



# Studies On Equilibrium Isotherms, Kinetic And Thermodynamic Parameters Of Pb<sup>2+</sup> Ion By Using New Composite Adsorbents

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## ARTICLE INFO ABSTRACT

The purpose of this study was to investigate the possibility of the utilization of low-cost adsorbents. Batch experiments were conducted to evaluate the removal of Pb<sup>2+</sup> ion from aqueous solutions by using various conditions of initial metal concentration, and contact time. The adsorption data was described by the Langmuir, Freundlich and BET adsorption Isotherm model. The best fit among the isotherm models was assessed by the linear coefficient of determination (R). The test results indicated that used materials be used as a cheap adsorbents for the removal of lead ions from aqueous solution. The kinetic experimental data properly correlated with the Pseudo first-order kinetic model, which indicates that, the Physical adsorption. From the thermodynamic data the overall adsorption is spontaneous, endothermic and increase in randomness.

**Keywords:** Low-cost adsorbent, Lead ions, adsorption Isotherm, Langmuir, Freundlich, BET, Kinetic and Thermodynamic equation

## 1.0. INTRODUCTION

Metal ions are highly toxic and hence they are to be necessarily removed from water and wastewater. Metallurgical metal processing and finishing and chemical industries are the major sources of discharge of effluents containing heavy metal ions [1]. Some of the industrial effluents are noted to possess high metal ion content, exceeding the tolerance limit. For example, industries like rayon, printed board, metallurgical, copper smelters, metal processing and finishing, non-ferrous and electroplating industries are the major sources that discharge copper(II) ions into the environment [2].

Magnesium powder is not suspected of being highly harmful to the environment. As magnesium oxide an aquatic toxicity rating of 1000 ppm has been established.[3]

The processes developed to remove heavy metal ions from water and wastewater include the techniques like decomposition, coagulation followed by filtration, chemical and electrochemical reduction and precipitation, complexing, solvent extraction, ion flotation, ion-exchange, reverse osmosis, electrolysis and adsorption [4]. Chemical treatment for the removal of heavy metal ions from water and wastewater has been well established over the years. Its major disadvantages are the cost of chemicals and the produced chemical sludge. Advanced biological treatments are suitable only for the reduction of oxygen demand and not suitable for the removal of metal ions. The metal ions are non-biodegradable, persistent and accumulate into the food chain. At low concentrations, the removal of metal ions is more effective by either ion-exchange or adsorption. Of these methods, adsorption technique is the most commonly used one, because it appears to be the most effective, efficient, quick, sludge-free and clean operation, which does not require a high degree of operator skill [5].

Although far more attention has been paid towards the studies on the adsorption of metal ions, only fewer attempts have been made on the studies on the kinetics and mechanism of adsorption of metal ions on low-cost adsorbents. The present study is therefore aimed at to study the removal of Lead(II) ions by adsorption on various low-cost adsorbents such as PFR and 20% (w/w) composite materials obtained by blending Sulphonated Carbons (AS, ML and MC) with PFR. Under various experimental conditions in

order to optimise the process parameters and to apply the various isotherms, first order and second order kinetic equations and to find out the thermodynamic parameters of the adsorption process. The results of the present study will be very much helpful in designing the low-cost effluent treatment plant for the removal of metal ions.

## 2.1. MATERIALS

Phenol- Formaldehyde resin (PFR) and Low-cost adsorbent materials such as AS3 [ 30% (w/w) Sulphonated Alangium Salvifolium L Carbon blended with PFR ], ML3 [ 30% (w/w) Sulphonated Madhucalongifolia L. Carbon blended with PFR ] and MC3 [ 30% (w/w) Sulphonated: Melia Composita Benth. Carbon blended with PFR ] were prepared by the methods which was given in the previous chapters. These adsorbent materials were sieved to 105-120 microns (Jayant, India). Lead sulphate (AnalaR samples purchased from E. Merck, India) are used as the source of lead(II) ion. All the other chemicals used in this study were of reagent grade, commercially obtained from Ranbaxy and SD fine chemicals, India. Double distilled water [6] was used for preparing all the solutions and reagents and employed throughout the experiment. Adsorption data of the replicates (Error  $\pm 1 - 2\%$ ) were reported.

## 2.2. CHARACTERISATION PROCEDURE

The samples synthesized by the above said methods were characterized by determining their various properties like, moisture, pH and electrical conductivity, absolute density, % of gravimetric swelling % of attritional breaking and surface area as per literature methods [7-11].

$$\text{Moisture content (percentage by mass)} = 100 (M - W)/M \quad \dots\dots\dots(1)$$

$$\text{Absolute density} = \frac{\text{Weight of the sample} \times \text{Density of the Medium}}{\text{Weight of equal volume of Medium}} \text{ gml}^{-1} \quad \dots\dots\dots(2)$$

$$\text{Percentage of swelling} = \frac{M_w - M_d}{M_d} \times 100 \quad \dots\dots\dots(3)$$

$$\text{Percentage of Attritional breaking} = \frac{(w_1 - w_2)}{w_1} \times 100 \quad \dots\dots\dots(4)$$

### 2.2.6. SURFACE AREA

Surface area of the adsorbent material was determined by following the acetic acid adsorption method [12, 13]. The adsorbent material (0.5 g) was added to each one of the 250 mL reagent bottles containing 50 mL of 0.05 M, 0.10, 0.15, 0.20 and 0.25 acetic acid solutions. A control experiment was also performed for each acid concentration without adsorbent. The bottles were tightly closed and kept for agitation at a speed of 200 rpm for a period of 60 min. in a thermostatic mechanical orbit shaker (NEOLAB, India) at  $30 \pm 1^\circ\text{C}$ . The solutions were filtered through whatman No.42 filter paper. The filtrate (10 ml) was then titrated against standardized sodium hydroxide solution (0.10 N) to find out the equilibrium concentration ( $C_e$ ) of acetic acid. The equilibrium concentration of acetic acid, remaining after adsorption, in each bottle ( $C_e$ ) was divided by the number of moles of acetic acid adsorbed per gram of the adsorbent to get the ratio  $C_e/n$ . The  $C_e/n$  values are linearly related to  $C_e$  values. The slope of the linear correlation of  $C_e/n$  with  $C_e$  yielded,  $N_m$  value (ie.  $N_m$  value =  $1/\text{slope}$ ). By substituting the value of  $N_m$  in the following equation, the surface area, A (in  $\text{m}^2 \text{g}^{-1}$ ) was calculated.

$$A = N_m N_A \sigma \quad \dots\dots\dots(5)$$

Where,  $N_A$  = Avogadro number ( $6.023 \times 10^{23}$ ),  $N_m$  = Number of moles of acetic acid per gram of adsorbent required to form monolayer coverage and  $\sigma$  = Molecular cross sectional area of acetic acid ( $21 \times 10^{-20} \text{ m}^2$ ).

