

EXPERIMENTAL INVESTIGATION ON ADSORPTION OF LEAD FROM AQUEOUS SOLUTION USING ACTIVATED CARBON FROM THE WASTE RUBBER TIRE: OPTIMIZATION OF PROCESS PARAMETERS USING CENTRAL COMPOSITE DESIGN

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ABSTRACT

Activated carbons prepared from waste rubber tires (RTAC) are used as practical adsorbents for the speedy evacuation and quick adsorption of lead ions from the wastewater effluents. Batch studies were done to evaluate the performance of RTAC for the adsorption of Pb²⁺ from aqueous solutions at various process parameters of pH (2-5), metal ion concentration (100 - 200 mg/L), the mass of the adsorbent (0.025 - 0.1 g), average particle size (85 - 200 Mesh) and solution temperature (308 - 323 K) at a maximum equilibrium agitation time of 60 minutes in an orbital shaker at 200 RPM. Taking into account exploratory results, Maximum evacuation of lead onto RTAC as adsorbent by 97.55 %. Optimized the adsorption efficiency using Central Composite Design (CCD) at pH = 4.98, Initial concentration 140.01 mg/L, the mass of the adsorbent is 0.12 grams and temperature of the metal solution is 314.46. Experimentation led above optimum conditions, the value of 3.64 % deviation is obtained with proposed value. Adsorption isothermal data were easily interpreted by Langmuir, Freundlich, Redlich-Peterson and Dubinin-Radushkevich (D-R), a Langmuir model with maximum adsorption capacity of 125 mg/g of lead ions on RTAC and kinetic data were appropriately equipped with the pseudo-second-order kinetic model. Consequences of thermodynamic investigations, properties of ΔH° , ΔG° and ΔS° are -63.976 KJ/mole, -5.787 KJ/mole and -0.196 KJ/mole.K, demonstrates the adsorption process is exothermic nature, feasible and spontaneous at lower temperature.

Keywords: Lead, Waste Rubber tire, Adsorption Isotherms, Kinetics, Central Composite Design (CCD), thermodynamic studies.

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INTRODUCTION

Heavy metal contamination has become one of the most serious problems that threaten biological community and human life because of the toxicity and strong tendency to concentrate in food chains¹. 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 problems². 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 respectively³.

The excellent properties of activated carbons (AC) as adsorbent materials have rendered the adsorption technology a versatile technique for wastewater remediation⁴. Hence, research of the recent past, mainly focused on utilizing low cost waste materials as alternative's to activated carbon from a Waste rubber tire is a mixture of different elastomers such as natural rubber, butadiene rubber, and styrene butadiene rubber plus other additives like carbon black, sulfur, and zinc oxide. Approximately 32% by weight of the waste tire is mainly constituted of carbon black in which the carbon content is as high as 70–75 wt. %⁵⁻⁷. One potential application for the waste rubber tire char is to produce activated carbon (RTAC) which is used as an adsorbent. RTAC is of high porosity and high surface area material manufactured by carbonization and activation of carbonaceous materials by either physical or chemical activation methods⁸⁻¹⁰. Appropriate activation conditions of temperature, time, etc. have been found to enhance both surface area and pore volume of activated carbons developed from carbon black¹¹ and this has resulted in improved adsorption behavior. Recent progress has shown the use of microwave assisted physical and chemical methods in the preparation of activated carbon from various low cost precursors as a substitute for conventional heating. The advantage associated with using microwave heating is that the treatment time and consumption of gases can be considerably reduced, which further results in the reduction in energy consumption as well. Also, the activated carbons prepared by microwave heating have been seen to demonstrate lesser oxygenated functionalities from their carbon surfaces¹². The objective of the present study was to prepare activate porous carbon from waste rubber tire 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 Optimization¹³. 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 in the 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 optimization¹⁴⁻¹⁶. It is used to examine the relationship between one or more response variables and a set of quantitative experimental variables or factors. This method is often employed after the vital controllable factors are identified and to find the factor settings that optimize the response. Designs of this type are usually chosen when a curvature in the response surface is suspected. The process optimization of the lead recovery from RTAC 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, mass of the adsorbent, temperature and pH of the solution to identify the optimum conditions using a central composite design (CCD).

EXPERIMENTAL

Preparation of activated carbon from waste rubber tire

The rubber tire pieces are cleaned thoroughly washed with deionized water. 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 20 min. The obtained carbonized product is now treated with 30% Hydrogen peroxide (H₂O₂) 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 H₂O₂ and dried at 110°C for 2hours in oven.

The dried material was activated to 900 °C for 2hr in a covered silica crucible by heating in a muffle furnace. The material was then treated with 1 M HCl solution to remove the ash content and was then washed with deionized water. 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 *Rubber tire activated carbon* (RTAC) was stored. The commercial activated carbon was cleaned, thoroughly washed with deionized water, and then dried in an oven at 100 °C for 2 hours.

Preparation of Adsorbate

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. The final concentration of metal ions in solution was analyzed by atomic AAS of Perkin Elmer model-3100, a flame type AAS.

Adsorption Experiment studies

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, contact time 2-90 min, metal ion concentrations 100-200 mgL⁻¹, the mass 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 5-90 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 contact time of 60 min and analyzed by AAS to assess the thermodynamic parameters and study the feasibility of the process with temperature.

Solute adsorption capacity

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

$$q = \frac{V(C_i - C_f)}{1000w} \quad (1)$$

Where q is the amount of metal adsorbed by RTAC adsorbent (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 (L) and w is the mass of the RTAC adsorbent.

Equilibrium isotherms for RTAC adsorbent

The adsorption isotherms indicate distribution of adsorbed molecules between the liquid phase and solid phase when the adsorption process reaches an equilibrium state. The analysis of the isotherm data by fitting them to different isotherm models is an important step to find the suitable model used for design purpose. The application of the isotherm equation is compared by judging the correlation coefficients R^2 . Isotherms are calculated under existing equilibrium conditions.

The Langmuir mathematical statement was used for the estimation of maximum adsorption capacity corresponding to the complete monolayer scope on the adsorbent surface, and after that no further adsorption happens. Thereby, the Langmuir represents the equilibrium distribution of metal ions between the solid and liquid phases. The linearized Langmuir equation was applied to analyze the data. The equation is given as:

$$q_{eq} = \frac{q_{max} K_L C_{eq}}{1 + K_L C_{eq}} \quad (2)$$

Where q_{max} is the adsorption binding capacity, that is, the maximum adsorption upon complete saturation of adsorbent surface, and K_L (L/g) is an affinity of adsorbent towards adsorbate respectively. C_e is the equilibrium concentration of adsorbate (mg/L), q_e is the amount of metal adsorbed per gram of the adsorbent at equilibrium (mg/g). The effect of isotherm predicts whether an adsorption process is favorable or unfavorable. The essential feature of the Langmuir isotherm can be expressed by means of R_L , a dimensionless constant referred to a separation factor or equilibrium parameter. R_L is calculated using the following equation:

$$R_L = \frac{1}{1 + K_L C_i} \quad (3)$$

The value of the separation factor R_L describes the nature of adsorption of the isotherm accordingly:

Separation factor (R_L)	Nature of adsorption
$R_L=0$	Irreversible
$0 < R_L < 1$	Favorable
$R_L = 1$	Linear
$R_L > 1$	Unfavorable

Freundlich isotherm model describes the ratio of the amount of metal adsorbed onto a given mass of adsorbent to the concentration of the metal in the solution. This model can be applied to multi-layer adsorption, with non-uniform distribution of adsorption heat and affinities over the heterogeneous surface and can be represented by the equation in linear form as

$$\ln q_{eq} = \ln K_f + \frac{1}{n_f} \ln c_{eq} \quad (4)$$

Where K_f and n are Freundlich constants related to adsorption capacity and adsorption intensity. At present, Freundlich isotherm is widely applied in heterogeneous systems, particularly for organic compounds or highly interactive species on activated carbon and molecular sieves.

