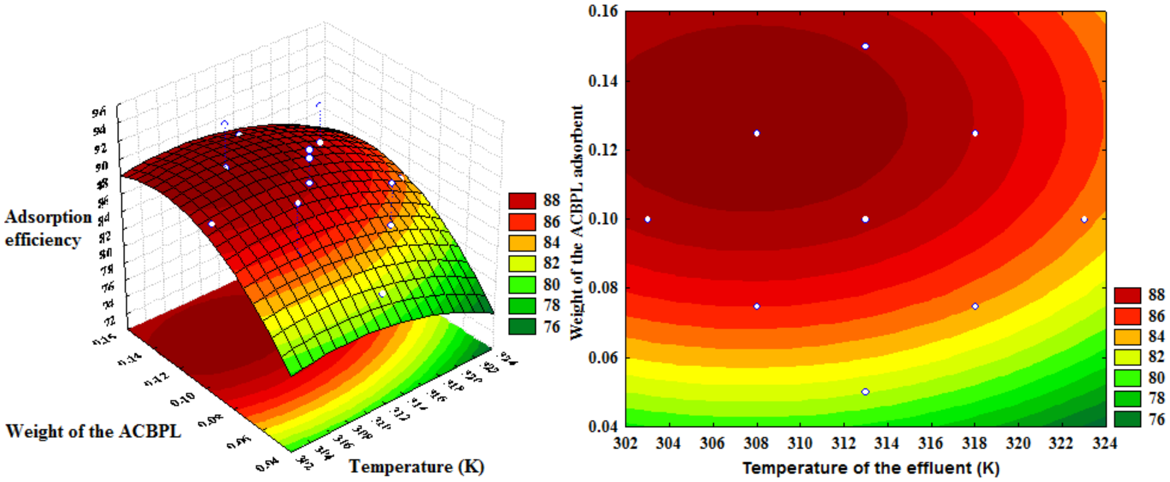

Fig 19(*b*): Surface and contour plots of Temperature Vs Weight of the adsorbent for the adsorption of Lead onto ACBPL adsorbent.

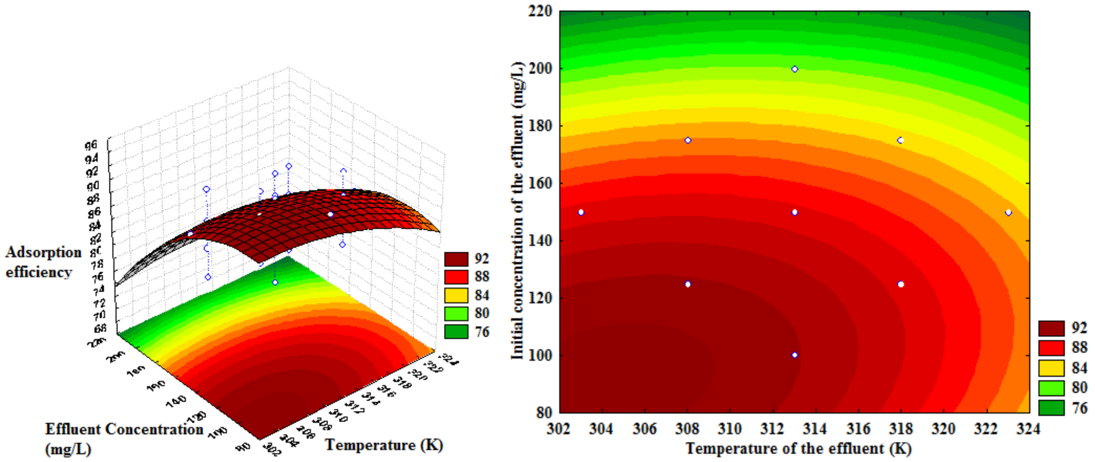

Fig 19(*c*): Surface and contour plots of Temperature Vs Initial concentration of the Solution for the adsorption of Lead onto ACBPL adsorbent.

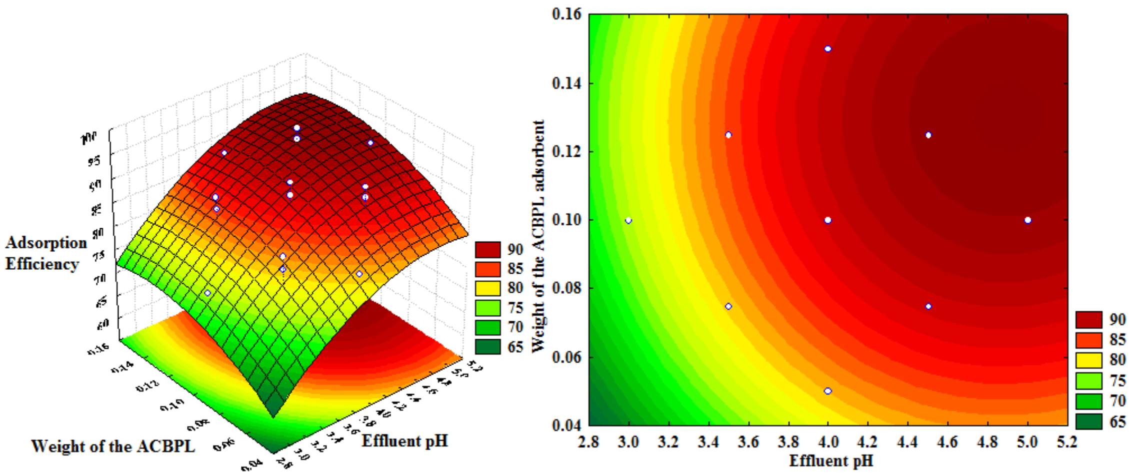

Fig 19(*d*): Surface and contour plots of Solution pH Vs Weight of the adsorbent for the adsorption of Lead onto ACBPL adsorbent.