### 2.2.7. ADSORPTION EXPERIMENTS

Adsorption experiments were carried out at room temperature ( $30 \pm 1^\circ\text{C}$ ) under batch mode [14]. Stock solution of  $\text{Pb}^{2+}$  ion (1000 ppm) was suitably diluted to the required initial concentration of  $\text{Pb}^{2+}$  ion with DD water. 250 mL of the  $\text{Pb}^{2+}$  solution of known initial concentration ( $C_i$ ) was taken in four different 500 mL leak – proof corning reagent bottles was shaken with a required dose of adsorbents ( $2 \text{ gL}^{-1}$  or specified amount) for a specific period of contact time (35 min.) at 200 rpm agitation speed in a thermostatic orbit incubator shaker ( Neolab, India), after noting down the initial pH of the solution. The initial pH of the solution was adjusted to the required value (range: 5.0-9.2) by adding either 1M HCl or NaOH solution. Required amount of adsorbent material was exactly weighed and then transferred into each one of these bottles.

The  $\text{Pb}^{2+}$  ions solutions, after equilibrium for required period of contact time were filtered through filter paper (Whatmann No.1) and the first 10ml portion of the filtrate was rejected from each bottle. The filtration was continued and the filtrates were collected separately in clean dry conical flasks. Then, the final/ equilibrium concentration ( $C_e$ ) were obtained from the standard curve by the interpolation technique from the OD values measured spectrophotometrically using Systronics spectrophotometer [15]

$$\text{Percentage removal} = \frac{100 (C_i - C_e)}{C_i} \dots \dots \dots (6)$$

$$\text{Amount adsorbed (q)} = \frac{(C_i - C_e) \times V}{m} \dots \dots \dots (7)$$

Where,  $C_i$  and  $C_e$  are the initial and equilibrium (final) concentration of metal ions (in ppm), respectively,  $V$  is the volume of metal ion solution taken and  $m$  is the mass of adsorbent in  $\text{g L}^{-1}$ .

The adsorption data obtained from the effect of initial concentration of metal ions and contact time respectively were used in fitting the various isotherms model and first order and second order kinetic equations and then determined the thermodynamic parameters such as change in free energy ( $\Delta G$ ), change in free enthalpy ( $\Delta H$ ) and change in entropy ( $\Delta S$ ).

### 3.0. RESULTS AND DISCUSSION

The adsorption experiments were carried out at  $30^\circ\text{C}$  (error:  $\pm 1^\circ\text{C}$ ) under batch mode [14] under different experimental conditions in order to study the effect of initial concentration of metal ions and contact. The results obtained are analysed and discussed below:

The absolute density in both hydrated (wet) and dehydrated (dry) of all adsorbents are presented in Table 1. It is found that the order of decreasing absolute density in both wet (hydrated) and dry (dehydrated) are as follows

**PFR > ML3 > AS3 > MC3**

**Table 1 Physico-chemical characterisation of Adsorbents.**

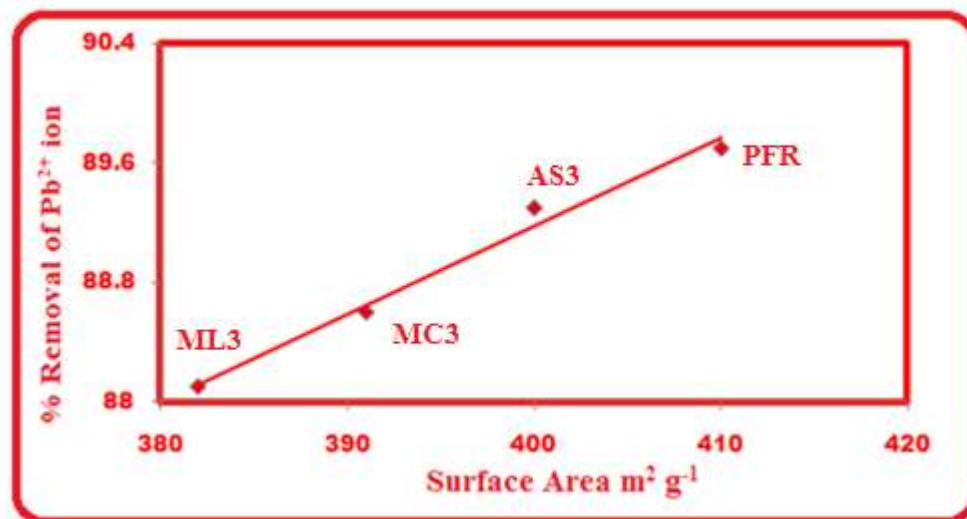
Properties		PFR	AS 3	ML 3	MC3
Absolute Density ( $\text{g mL}^{-1}$ )	Dry	1.910	1.553	1.587	1.36
	Wet	1.952	1.651	1.645	1.43
% of Gravimetric swelling		98.25	66.82	53.31	57.54
% of Attritional breaking		7.96	11.66	23.24	24.65
pH		6.3	6.1	5.9	5.9
Conductivity ( $\text{ohm/cm}$ ) $\times 10^{-3}$		0.96	0.74	0.66	0.64
% of Moisture		0.32	0.48	0.41	0.40
Surface Area $\text{m}^2 \text{g}^{-1}$		415	396	386	388
Description		Brown powder	Black powder	Black powder	Black powder

This indicates all adsorbents are more closely packed. Gravimetric swelling percentage shows that adsorbent materials are macro reticular having non-gel pores.

The percentage of attritional breaking data revealed that mechanical stability of all adsorbents. The increasing orders of mechanical stability of adsorbents are

**PFR > AS3 > ML3 > MC3**

Table 1 indicates that all adsorbents are acidic in nature. Electrical conductivity of all adsorbents are very low and in the order of  $(0.64-0.96) \times 10^{-3} \text{ ohm/cm}$ . From the Table 1 shown that the lower moisture content of the various adsorbents (range 0.32-0.48%) is mainly due to the method of preparation viz., high temperature employed during carbonisation and activation. Hence the moisture content of the adsorbents does not affect their adsorptive power [7]



**Fig. 1. % Removal of  $\text{Pb}^{2+}$  ion Versus Surface Area**

Fig. 1 shown that the % removal of  $\text{Pb}(\text{II})$  ion Vs surface area of adsorbents which indicates that amount of % removal  $\text{Pb}(\text{II})$  ion increases with increasing surface area of the adsorbents [12-13].