Redlich–Peterson isotherm is the three parameter model and highlighting both Langmuir and Freundlich isotherms. It system can be represented as

$$q_{eq} = \frac{AC_{eq}}{1 + BC_{eq}^g} \quad (5)$$

where A (L/g) and B (L/mg) are the Redlich-Peterson isotherm constants and g is the Redlich Peterson isotherm exponent, which is in between 0 and 1. The linearized form of the equation is given by:

$$\ln \left(\frac{AC_{eq}}{q_{eq}} - 1 \right) = g \ln(C_{eq}) + \ln(B) \quad (6)$$

Dubinin–Radushkevich isotherm¹⁷, is an empirical model, applied to examine the adsorption mechanism¹⁸ with a Gaussian energy distribution onto a heterogeneous surface.¹⁹⁻²¹ The model has frequently effectively fitted high solute affinity and the intermediate range of concentrations. The methodology was usually applied to differentiate the physical and chemical adsorption of metal ions, with its mean free energy. The D–R equation has been computed by

$$q_e = q_o e^{-K_d \varepsilon^2} \quad (7)$$

The parameter ε is computed by an empirical equation has been represented by-

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (8)$$

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-

$$E = \frac{1}{\sqrt{-2K_d}} \quad (9)$$

Experimental design using response surface methodology (RSM)

RSM is an efficient statistical method to assess the optimum operational conditions of the process or to resolve the range of process parameters that meets the process specifications with a minimum number of experiments as well as to inspect the relationship between one or more response variables and a set of quantitative experimental variables or factors. To provide efficient conditions for the 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.²² 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.²³ For a full factorial -

$$\alpha = \left[2^{\frac{n}{4}} \right] \quad (10)$$

In this study four parameters: pH of the solution, initial lead concentration in the solution (C_o), mass of adsorbent (w) and temperature of the solution are considered and thus $n = 4$ and $\alpha = 2$ from equation-10. Moreover, the total number of test points (N) in a CCD is ascertained from the accompanying mathematical statement:

$$N = 2^n + 2n + n_o \quad (11)$$

n_o is the number of central points. Thus, total number of experimental runs, $N = 26$ are considered and accordingly ($n = 4$; $n_o = 2$ and $\alpha = 2$ from equation-11).

Along these lines, CCD with four factors is applied using STATISTICA 6.0 with the limits of initial pH = 2 – 5.5, $w = 0.025 - 0.15$ g, $C_o = 100 - 200$ mg/L as appeared in Table-3. Compatibility of the process is assessed by analyzing the response of adsorbent for lead ions. The response (Y) is % adsorption of lead. 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 model²⁴.

$$Y = \beta_o + \sum_{i=1}^k \beta_i x_i + \sum_{i=1}^k \beta_{ii} x_i^2 + \sum_{i < j}^k \beta_{ij} x_i x_j + \epsilon$$

$$Y = \beta_o + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_4 x_4 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{33} x_3^2 + \beta_{44} x_4^2 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{14} x_1 x_4 + \beta_{23} x_2 x_3 + \beta_{24} x_2 x_4 + \beta_{34} x_3 x_4 + \epsilon \quad (12)$$

Where y is the response, β_o is the constant, β_i is the incline or straight impact of the data element x_i , β_{ii} is the quadratic effect of input factor x_i , β_{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.

RESULTS AND DISCUSSION

Determination of Equilibrium Agitation time for RTAC adsorbent

The agitation time is the most essential parameter for RTAC adsorbent. The adsorption experiments were conducted for different lead concentrations from 100 mg/L - 200 mg/l with the function of agitation time and adsorption capacity of RTAC are demonstrated in Figure-1. The adsorption effectiveness of lead ions

increases gradually with increasing contact times and reaches equilibrium at around 60 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 RTAC by the thermal-chemical treatment process during the preparation of RTAC from waste rubber tires. The outcomes in the Fig.1.depicts that the percentage adsorption, increased from 86.59 to 97.55% at a contact time of 60 min with 100 mg/L metal concentration. At this optimum agitation time, the clump of the batch experiments were led to make sure that equilibrium is reached. The Figure-2. shows that the maximum metal uptake on the adsorbent surface at 60 min agitation time is 24.034 mg/g.

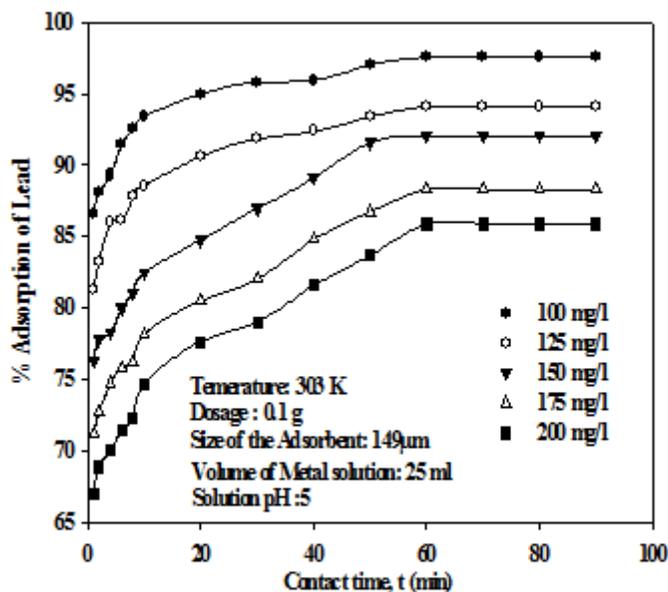


Fig.-1: Effect of contact time on % Adsorption of Lead using RTAC as an adsorbent

Effect of pH on metal ion binding

The variation of pH of metal solution is highly effected on the adsorption process for removal of metal ions from aqueous solutions using RTAC as an adsorbent. 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 time of agitation 60 min is shown in Figure-4. The effect of pH on adsorption of lead at constant temperature (303 K) and time of agitation 60 min is shown in Figure- 4. It was observed that adsorption capacity 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 RTAC 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, adsorbent surface is more negatively charged and the functional groups of the RTAC were more competent to bind the metal ions at the surface. The maximum removal of efficiency 97.55% is obtained at pH 5.0.

Effect of solute concentration on percentage adsorption and metal uptake

The Figure-5 demonstrates the adsorption behavior by using RTAC adsorbent at the different solute concentration in stock solution from 100 mg/l -200mg/l, optimum pH 5.0, agitation time 60 min, the weight of RTAC adsorbent is 0.1 grams and the temperature is 303K. The outcomes got from the data, investigated that the adsorption efficiency has declined from 97.55 % - 85.89 % and the amount of lead deposited on the surface of the RTAC adsorbent is increased from 24.034mg/g-26.987mg/g with increases solute concentration. At lower concentrations, all lead ions present in solution could interact with the binding sites and accordingly the rate adsorption was higher than those at higher initial lead ion concentrations. At higher concentrations, the lower adsorption yield is due to the saturation of adsorption sites.

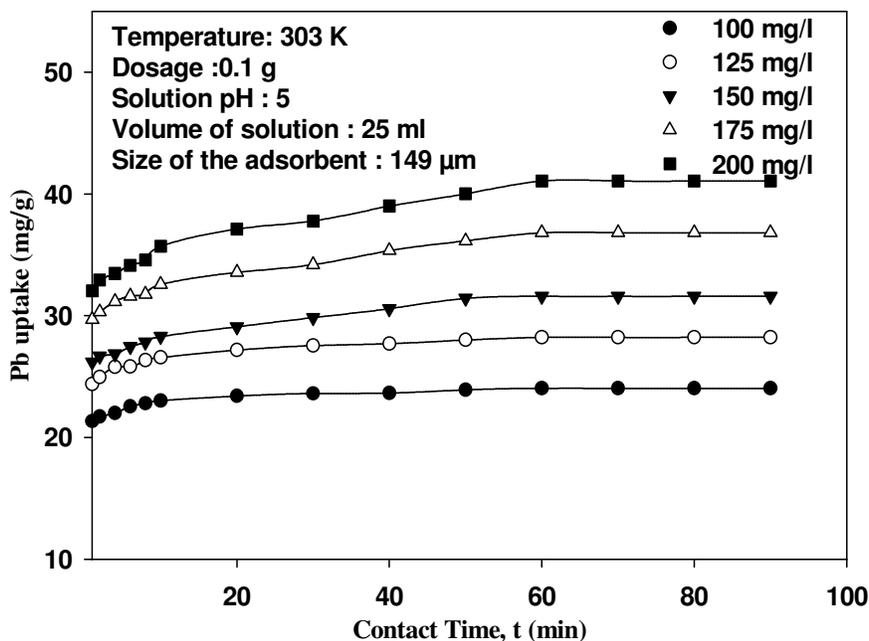


Fig.-2: The effect of contact time on Lead uptake using RTAC as an adsorbent



Fig.-3: Activated carbon from waste rubber tire

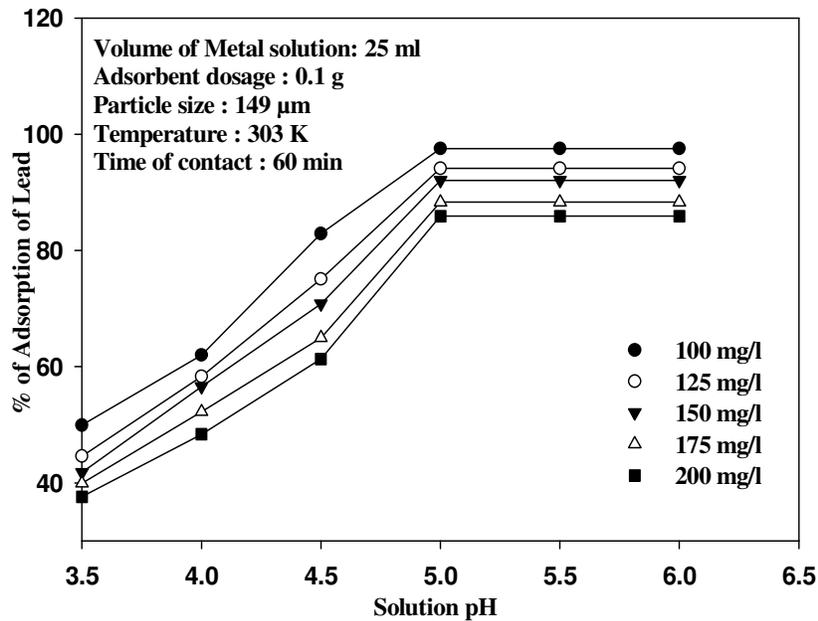


Fig.-4: Effect of solution pH on percentage adsorption of Lead using RTAC as an adsorbent