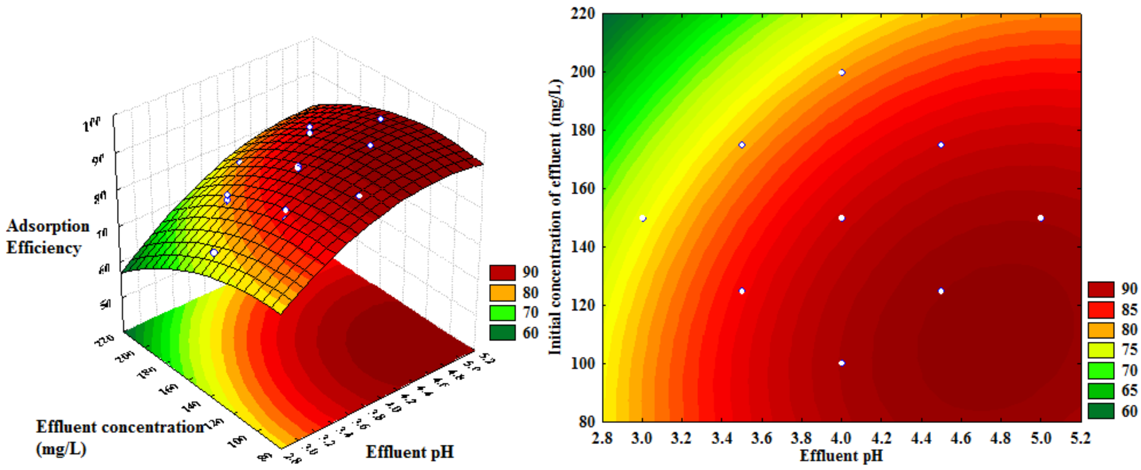

Fig 19 (*e*): Surface and contour plots of Weight of the adsorbent Vs Initial concentration of the solution for the adsorption of Lead onto ACBPL adsorbent.

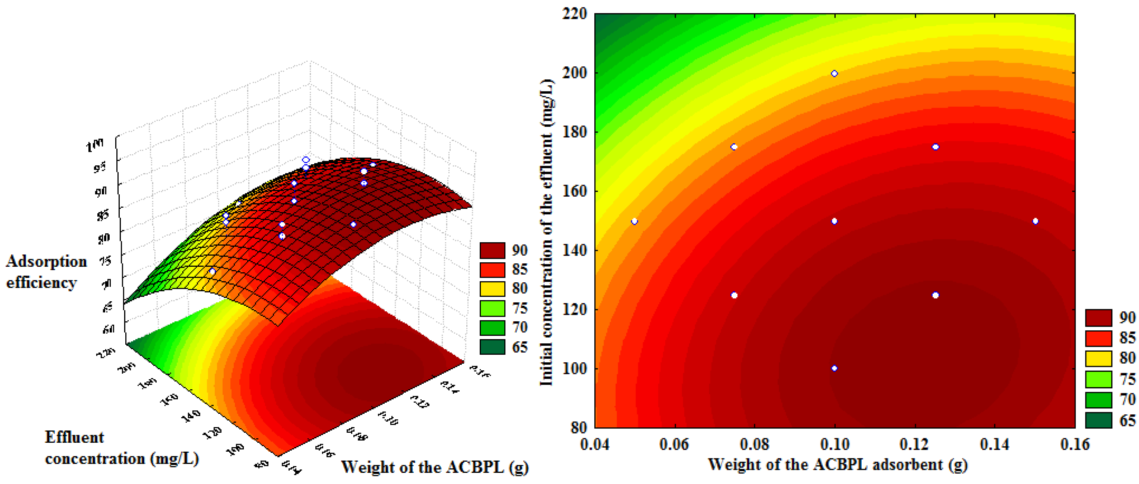

Fig 19(*f*): Surface and contour plots of Solution pH Vs Initial concentration of the solution for the adsorption of Lead onto ACBPL adsorbent.

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CONCLUSIONS

- Adsorption experiment was performed under the following conditions are *pH* : 5.0,C_i : 100 mg/L, *w* = 0.1 g, *T*: 303 K and *t* : 30 min, the maximum adsorption efficiency of lead onto ACBPL as adsorbent by 98.52 %.
- Thethermodynamic feasibility of adsorption process described that the negative sign values of ΔG^o, ΔH^o and ΔS^orevealed that the adsorption process is exothermic, increase the adsorption efficiency and Pb deposition on the ACBPL surface at lower temperatures.
- The adsorption activation energy values declined with increasing temperature from 1.29 KJ/mole – 0.223 KJ/mole. It was observed that the scope of an ordinary free energy credited to physical adsorption and the force of attraction between the adsorbate and adsorbent is very weak, therefore this type of adsorption can be easily reversed by heating or by decreasing the pressure.
- The results were analyzed statistically and the optimum conditions identified as pH: 4.77, C_i: 105.70 mg/L, *w*: 0.123 grams and *T*: 305.31. The predicted value of adsorption efficiency of Pb on ACBPL adsorbent used CCD is 95.55% .Under the optimum conditions experiment was conducted to lead the adsorption efficiency is 94.04 %.
- Surface and contour plots described that the adsorption efficiency is highly influenced by solution pH, Initial concentration of the solution and weight of the ACBPL adsorbent.

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