### 3.1. Effect of Initial Concentration

The effects of initial concentration of metal ions on the extent of removal of lead (II) ions by adsorption on various low-cost adsorbents were studied. The relevant data are given in Table 2. The percentage removal of metal ions decreased with the increase in initial concentration. The exponential decrease in the extent of removal (in terms of percentage removal) of metal ions with the increase in initial concentration of metal ions may be due to the reduction in immediate solute adsorption due to the lack of available active sites on the surface of adsorbent compared to the relatively large number of active sites required for the high initial concentration

**Table 2 Effect of initial concentration of  $Pb^{2+}$  ion on the % removal and amount adsorbed by various adsorbents. Contact time-35 min, pH-8.3, Particle size-105-120 $\mu$ , Dose : 2g/L**

Adsorbents	Parameter	Pb <sup>2+</sup> Concentration in ppm			
		10	20	30	40
PFR	C <sub>i</sub>	10	20	30	40
	C <sub>e</sub>	1.26	2.38	3.08	4.17
	% of Removal	87.4	88.1	89.7	89.5
	Amount Adsorbed	4.37	8.81	13.46	17.92
ML3	C <sub>i</sub>	10	20	30	40
	C <sub>e</sub>	1.41	3.11	3.66	4.92
	% of Removal	85.9	84.5	87.8	87.7
	Amount Adsorbed	4.30	8.45	13.17	17.54
MC3	C <sub>i</sub>	10	20	30	40
	C <sub>e</sub>	1.38	2.98	3.44	4.88
	% of Removal	86.2	85.1	88.53	87.8
	Amount Adsorbed	4.32	8.51	13.28	17.56
AS3	C <sub>i</sub>	10	20	30	40
	C <sub>e</sub>	1.32	2.58	3.22	4.68
	% of Removal	86.8	87.1	89.3	88.3
	Amount Adsorbed	4.34	8.71	13.39	17.66

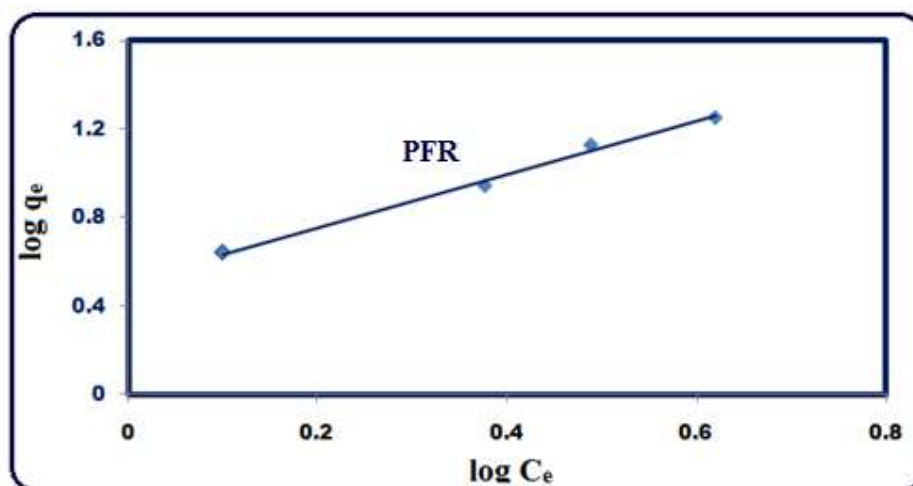
On the contrary the amount adsorbed increases (Table 2) with the increase in initial concentration. Similar results have been reported in literature on the extent of removal of metal ions [14,16-18]. The optimum initial concentration of lead(II) ions is fixed as 30 ppm, since the maximum extent of removal occurred at this concentration.

#### 3.1.1 ADSORPTION ISOTHERMS

In order to determine the adsorption capacity and potential, the study of adsorption isotherm is essential, in selecting the adsorbent for the removal of metal ions [19]. The adsorption data were analysed with the help of Freundlich, Langmuir and BET adsorption isotherms [20].

##### (1) Freundlich isotherm : $\log q_e = \log K + 1/n \log C_e \dots (8)$

Where, K and n are Freundlich constants indicating sorption capacity ( $mg\ g^{-1}$ ) and intensity, respectively. 'q<sub>e</sub>' is the amount of adsorbate adsorbed,  $q_e = (C_i - C_e) / m$ , C<sub>i</sub> and C<sub>e</sub> are initial and equilibrium concentrations; 'm' is mass of adsorbent; 'K' and 'n' can be determined from linear plot of log q<sub>e</sub> against log C<sub>e</sub> (Figures 2-5).