Effect of adsorbent concentration on adsorption efficiency

The experiments were carried out by varying adsorbent doses in the range 0.025-0.15 g at 25 °C and the agitation time is 60 min. The effect of mass of the RTAC adsorbent on the adsorption of lead ions shown in Figure-6. The data revealed that the adsorption efficiency (74.71% – 97.55 %) of lead ions on RTAC was increased with subsequent increasing the adsorbent dose up to 0.1 grams. After that, the adsorption efficiency is almost becoming constant at higher dosage from 0.1 g to 0.15g. This behavior could be explained by the formation of aggregates of the RTAC at higher doses, which decreases the effective surface area for adsorption.

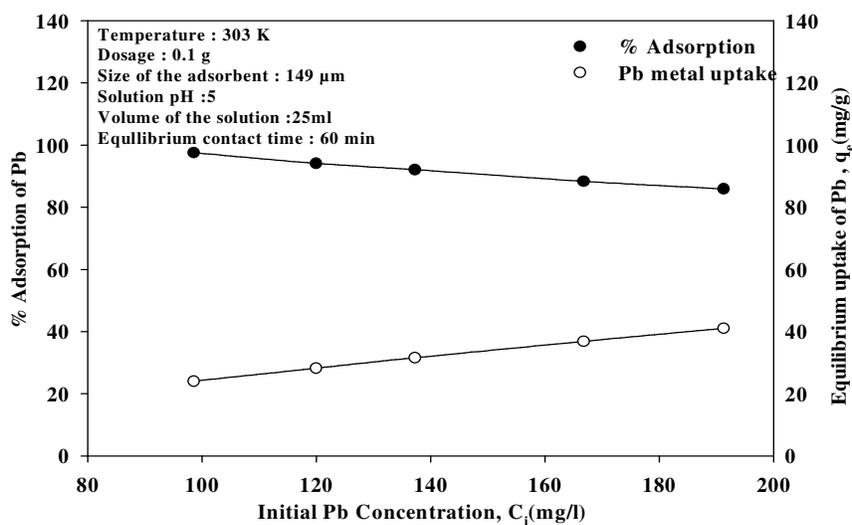


Fig.-5: Effect of Initial Concentration of Pb on percentage adsorption and Pb uptake using RTAC as an adsorbent

Therefore; the doses 0.1 g for lead removal was selected as the optimum doses of the adsorbent for the rest of the study. The maximum metal uptake on the adsorbent surface is 24.03 mg/g of 25 ml of a given metal solution.

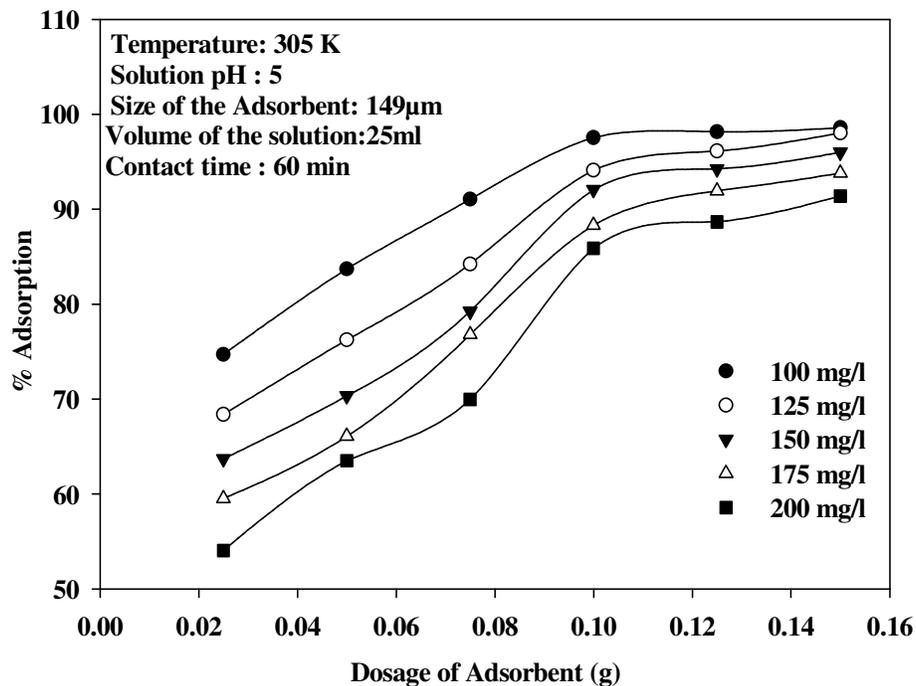


Fig.-6: The effect of adsorbent dosage on % Adsorption of Lead using RTAC as Adsorbent.

Modeling of Adsorption Isotherms

Freundlich Isotherm

From the Freundlich isotherm model, gives the straight line relationship with correlation coefficient is approached to unity (0.998) indicates that at lower concentrations, this model fitted for the removal of lead using RTAC adsorbent. The constant K_f is an estimated marker of adsorption capacity, while $1/n$ is a function of the strength of adsorption in the adsorption process. Figure-7 shows that the $1/n$ is diminished from 0.953 to 0.393, while K_f increased from 1.181(mg/g)/(L/g)ⁿ to 7.81 (mg/g)/(L/g)ⁿ with increased temperature (303K - 323K) and solute concentration (100 mg/L – 175 mg/L). These outcomes revealed that the adsorption lead from solution using RTAC was favorable and this might be because of the chemical interactions between adsorbent and adsorbate. As the temperature increases, the constants K_f and n change to reflect the empirical observation that the quantity adsorbed rises more slowly and higher pressures are required to saturate the surface.

Langmuir Isotherm

In Figure-8 $1/q_e$ was plotted against $1/C_{eq}$ yielding a straight line with $R^2(0.999)$ indicating that adsorption data fitted well with the Langmuir model. The value of Q_{max} (125 mg/g for lead) was calculated from the slope of the linear plot, whereas the value of K_L (0.008 for lead) was derived from the intercept. The value of the separation factor R_L is 0.56 was obtained by taking a solute concentration is 100 mg/L. The values of R_L at different concentrations are shown in Figure-9 and Table-1. The R_L values indicated that adsorption is higher at lower concentrations than higher concentrations. However, the RTAC would be an effective adsorbent for removing lead from solution.

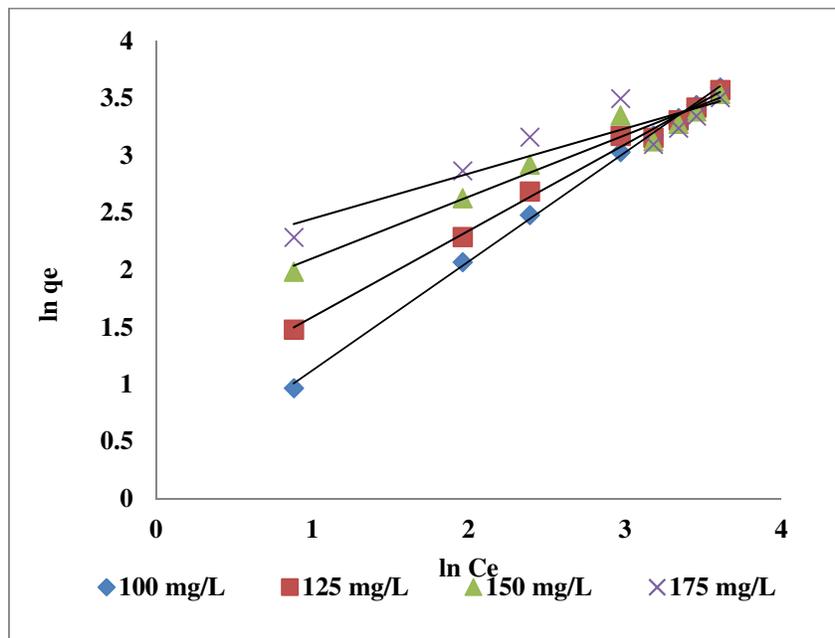


Fig.-7: Freundlich isotherms at four different concentrations for removal of Lead.