**Fig.2. Freundlich isotherm plot for the removal of  $Pb^{2+}$  ion by PFR**

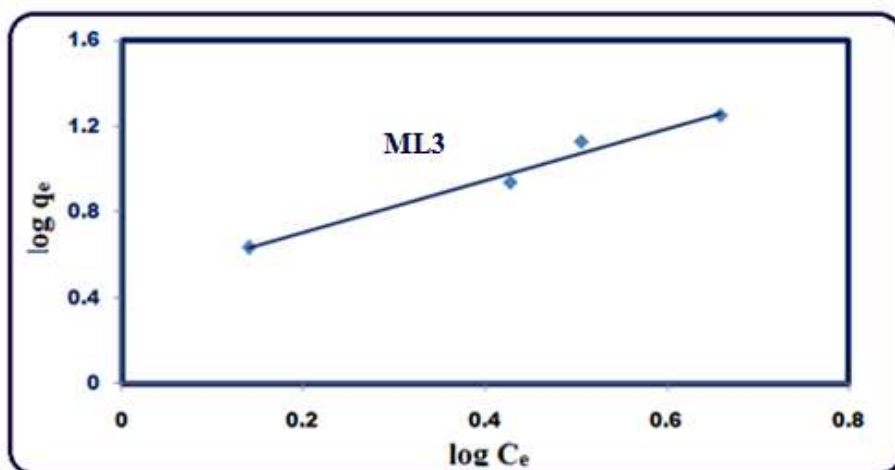


Fig.3.Freundlich isotherm plot for the removal of Pb<sup>2+</sup> ion by ML3

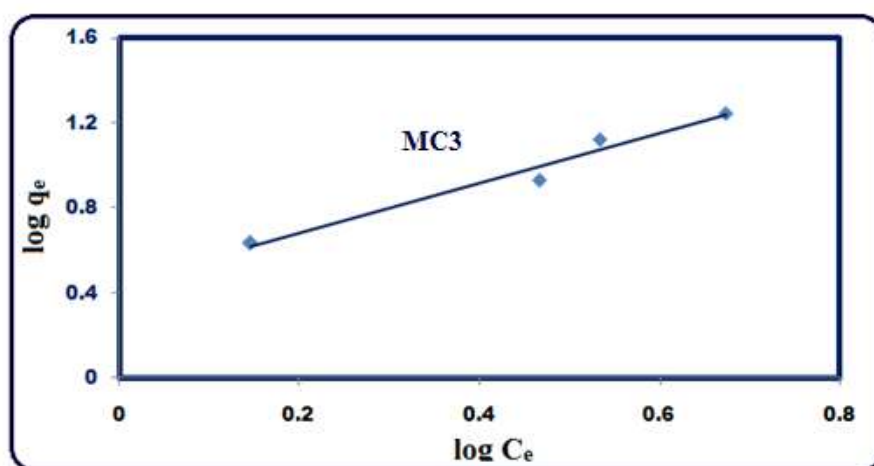


Fig.4.Freundlich isotherm plot for the removal of Pb<sup>2+</sup> ion by MC3

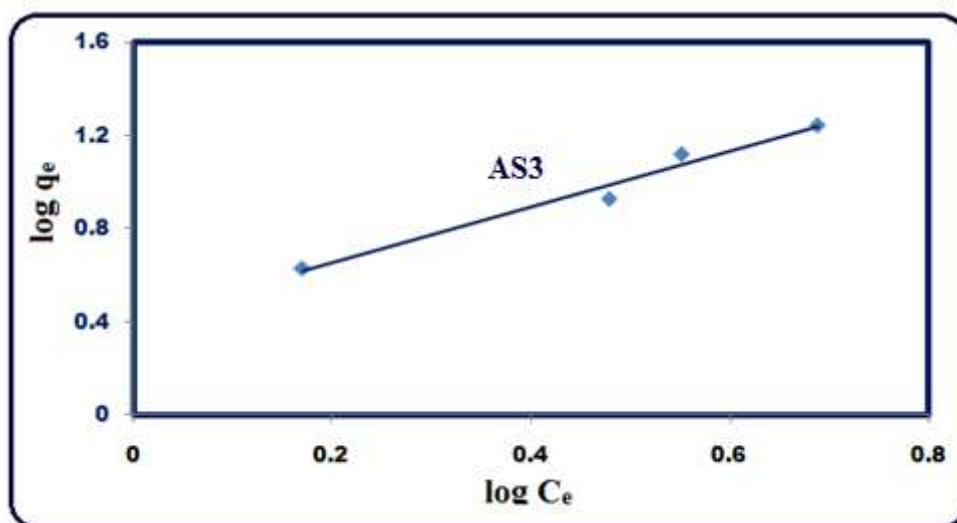


Fig.5.Freundlich isotherm plot for the removal of Pb<sup>2+</sup> ion by AS3

**(2). Langmuir Isotherm:  $1/q_e = (1/Qb) \times 1/C_e + (1/Q)$  .....(9)**

Where, K and (1/n) are measures of adsorption capacity and intensity of adsorption, respectively; q<sub>e</sub> is the amount adsorbed per unit mass of adsorbent; C<sub>e</sub> is the equilibrium concentration (ppm); Q and b are the Langmuir constants, which are the measures of monolayer (saturation) adsorption capacity (in mgg<sup>-1</sup>) and surface energy (in Lmg<sup>-1</sup>), respectively. By plotting 1/q<sub>e</sub> Vs 1/C<sub>e</sub> one get on Q and b (Figures 6-9). Further,

the essential characteristics of the Langmuir isotherm can be described by a separation factor  $R_L$ , which is defined by the following equation [21,22].  $R_L = 1/(1 + b C_i)$  ----- (10)

Where,  $C_i$  is the optimum initial concentration (ppm) of metal ions and  $b$  is the Langmuir constant. The value of separation factor  $R_L$  indicates the shape of the isotherm and nature of the adsorption process as given below:

$R_L$ value	Nature of the process
$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$0 < R_L < 1$	Favourable
$R_L = 0$	Irreversible