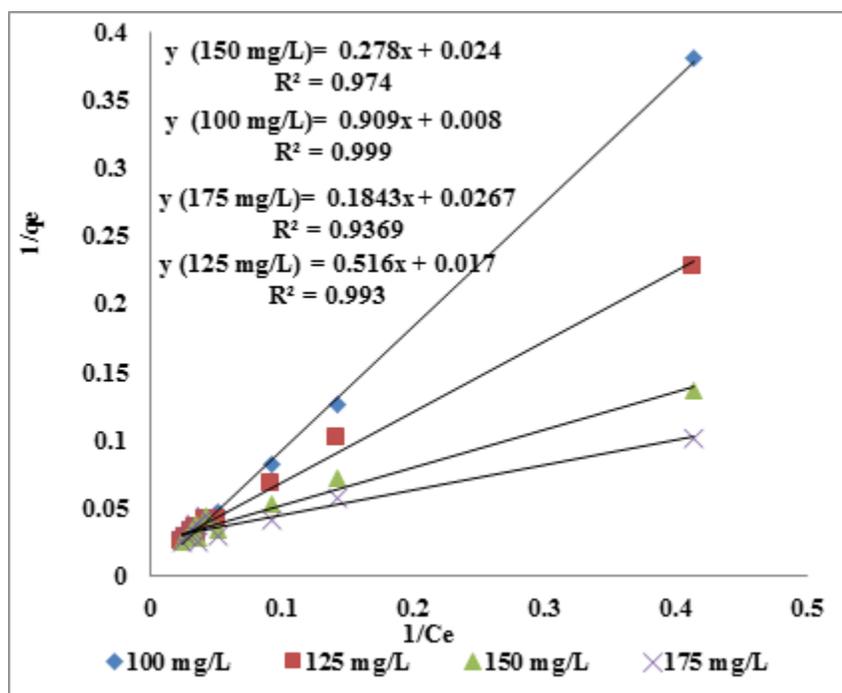


Fig.-8: Langmuir isotherms at four different concentrations for the removal of Lead.

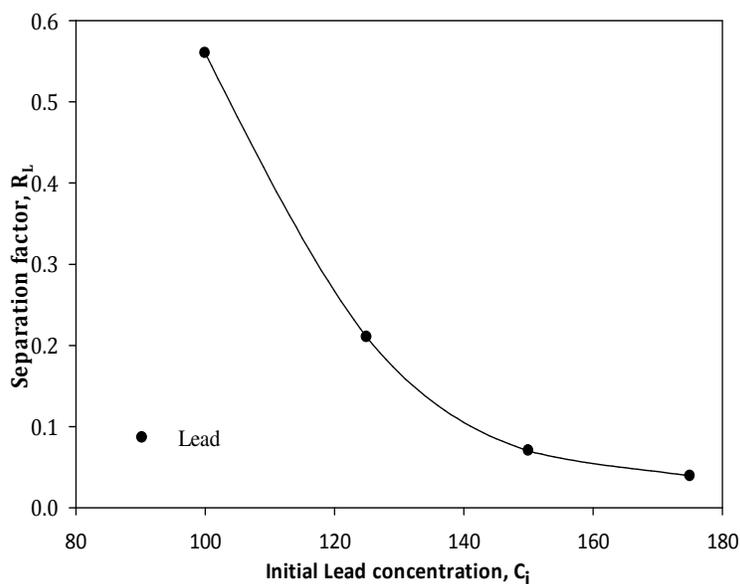


Fig.-9: The values of separation factor

Redlich-Peterson Isotherm

$$\ln\left(\frac{AC_{eq}}{q_{eq}} - 1\right)$$

Fig.10. Shows the plot between $\ln(C_{eq})$ versus $\ln\left(\frac{AC_{eq}}{q_{eq}} - 1\right)$. The calculated Redlich-Peterson constants and their corresponding linear regression coefficient of determination are shown in Table-2.

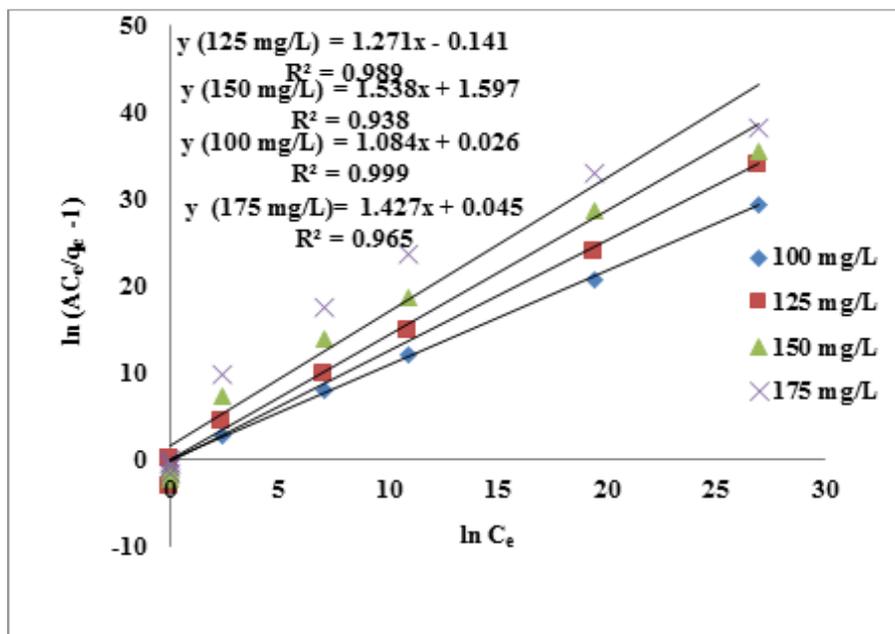


Fig.-10: Redlich-Peterson isotherms at four different concentrations.

D–R Isotherm

The mean free energy change of adsorption (E) can be ascertained utilizing equation- (9). The magnitude of E can be utilized for assessing the kind of adsorption. The adsorption behavior can be depicted as the physical adsorption when the mean adsorption energy (E) is somewhere around 1.0 and 8.0 kJ/mol. However, the chemical adsorption is more than 8.0 kJ/mol of the mean adsorption energy²⁵. The mean adsorption energy to lead was exhibited in Table-2. E worth was figured as 2.236 kJ/mol for lead and observed to be in the scope of an ordinary free energy credited to physical adsorption. One of the remarkable feature of the D–R isotherm model lies on the fact that it is temperature-dependent, which, when adsorption data at diverse temperatures are plotted as a function of the logarithm of the amount adsorbed ($\ln q_e$) vs ϵ^2 the square of potential energy (Fig.-11), all suitable data will lie on the same curve, named as the characteristic curve²⁶⁻²⁷. The equilibrium data were fitted to all the four equilibrium models. The calculated isotherm constants are given in Table-1. The best fit equilibrium model was determined based on the linear regression correlation coefficient R^2 . From the table for 100 mg/l of metal solution, it was observed that the adsorption data were very well represented by Langmuir isotherm for the lead with an average higher correlation coefficient of 0.999, followed by Redlich-Peterson, Freundlich, Dubinin – Radushkevich isotherms and with a correlation coefficient of 0.998, 0.998 and 0.824 respectively.

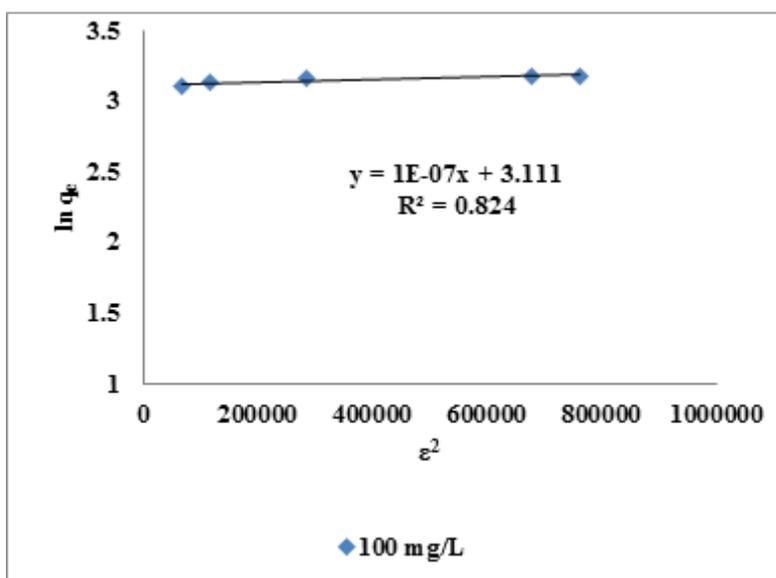


Fig.-11: Dubinin - Radushkevich isotherms for adsorption of lead onto RTAC adsorbent.

Table-1: The values of various isotherms constants for lead adsorption on to RTAC adsorbent using different initial concentrations; $C_i=100 - 200$ mg/L, 0.1g of adsorbent, particle size 149 μm , 303-323 K, pH 5.0 and 60 min.

Isotherm model	Parameter	Lead concentration (mg/L)			
		100	125	150	175
Freundlich	K_f (mg/g)/(L/g) ⁿ	1.181	2.30	4.77	7.81
	n_f (L/g)	1.049	1.32	1.85	2.54
	R^2	0.998	0.993	0.958	0.834
Langmuir	q_{max} (mg/g)	125	58.82	41.6	37.45
	K_L (L/g)	0.008	0.03	0.086	0.14
	R^2	0.999	0.993	0.974	0.936
Redlich-Peterson	A(L/g)	4.39	2.42	1.9	1.41
	B(L/mg)	1.026	0.868	4.93	1.04

	g	1.084	1.271	1.538	1.42
	R ²	0.999	0.989	0.938	0.965
R - D	q ₀ (mg/g)	22.42			
	K _d (Mol ² kJ ⁻²)	1*10 ⁻⁷			
	E (kJ/Mole)	2.236			
	R ²	0.824			

Thermodynamic feasibility study of Lead adsorption

Based on the values of thermodynamic parameters like Enthalpy change (ΔH°), Entropy change (ΔS°), and Gibb's free energy (ΔG°) to verify the thermodynamic feasibility of an adsorption process. The experiments conducted for different concentrations (100 mg/L – 200 mg/L) of metal solutions with the solution temperature is varied in the range of 303 – 323 K and adsorption data are obtained, keeping all other parameters constant. It is found that % adsorption decreases with increasing temperature. The Van't Hoff equation is described the thermodynamic parameters is given by using the following nonlinear equation,

$$\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2} \quad (13)$$

$$\ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (14)$$

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

$$\Delta G^\circ = -RT \ln K \quad (15)$$

Where, R is gas constant (8.314 J/mol K) and K is the adsorption equilibrium constant equivalent to q_e/C_e . Van't Hoff plot with $\ln K$ as a function of $1/T$ yields a straight line and ΔH° and ΔS° can be evaluated from the slope and intercept, respectively. The Van't Hoff plot is drawn in Fig.14 for the present data. The values of ΔH° , ΔS° and ΔG° for various initial concentrations of lead at different temperatures are appear in table.3. The negative values of ΔH° (-63.976 kJ/mole), ΔS° (- 0.196 kJ/mole.K) and ΔG° (- 5.787 kJ/mole) indicates that the process of lead adsorption is spontaneous at lower temperatures and the reverse reaction is taking place at higher temperatures. The RTAC adsorbent used in this study has higher affinity at lower temperatures. The negative value of ΔH° reveals that adsorption of lead onto RTAC is exothermic. The negative value of ΔS° suggests the disorder of the system decreases at the solid/solution interface.

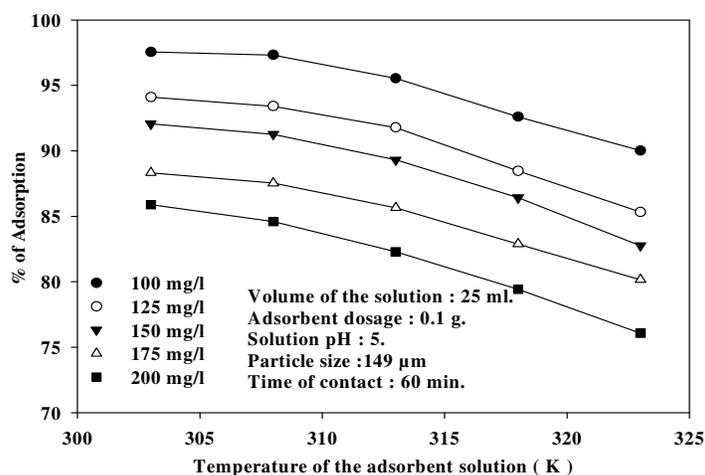


Fig.-12: Effect of temperature on percentage adsorption of Lead onto RTAC adsorbent.

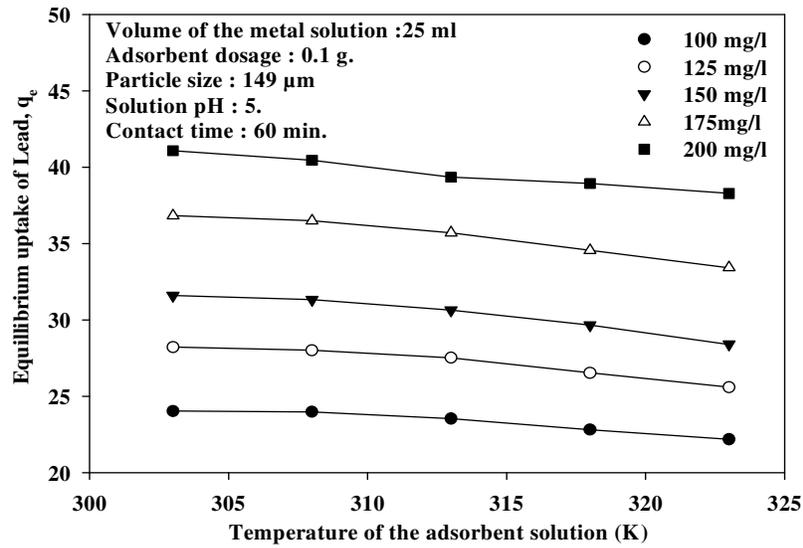


Fig.-13: Effect of temperature on Lead uptake onto RTAC adsorbent.

Table-2: Thermodynamic energy parameters for the adsorption of Lead for different initial concentrations with varying temperatures.

Initial concentration (mg/L)	$-\Delta H^\circ$ (kJ/mol)	$-\Delta S^\circ$ (kJ/mol.K)	$-\Delta G^\circ$ (kJ/mol)				
			30°C	35°C	40°C	45 °C	50 °C
100	63.976	0.196	5.78	5.65	4.36	3.01	2.18
125	41.869	0.125					
150	35.883	0.108					
175	25.806	0.079					
200	16.927	0.052					

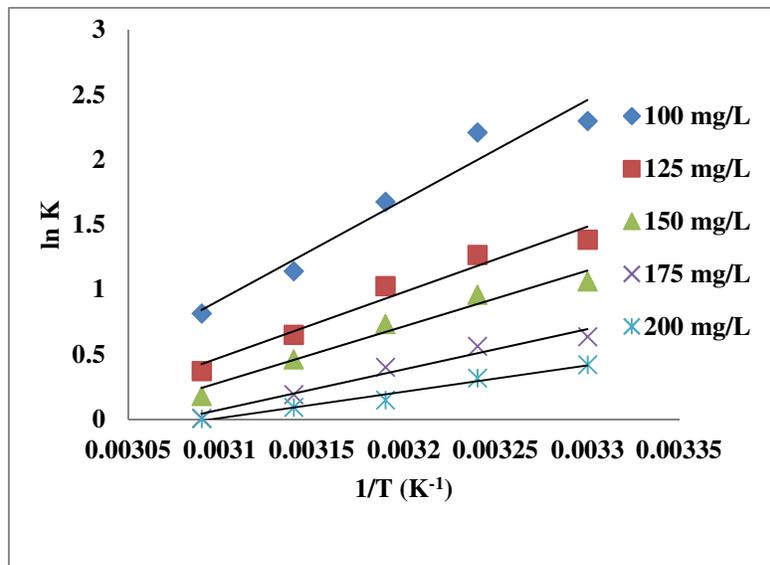


Fig.-14: Plot for estimation of thermodynamic energy properties using Van't- Hoff relation.

Adsorption Kinetics Modeling

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 RTAC. A number of models with varying degrees of complexity have been developed to describe the kinetics of metal adsorption in batch systems. 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-

$$\ln(q_e - q_t) = -k_f t + \ln q_e \tag{16}$$

Where q_t (mg/g) is the mass of metal adsorbed at time t , and k_f (min^{-1}) is the first-order reaction rate equilibrium constant. The equation can be written as

$$q_t = q_e (1 - e^{-k_f t})$$

The validity of pseudo – first order kinetic model for the adsorption of lead using RTAC as adsorbent was evaluated separately using the plot of $\ln (q_e - q_t)$ versus t at different initial concentration (100 – 200 mg/L) of lead at optimum solution pH 5 and temperature is 303 K. Figure-15 shows the linear plot of pseudo-first-order kinetic model. Second-order kinetic model is expressed as-

$$\frac{t}{q_t} = \frac{1}{q_e} t + \frac{1}{k_s q_e^2} \tag{17}$$

where k_s ($\text{g mg}^{-1} \text{min}^{-1}$) is the second-order reaction rate equilibrium constant. A plot of t/q_t against t should give a linear relationship for the applicability of the second-order kinetic model is shown in Figure-16. The validity of the kinetic models is checked and shown in Table-3. 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-

$$q = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \tag{18}$$

Where α initial rate and β is represents activation energy required for chemisorption (g/mg).