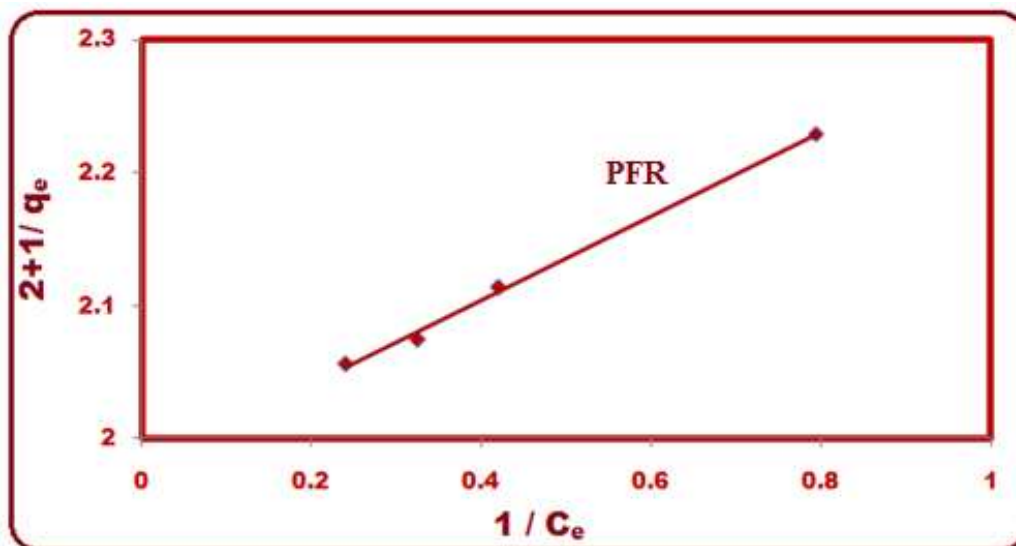


Fig 6 Langmuir isotherm plot for the removal of  $Pb^{2+}$  ion by PFR

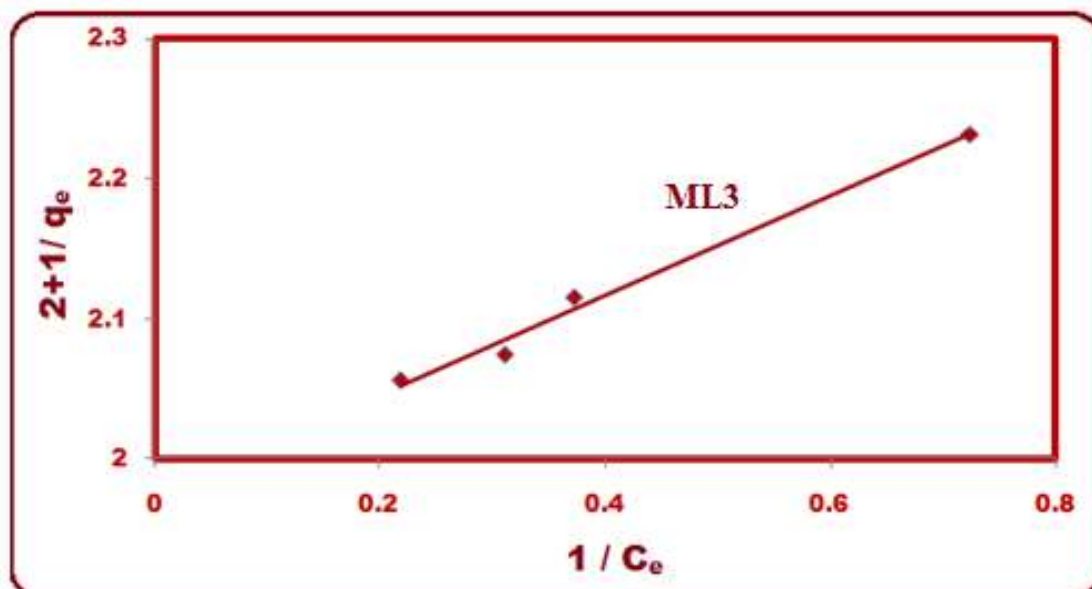


Fig 7 Langmuir isotherm plot for the removal of  $Pb^{2+}$  ion by ML3



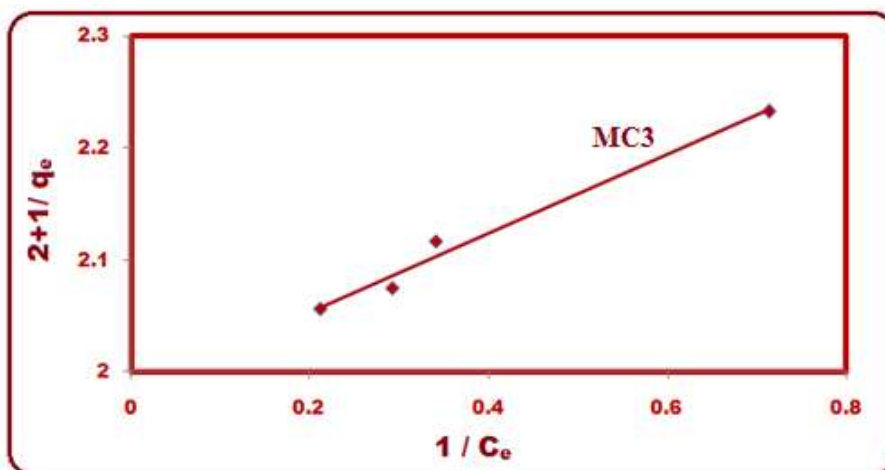


Fig 8 Langmuir isotherm plot for the removal of  $Pb^{2+}$  ion by MC3

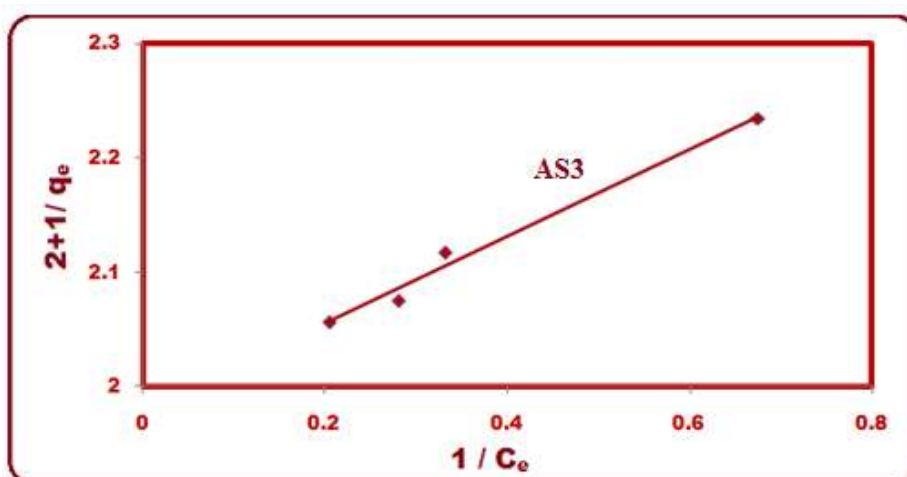


Fig .9 Langmuir isotherm plot for the removal of  $Pb^{2+}$  ion by AS3

( 3) BET isotherm:  $C_e / (C_s - C_e)q_e = 1/bQ + (b-1)/bQ (C_e / C_s) \dots(11)$

Where,  $Q$  is the maximum adsorption at monolayer ( $mg\ g^{-1}$ ),  $C_e$  is the equilibrium concentration of  $Pb(II)$  ion in ppm.  $C_s = (C_i - C_e)$  is the saturation concentration of the solute in ppm.  $q_e$  is the amount of  $Pb(II)$  ion adsorbed per unit weight of Adsorbent at equilibrium concentration ( $mg\ g^{-1}$ ) and  $b$  is the BET constant expressive of the energy of interaction with surface. By an linear plot of  $C_e / (C_i - C_e)q_e$  Vs  $C_e / C_i$  one who obtained the  $Q$  and BET constant 'b' (Figures 10-13) values.