The constants are obtained from the slope and intercept of a straight line plot of q versus $\ln t$ shown in Figure-17. The correlation coefficients summarized in Table-3, indicates that the Elovich model is not well suitable for removal of lead using RTAC from a given experimental data.

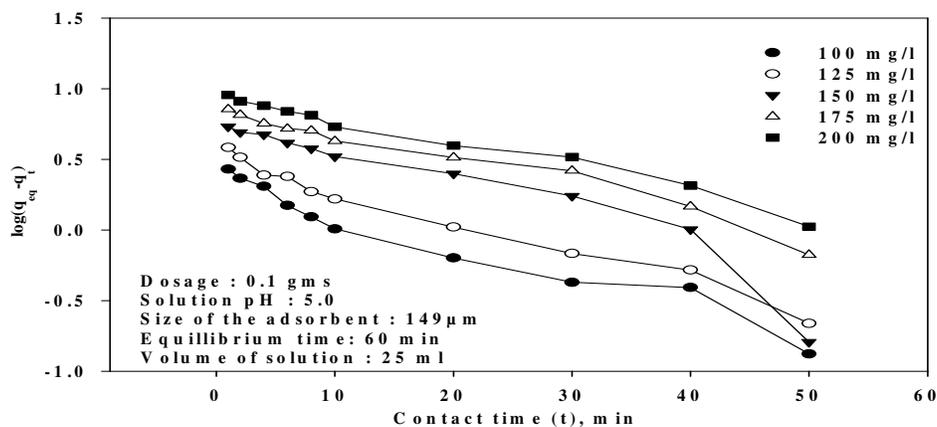


Fig.-15: First order Kinetic model for adsorption of lead on to RTAC as adsorbent.

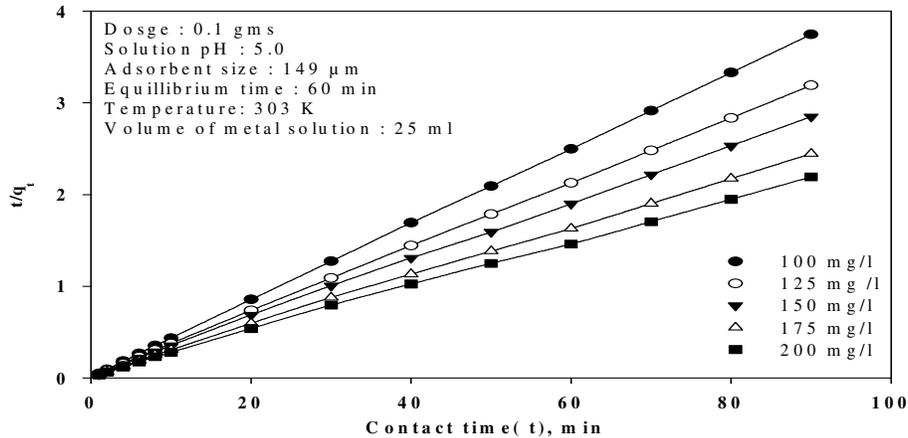


Fig.-16: Second order Kinetic model for adsorption of lead on to RTAC as adsorbent.

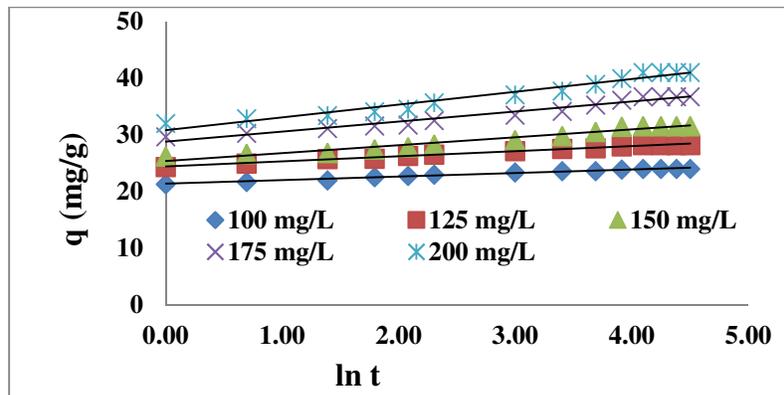


Fig.-17: Elovich kinetic model for the adsorption of lead on to RTAC adsorbent.

Table-3: Kinetic rate constants and q_e values for lead adsorption onto RTAC using different initial concentrations; $C_i = 100 - 200$ mg/L, 0.1g of adsorbent, particle size 149 μm , 303 K, pH 5.0 and 60 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	0.023	1.42	0.949	0.098	24.3	0.999	1.572	2.41×10^{14}	0.982
125	0.022	1.66	0.974	0.064	28.57	0.999	1.119	6.72×10^{11}	0.992
150	0.025	2.22	0.895	0.029	32.25	0.999	0.715	1.071×10^8	0.956
175	0.018	2.34	0.966	0.021	37.17	0.999	0.561	1.87×10^7	0.962
200	0.017	2.58	0.974	0.016	41.67	0.999	0.44	1.7×10^6	0.959

Experimental design using the CCD model

Development and Statistical analysis

In the present study RSM was used to optimize different parameters which include pH, metal ion concentration, mass of the adsorbent and the temperature of the metal solution as shown in Table-4. CCD is applied to obtain a correlation between the adsorption of Lead from the aqueous solution and the process variables investigated. The quadratic model suggested by the software was selected. Experiments

were planned to obtain a quadratic model consisting of 26 trials and 1 replicate at the center point. The design of this experiment is given in Table-5, along with the experimental values and predicted values.

Regression analysis is performed to fit the response function of lead adsorption. The coded values of variables in equation- 18 represent % lead adsorption (Y) as a function of pH (X_1), concentration (X_2), dosage (X_3) and temperature (X_4). 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 Lead:

$$\% \text{ Adsorption of Lead (Y)} = -7779.95 + 86.38 X_1 - 1.71 X_2 - 375.23 X_3 + 49.62 X_4 - 9.35 X_1^2 - 3653 X_3^2 - 0.08 X_4^2 + 0.18 X_1 X_2 + 45.40 X_1 X_3 - 0.07 X_1 X_4 + 1.83 X_2 X_3 + 0.01 X_2 X_4 + 2.4 X_3 X_4$$

Where X_1 , X_2 , X_3 and X_4 are the code values for the independent variables, $X_1 X_2$, $X_1 X_3$, $X_1 X_4$, $X_2 X_3$, $X_2 X_4$, $X_3 X_4$, X_1^2 , X_2^2 , X_3^2 and X_4^2 are the significant model terms for the adsorption of Lead.

The significance of the second-order polynomial equation is estimated by the F -test of ANOVA as represented in Table-6. Probability $>F$ value indicates the adequacy of any model. The model has prob $>F$ values less than 0.0001 means that the experimental data obtained can be experimentally explained with 99% accuracy by the model generated by RSM²⁸ whereas a low p -value (<0.05) indicates that the model is considered to be statistically significant. The F -value of 165.364 and p -value of <0.0001 represent that the model is 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 , 99.7% (0.997) value which is close to 1²⁹. In this model X_1 , X_2 , X_3 and X_4 represents the pH, Concentration, Dosage and Temperature respectively. Table-5 gives a correlation between the experimental values and predicted values by establishing the validity of the model and also indicates that they are in a close agreement with each other. The actual and the predicted percentage adsorption of lead are shown in Figure-21.

Interaction effects of adsorption variables

The % adsorption of lead with the distinct consolidation of free variables is visualized through three-dimensional view of response surface plots (Figures-18 to 24). All the response surface plots reveal that at low and high titers of the variables, the % absorption by the adsorbent is maximal; however, there exists a part where neither an expanding nor a diminishing pattern in the % adsorption is noticed. This exception confirms that there is a presence of ideal condition for the adsorption variables to encourage the % adsorption.

Optimization by response surface modeling

The optimum adsorption conditions determined using RSM for the adsorbent RTAC batch studies are pH 4.98, metal ion concentration 140.01 mg/L, adsorbent dosage 0.12g and temperature 314.46. The model approval has been characterized at optimum levels of the process variables, anticipated by the model to accomplish the maximum % adsorption of 92.16.

Table-4: Range of process parameters used in Central Composite Design for the adsorption of Lead onto RTAC adsorbent.

Variable	Process parameter	Range of Process parameters				
		-2	-1	0	1	2
X_1	Solution pH	3	3.5	4	4.5	5
X_2	Initial Metal concentration (mg/L)	100	125	150	175	200
X_3	Adsorbent dosage (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 along with predicted & experimental values of percentage adsorption of Lead onto RTAC adsorbent.