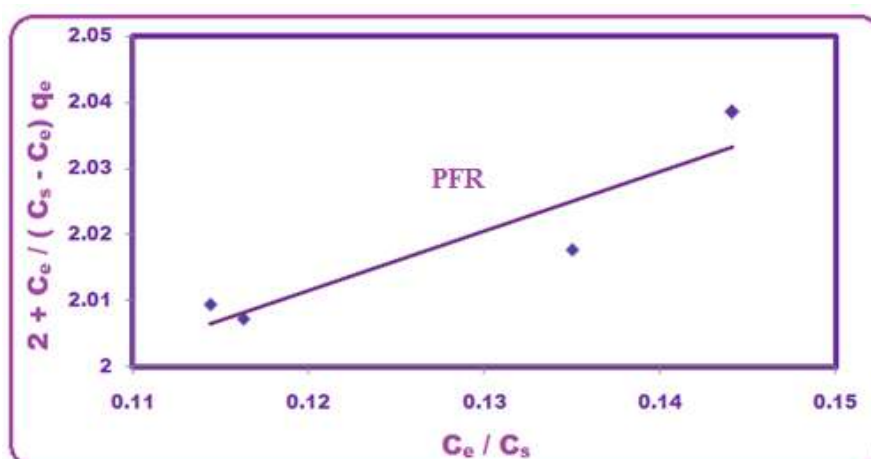


Fig 10 BET isotherm plot for the removal of  $Pb^{2+}$  ion by PFR

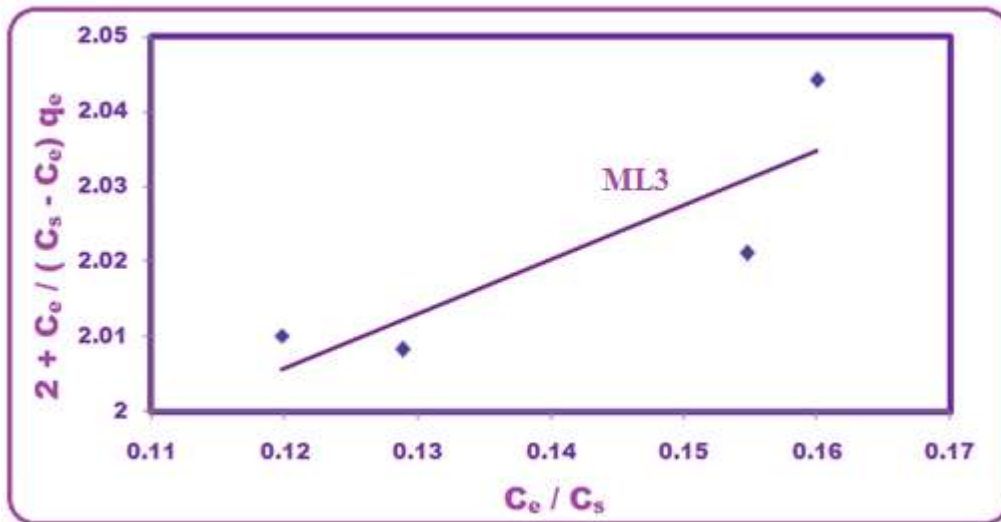


Fig 11 BET isotherm plot for the removal of  $Pb^{2+}$  ion by ML

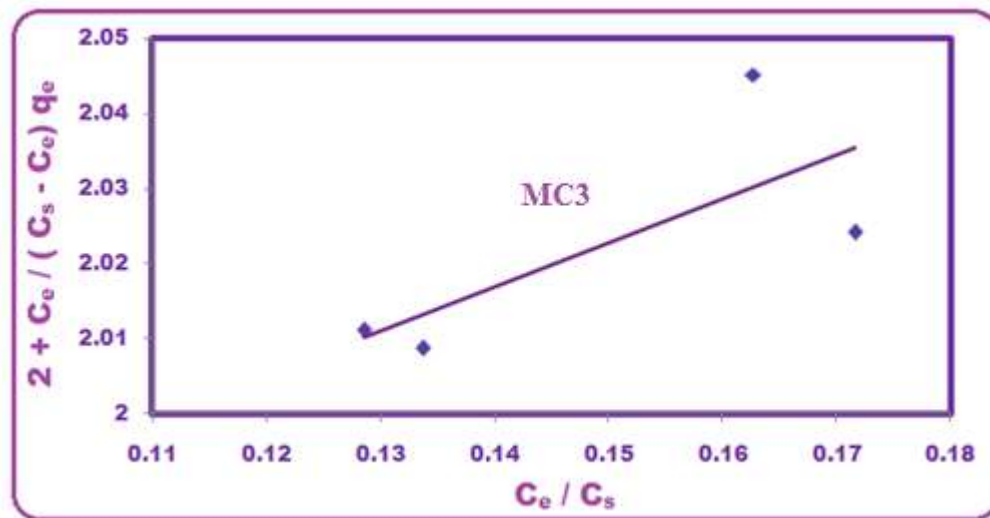


Fig 12 BET isotherm plot for the removal of  $Pb^{2+}$  ion by MC 3

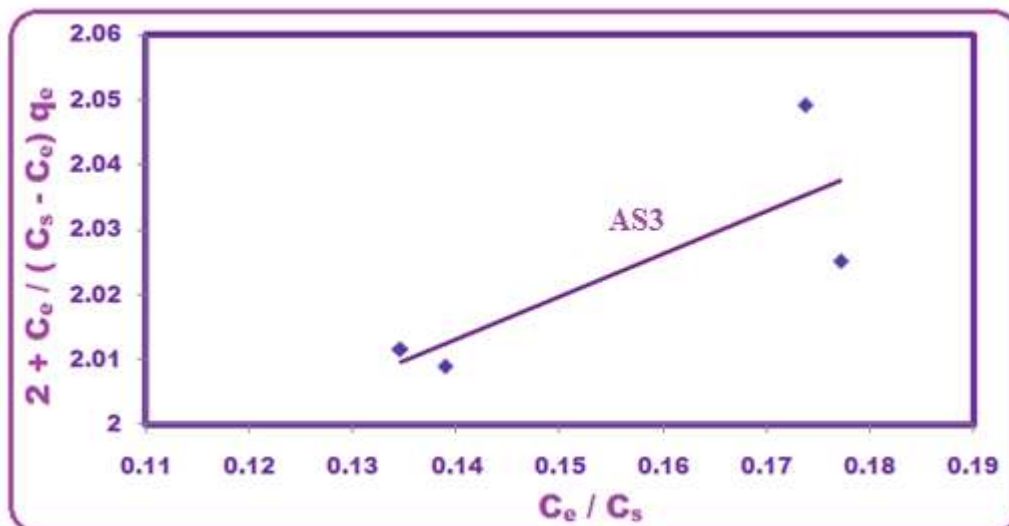


Fig 13 BET isotherm plot for the removal of  $Pb^{2+}$  ion by AS3

From the Table 3 it is observed that there is a slight increase in K values and slight decrease in 'n' values for all the adsorbents. Increase in the adsorption capacity K may be attributed to the widening of pores at which,



may allow more number of adsorbate in a large surface area. The intensity of adsorption 'n' is an indicative of the bond energies and interaction between Pb (II) ion and adsorbents. The values of 'n' are nearly '1' indicate the adsorption is more favourable.

**Table3 Results from correlation analysis on testing the applicability of adsorption isotherms for the removal of Pb<sup>2+</sup> by various adsorbents..**

Parameter	Lead (II) ion			
	PFR	ML3	MC3	AS3
<b>Freundlich isotherm</b>				
<b>n</b>	<b>0.833</b>	<b>0.820</b>	<b>0.838</b>	<b>0.853</b>
<b>K</b>	<b>3.281</b>	<b>2.691</b>	<b>2.821</b>	<b>2.912</b>
<b>Correlation coefficient (r)</b>	<b>0.9969</b>	<b>0.9892</b>	<b>0.9821</b>	<b>0.9920</b>
<b>Langmuir isotherm</b>				
<b>Q (mgg<sup>-1</sup>)</b>	<b>34.48</b>	<b>40.16</b>	<b>47.62</b>	<b>57.22</b>
<b>b (Lmg<sup>-1</sup>)</b>	<b>0.0912</b>	<b>0.0725</b>	<b>0.0501</b>	<b>0.0523</b>
<b>Correlation coefficient (r)</b>	<b>0.9986</b>	<b>0.9990</b>	<b>0.9983</b>	<b>0.9996</b>
<b>R<sub>L</sub></b>	<b>0.268</b>	<b>0.315</b>	<b>0.325</b>	<b>0.401</b>
<b>BET isotherm</b>				
<b>Q (mgg<sup>-1</sup>)</b>	<b>0.998</b>	<b>1.262</b>	<b>1.262</b>	<b>1.323</b>
<b>b (Lmg<sup>-1</sup>)</b>	<b>10.32</b>	<b>9.87</b>	<b>9.87</b>	<b>9.44</b>
<b>Correlation coefficient (r)</b>	<b>0.9215</b>	<b>0.8515</b>	<b>0.7860</b>	<b>0.8012</b>

In this study, linear plot of  $1/q_e$  Vs  $1/C_e$  was obtained which showed that the adsorption followed Langmuir isotherm model (Figs 6-9). The values of Q (34.48- 57.22 mg/g) and b (0.0501-0.0912 L/mg<sup>-1</sup>) were determined from the slope and intercept of the plot, respectively. The applicability of Langmuir isotherm suggested monolayer coverage of Pb(II) on the surface of adsorbent prepared from various plant materials. The essential characteristics of Langmuir isotherm can be expressed in terms of dimensionless Separation Factor.

The parameter,  $R_L$  indicates the shape of the isotherm. The  $R_L$  values obtained were in between 0 and 1 (0.268 to 0.401), which indicates favourable adsorption of Pb(II) onto various adsorbents [21].

The mechanism of metal ion adsorption on porous adsorbents may involve three steps: (i) diffusion of the ions to the external surface of adsorbent; (ii) diffusion of ions into the pores of adsorbents; (iii) adsorption of the ions on the internal surface of adsorbent.

It can be seen from the Table3 that among the linear form of all three adsorption isotherm models used i. e. Langmuir, Freundlich and BET Model, the values of correlation Coefficient, R are more than 0.99 for Langmuir adsorption isotherm. The best adsorption isotherm fitting was found in the following order for various adsorbents.

### Langmuir > Freundlich > BET

#### 3.2. EFFECT OF CONTACT TIME

In the adsorption system, contact time plays a vital role, irrespective of the other process parameters affecting the kinetics of adsorption. The effect of contact time on the extent of removal of metal ions was studied (Fig. 14 and Fig. 15). The extent of removal of metal ions increased with the increase in contact time and reached a constant value with the increase in contact time. The relative increase in the extent of removal of lead (II) ion, after 35 minutes of contact time is found to be less. The optimum contact time at which the maximum removal occurred is fixed as 35min. for Pb(II) ions. Similar results have been reported in literature for the removal of metal ions [14, 23-25].

#### 3.3. KINETICS OF ADSORPTION

The kinetics of adsorption of metal ions has been studied by applying the following pseudo first order kinetic equations [26] and pseudo second order kinetic equations

$$\text{First order kinetics model: } \log(q_e - q_t) = \log q_e - k_1 t / 2.303 \quad \text{-----(12)}$$

Where,  $q_e$  and  $q_t$  are the amounts of metal ion adsorbed per unit mass of adsorbent at equilibrium and at time  $t$  (min), and  $k_1$  (min<sup>-1</sup>) is the first order rate constant. Values of  $k_1$  can be obtained from linear plots of  $\log(q_e - q_t)$  versus 't' and are given for Pb(II) adsorption on various adsorbents shown in Fig 14

$$\text{Pseudo second order kinetics: } t/q_t = 1/k_2 q_e^2 + t/q_e \quad \text{-----(13)}$$

where  $q_e$  and  $q_t$  are the amounts of metal ion adsorbed per unit mass of adsorbent at equilibrium and at time  $t$  (min), and  $k_2$  ( $\text{min}^{-1}$ ) is the second order rate constant. Values of  $k_2$  can be obtained from linear plots of  $t/q_t$  versus  $t$ .

**3.3.1. FITNESS OF THE KINETIC MODELS**

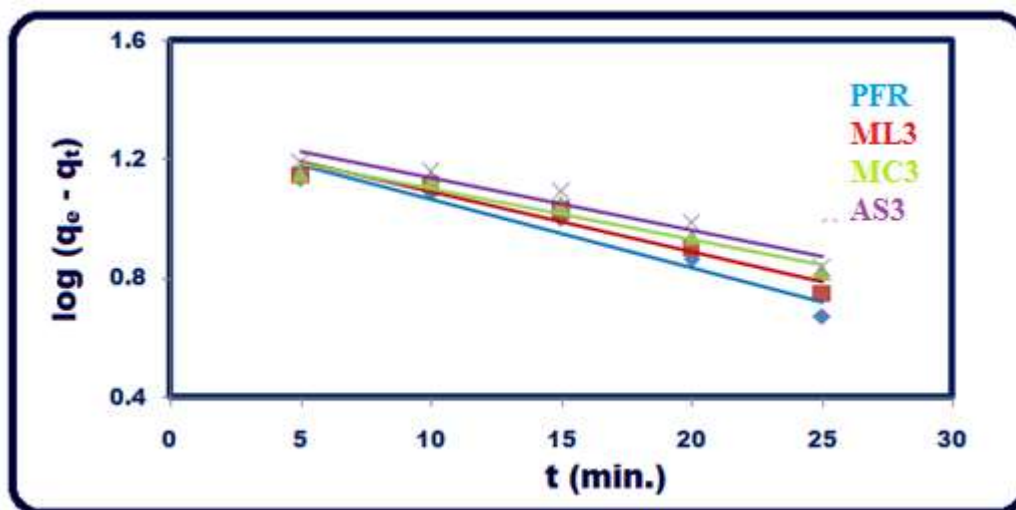
The best-fit among the kinetic models was assessed by the **squared sum of errors (SSE)** values. It is assumed that the model which gives the lowest SSE values is the best model for the particular system [27, 28]. The SSE values were calculated by the equation

$$SSE = \sum \frac{(q_{e(expt.)} - q_{e(cal.)})^2}{q_{e(expt.)}^2}$$

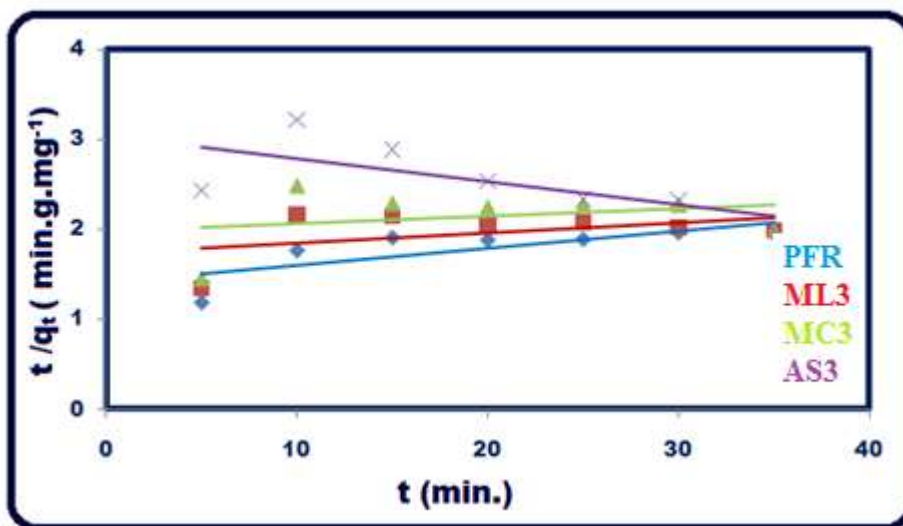
.....(14)