Experiment runs	Experimental value of % Adsorption of Lead	Predicted value of % Adsorption of Lead
1	72.16	72.71
2	74.05	74.33
3	74.73	73.74
4	77.34	76.56
5	50.24	50.27
6	55.23	54.50
7	55.47	55.87
8	61.86	61.29
9	86.63	86.93
10	88.45	87.81
11	89.75	90.23
12	92.6	92.30
13	72.84	73.37
14	76.13	76.86
15	81.78	81.23
16	86.72	85.92
17	54.14	54.77
18	93.76	93.61
19	88.45	88.73
20	59.71	59.91
21	70.17	69.37
22	78.17	79.46
23	73.05	72.40
24	77.57	78.70
25	83.4	83.55
26	83.7	83.55

Table-6: Analysis of variance for removal of Lead using RTAC as adsorbent

Variables	SS	DF	MS	F	P (Prob >F)
X ₃	152.611	1	152.611	165.364	0.000000
X ₃ ²	90.985	1	90.985	98.587	0.000001
X ₄	59.598	1	59.598	64.578	0.000006
X ₄ ²	69.687	1	69.687	75.511	0.000003
X ₁ X ₂	78.854	1	78.854	85.444	0.000002
X ₁ X ₃	5.153	1	5.153	5.583	0.037618
X ₁ X ₄	0.555	1	0.555	0.601	0.454392
X ₂ X ₃	20.839	1	20.839	22.581	0.000598
X ₂ X ₄	6.812	1	6.812	7.381	0.020044
X ₃ X ₄	1.440	1	1.440	1.560	0.237545
Error	10.152	11	0.923		
Total SS	3994.534	25	R ² = . 9746	R ² (Adj) = . 99422	

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

Table-7: Regression coefficients for removal of Lead using Response surface methodology

Adsorption parameter (Mean value)	Regression Coefficient	Standard Error	t-Value	p-Value
X ₁	-7779.95	927.3439	-8.3895	0.000004
x ₁ ²	86.38	31.1518	2.7729	0.018133
x ₂	-9.35	0.9198	-10.1683	0.000001
X ₂ ²	-1.71	0.6175	-2.7667	0.018336
X ₃	-0.00	0.0004	-10.0270	0.000001
X ₃ ²	-375.23	613.4817	-0.6116	0.553203**
x ₄	-3653.00	367.9076	-9.9291	0.000001
X ₄ ²	49.62	5.7811	8.5837	0.000003
X ₁ X ₂	-0.08	0.0092	-8.6897	0.000003
x ₁ x ₃	0.18	0.0192	9.2436	0.000002
x ₁ x ₄	45.40	19.2133	2.3629	0.037618
x ₂ x ₃	-0.07	0.0961	-0.7755	0.454392**
x ₂ x ₄	1.83	0.3843	4.7519	0.000598
x ₃ x ₄	0.01	0.0019	2.7169	0.020044

**insignificant (P ≥ 0.05)

Table-8: Optimized process parameters for adsorption of lead on to RTAC adsorbent

Process parameters	Observed limits of process parameters	Critical values of process parameters	Observed limits of process parameters
pH	3.0	4.98	5.00
Initial Concentration (mg/L)	100.0	140.01	200.00
Dosage (g)	0.1	0.12	0.15
Temperature (K)	303.0	314.46	323.00

The predicted value of % adsorption of Lead on RTAC adsorbent using RSM is: 95.64802

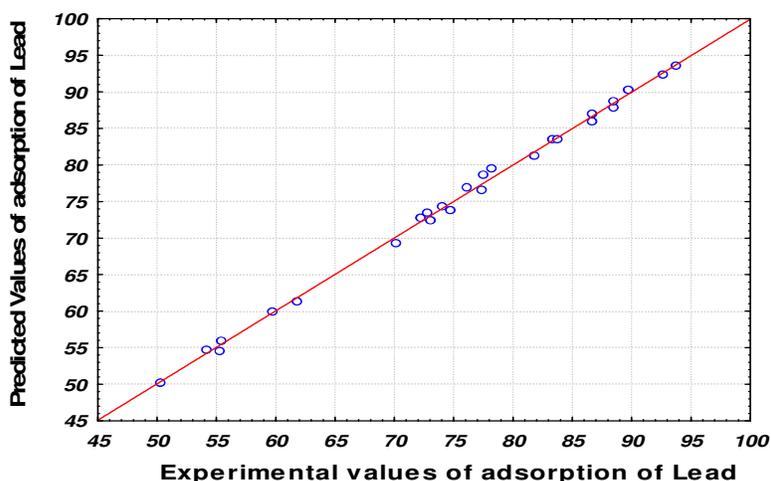


Fig.-18: Correlation plot of experimental values Vs predicted values for the adsorption of Lead.

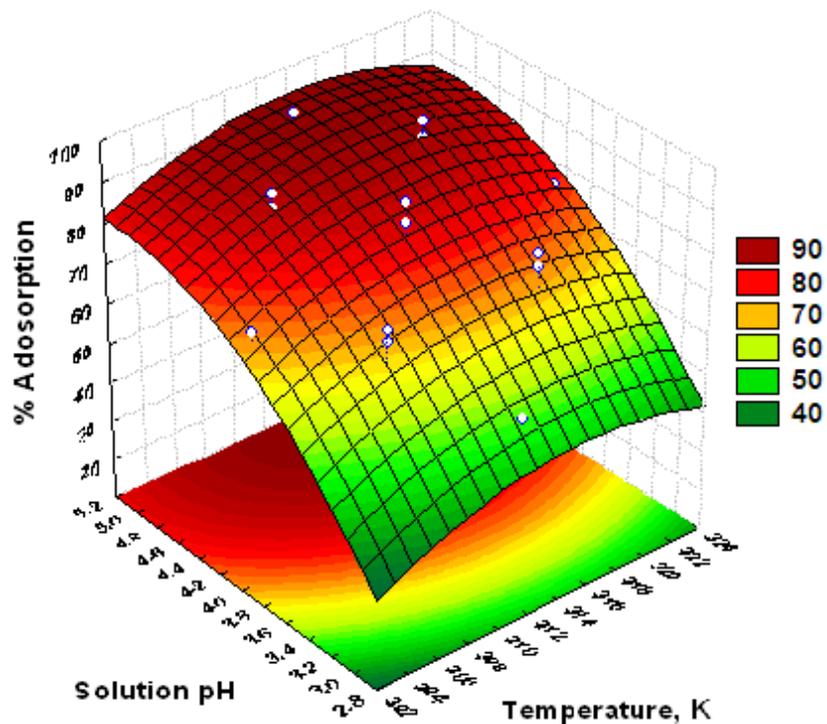


Fig.-19: Response surface plots of Temperature Vs Solution pH for the adsorption of Lead onto RTACadsorbent.

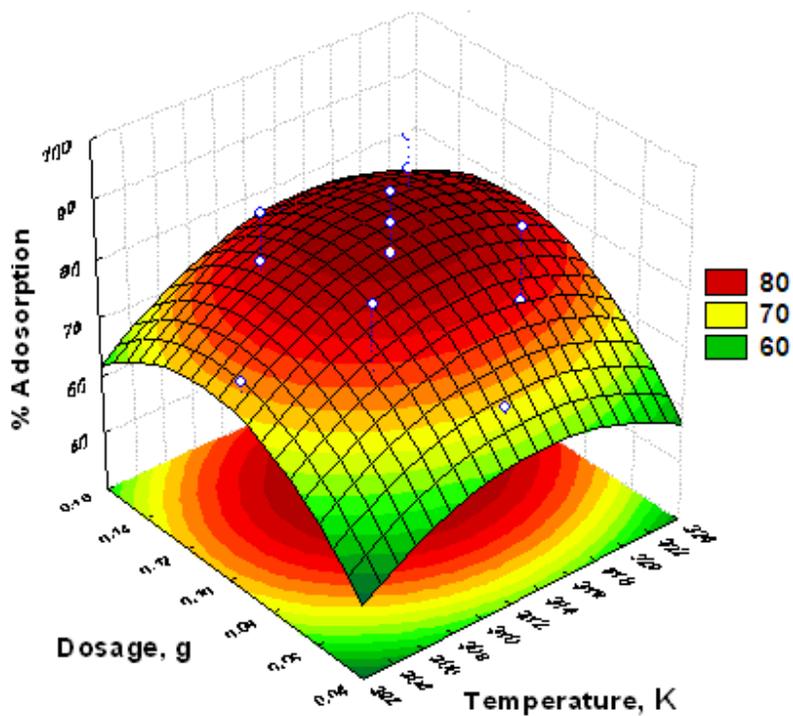


Fig.-20: Response surface plots of Temperature Vs Adsorbent dosage for the adsorption of Lead onto RTAC adsorbent.