**Table 4 Correlation coefficient obtained from pseudo first and second order kinetic model**

Adsorbents	Correlation coefficient (R)	
	pseudo First order	pseudo Second order
PFR	0.9896	0.7325
ML3	0.9825	0.4254
MC3	0.9931	0.2622
AS3	0.9902	0.7012



**Fig. 14. Test of pseudo first order equation for adsorption of  $\text{Pb}^{2+}$  ion by various adsorbents**



**Fig 15. Test of pseudo second order equation for adsorption of  $\text{Pb}^{2+}$  ion by various adsorbents**

The present data of Pb<sup>2+</sup> ion fit the pseudo first order kinetic model to an acceptable degree and with a correlation coefficient not less than 98%. Based on the correlation coefficient and lowest SSE values (Table 4 and 5), the adsorption of Pb (II) ion is best described by the First order rate equation.

**Table 5. Fitness of the kinetic models**

Adsorbents	Graph	R	K <sub>1</sub>	log q <sub>e</sub>	Q <sub>e(cal.)</sub>	Q <sub>e(expt.)</sub>	SSE
PFR	log(q <sub>e</sub> -q <sub>t</sub> ) vs t	0.9896	0.0652	1.328	21.28	17.92	0.0352
ML 3		0.9825	0.0602	1.350	22.38	17.54	0.0762
MC 3		0.9931	0.0570	1.333	21.52	17.56	0.0509
AS 3		0.9902	0.0520	1.364	23.12	17.66	0.0956

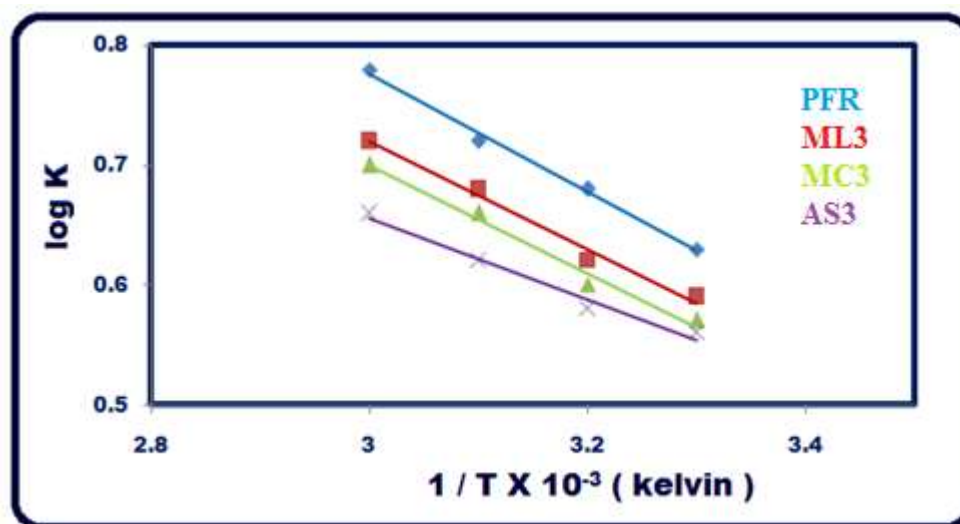
### 3.4. Thermodynamic Studies

Thermodynamic parameters such as change in free energy (ΔG°, kJ/mol), enthalpy change (ΔH°, kJ/mol) and entropy change (ΔS°, J/K/mol) were determined using the following equations [29,30].

$$K_c = q_e / C_e \dots(15), \quad \Delta G^\circ = -RT \ln K_c \dots(16) \text{ and}$$

$$\log K_c = \Delta S^\circ / (2.303R) - \Delta H^\circ / (2.303RT) \dots(6.17)$$

Where, K<sub>c</sub> is the equilibrium constant, q<sub>e</sub> and C<sub>e</sub> are the concentrations (mg/L) of metal ion in the solid and in the liquid phase, respectively, at equilibrium, T is the temperature in Kelvin and R is the gas constant. The ΔH° and ΔS° values obtained From the slope and intercept of Van't Hoff plots are presented in Figure 16 and Table 6.



**Fig .16 Van't Hoff plots for the adsorption of Pb (II) ion on various adsorbents**

**Table 6 Thermodynamic parameters for the removal of Pb<sup>2+</sup> ion by various adsorbents**

Samples	-ΔG KJ. mol <sup>-1</sup>	ΔH KJ. mol <sup>-1</sup>	ΔS KJ.K <sup>-1</sup> mol <sup>-1</sup>
RFR	3.65	9.38	0.021
ML3	3.12	7.56	0.016
MC3	3.33	8.02	0.017
AS3	3.45	8.54	0.019

The thermodynamic parameters can be calculated from Vant Hoff plot (Fig.16). The positive value of ΔH° (7.56 to 9.38 kJ/mol.) for the adsorption of Pb<sup>2+</sup> by all adsorbents showed physical adsorption (<40 kJ/mol<sup>-1</sup>) and endothermic nature of the overall process and negative ΔG° value (-3.12 to -3.65 kJ/mol) indicates that the adsorption process is spontaneous [31, 32]. The positive value of ΔS (0.016 to 0.021 kJ.K<sup>-1</sup>mol<sup>-1</sup>) indicates that the increase in randomness adsorption process due to the increase of other eliminated ions into the solution.

### 4.0. Conclusion

The conclusions derived from the present studies are:

The percentage removal of Pb (II) ions increases with the increases in initial concentration and optimum concentration is 30ppm. The percentage removal of Pb (II) ions increases with the increase in contact time and optimum contact time is 35 minutes. The adsorption data obeyed the Langmuir isotherms and indicate the formation of unimolecular layer of adsorbents. The adsorption process obeys pseudofirst order kinetic equations. Hence AS<sub>3</sub>, MC<sub>3</sub> and ML<sub>3</sub> could be used as an adsorbent for the effluent treatment, especially for the removal of metal ions. I.e. lead metal ions.

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