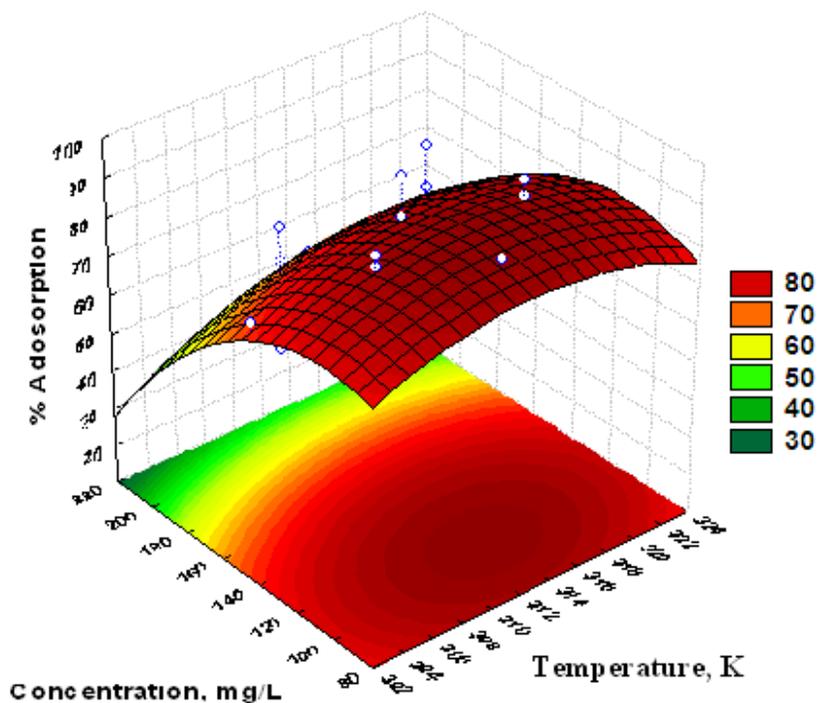


Fig.-21: Response surface plots of Temperature Vs Initial concentration of the Solution for the adsorption of Lead onto RTAC adsorbent.

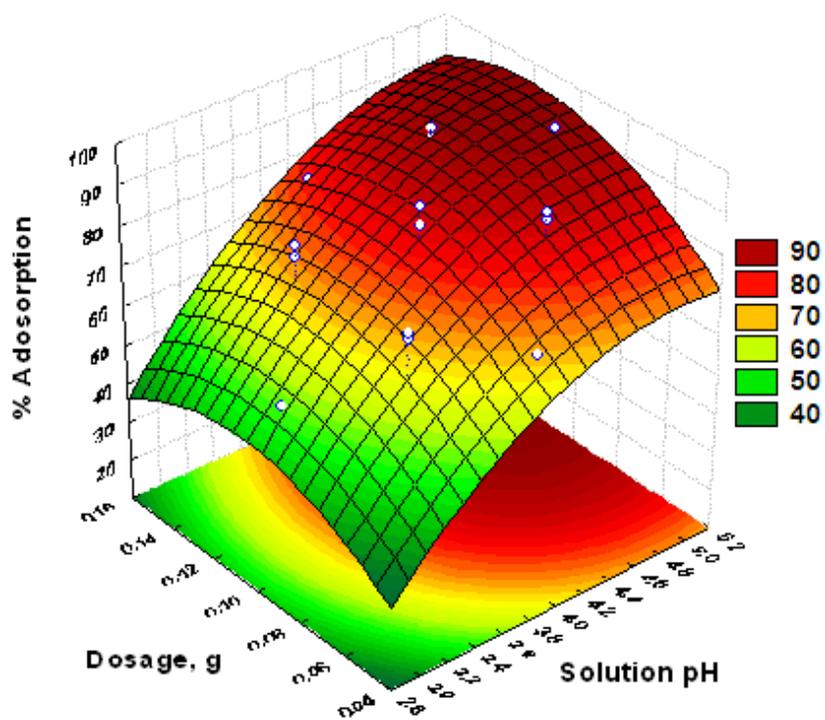


Fig.-22: Response surface plots of Solution pH Vs Adsorbent dosage for the adsorption of Lead onto RTAC adsorbent.

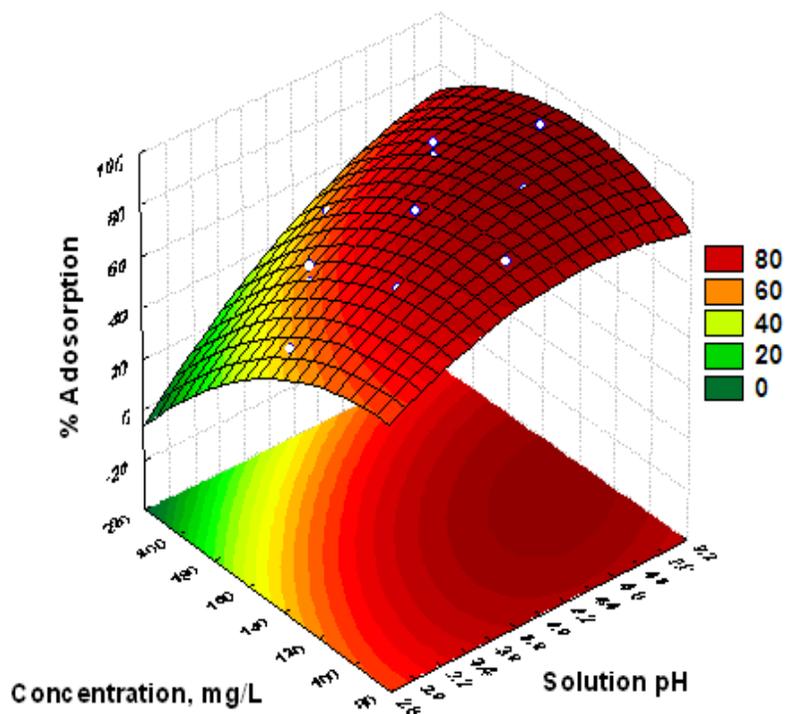


Fig.-23: Response surface plots of Adsorbent dosage Vs Initial concentration of the solution for the adsorption of Lead onto RTAC adsorbent.

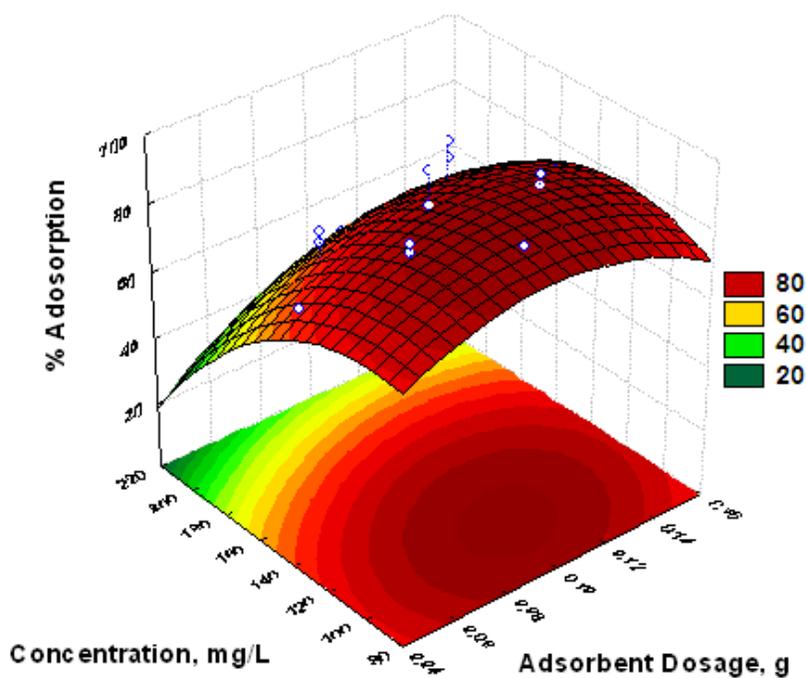


Fig.-24: Response surface plots of Solution pH Vs Initial concentration of the solution for the adsorption of Lead onto RTAC adsorbent.

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CONCLUSIONS

The maximum adsorption of lead onto the RTAC was at pH 5.0, contact time 60 min with the percentage removal of 97.55%.

Adsorption isothermal data were easily interpreted by a Langmuir model with maximum adsorption capacity of 125 mg/g of lead ions on RTAC and kinetic data were appropriately equipped with the pseudo-second-order kinetic model.

Consequences of thermodynamic investigations, properties of ΔH° , ΔG° and ΔS° are -63.976 KJ/mole, -5.787 KJ/mole and -0.196 KJ/mole.K, and -0.196 KJ/mole.K, demonstrates the adsorption process is exothermic nature, feasible and spontaneous at lower temperature.

The adsorption data were very well represented by Langmuir isotherm for the lead with an average higher correlation coefficient of 0.999, followed by Redlich-Peterson, Freundlich, Dubinin-Radushkevich isotherms and with a correlation coefficient of 0.998, 0.998 and 0.824 respectively.

The mean adsorption energy to lead figured as 2.236 kJ/mol, observed to be in the scope of an ordinary free energy credited to physical adsorption.

Optimized the adsorption efficiency using Central Composite Design (CCD) at pH = 4.98, Initial concentration 140.01 mg/L, the mass of the adsorbent is 0.12 grams, temperature of the metal solution is 314.46 and R^2 value is 0.9746. Experimentation led above optimum conditions, the value of percentage adsorption is 92.16.

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