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EQULIBRIUM ISOTHERMS, KINETIC AND THERMODYNAMIC ADSORPTION OF Pb^{2+} ION BY USING NEW LOW-COST ADSORBENTS

P. Selvarani [1], R. Pandimeena[2], Rane Caroleena Ganesh[3], R.K. Seenivasan[4*]
[1&2] Research and Development Centre, Bharathiar University, Coimbatore, Tamil Nadu, India
[3] Department of Chemistry, Sidharth College, Badlapur, University of Mumbai, India
[4*]Department of chemistry,Government Arts College, Melur,
Madurai- 625106, Tamilnadu, India
Corresponding Author Email id: rkseenivasan@gmail.com

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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^{2+} *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

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 rayan, 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].

The excess copper level will cause many ill-effects [1], such as lung cancer, Wilson's disease (in which the excess copper will deposit on brain, skin, pancreas and myocardium), genetic recessiveness*etc.* The major sources of lead (II) ions are automobiles, metallurgical, metal processing and finishing, mining, chemical and paint industries. Lead (II) ions are also highly toxic to most of the animals and plants, inhibit δ-aminolevulinatedehydrase and haemoglobin synthesis, produce anemia, affect gastrointestine and toxic to central nervous system. Inhale magnesium oxide fume, they may suffer to humans. On an environmental spectrum of 0 - 3 Magnesium oxide fume registers 0.8. A score of 3 represents a very high hazard to the environment and 0 a negligible hazard. This ranking include the extent of the material's toxic or poisonous nature and/or its lack of toxicity, and the measure of its ability to remain active in the environment and whether it accumulates in living organisms. It does not take into exposure to the substance.

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]

Removal and recoveries of these toxic metal ions are the best approaches to control the metal pollution problem and safeguard the environment and human health.

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 less attempt has 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 RFR and 30% (*w/w*) composite materials obtained by blending Sulphonated Carbons(PG, MI and MC) with RFR. 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.

MATERIALS AND METHODS

MATERIALS

Resorcinol- Formaldehyde resin (RFR) and Low-cost adsorbent materials such as PG3 [30% (*w/w*) Sulphonated *Psidium Guajava* L. Carbon blended with RFR], MI3 [30% (*w/w*) Sulphonated *Mangifera Indica* L Carbon blended with RFR] and MC3[30% (*w/w*) Sulphonated *Morinda Citrifolia* **L.**Carbon blended with RFR] 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 ±1 – 2%) were reported.

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.

MOISTURE CONTENT

About 2 g of the adsorbent material was weighed in a petridish and placed in a hot air- oven at 110 °C for about 4 hours. The dish was covered, cooled in a desiccators and weighed [7]. Heating, cooling and weighing was repeated at 30 min. intervals of time, until the difference between the consecutive weighing was less than 1 mg.

Moisture content (percentage by mass) = $\mathbf{100\ (M - W)/M}$ ……..….**(1)**

Where, M is the initial mass of adsorbent taken (g) and W is the mass of adsorbent after drying (g).

pH AND ELECTRICAL CONDUCTIVITY

Adsorbent (100 mg) was mixed well with 50 mL of DD water (pH = 6.7 and conductivity 0.06 μS m^{-1}) and equilibrated for 1 hour by agitating it at 200 rpm in a thermostatic orbit shaker incubator (NEOLAB, India). The supernatant liquid was tested for pH using digital pH meter (Systronic's, India) and electrical conductivity (in ohm^{-1} cm^{-1}) with the conductivity meter (Systronic's CM – 335, India), and a cell (with cell constant of 1 cm^{-1}) at room temperature[8].

DETERMINATION OF ABSOLUTE DENSITY (WET & DRY)

The absolute density of the samples was determined in both hydrated and dehydrated states with the aid of a specific gravity bottle in water and toluene media, respectively [9].

The weight of empty specific gravity bottle (w_1, g) and with the sample (w_2, g) was found out.

The bottle was then filled was the medium (solvent) and the weight along with the sample was taken (w_3, g). Finally the weight of the bottle filled with the medium alone was taken as (w_4, g).

The absolute density of the sample was calculated as follows;

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

DETERMINATION OF GRAVIMETRIC SWELLING PERCENTAGE

Swelling measurements were made by allowing the samples to equilibrate in water overnight. The weight of the swollen sample (wet weight) was taken as Mw and the corresponding dry weight M_d was determined after drying the same lot at 700°C for 12 hrs and then Gravimetric swelling percentage was determined using the formula [10],

$$\textbf{Percentage of swelling} = \frac{M_W - M_d}{M_d}\ \mathbf{x\ 100} \qquad \ldots\ldots\ldots\mathbf{(3)}$$

DETERMINATION OF % OF ATTRITIONAL BREAKING

The sample under investigation was sieved to give batches of particles of size greater than 200 micron sieve [11]. A known quantity of the samples (w_1, g) was swollen in water and shaken continuously for 6 hrs. The wet sample was separated by filtration and dried subsequently, it was sieved on a 200 micron mesh and the amount retained by the sieve was weighed (w_2, g)

$$\textbf{Percentage of Attritional breaking} = \frac{(w_1 - w_2)}{w_1} \times 100 \qquad \ldots\ldots\ldots\mathbf{(4)}$$

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 mL, 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 ± 1^0C. 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 (Ce) of acetic acid. The equilibrium concentration of acetic acid, remaining after adsorption, in each bottle (Ce) was divided by the number of moles of acetic acid adsorbed per gram of the adsorbent to get the ratio Ce/n . The Ce/n values are linearly related to Ce values. The slope of the linear correlation of Ce/n with Ce yielded, N_m value (ie. N_m value = 1/slope). By substituting the value of N_m in the following equation, the surface area, A (in $m^2 g^{-1}$) was calculated.

$$\mathbf{A = N_m N_A \sigma} \qquad \ldots\ldots\ldots \textbf{(5)}$$

Where,

N_A = Avogadro number (6.023×10^{23})

N_m = Number of moles of acetic acid per gram of adsorbent required to form monolayercoverage

σ = Molecular cross sectional area of acetic acid (21×10^{-20} m^2),

ADSORPTION EXPERIMENTS

Adsorption experiments were carried out at room temperature (30±1°C) under batch mode [14]. Stock solution of Pb^{2+} ion (1000ppm) was suitably diluted to the required initial concentration of Pb^{2+}ion with DD water. 250 mL of the 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 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 Pb^{2+} ion 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 spectro photometrically using Systronics spectrophotometer [15]

$$\textbf{Percentage removal} = \mathbf{100\,(C_i - C_e) / C_i} \ldots\ldots\ldots \textbf{(6)}$$

$$\textbf{Amount adsorbed (q)} = \mathbf{(C_i - C_e) \times V / m} \ldots\ldots\ldots \textbf{(7)}$$

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 gL^{-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 (ΔG), change in free enthalpy (ΔH) and change in entropy (ΔS).

RESULTS AND DISCUSSION

The adsorption experiments were carried out at 30°C (error:±1°C) under batch mode [14] under different experimental conditions in order to study the effect of initial concentration of metal ions and contact.

Table.1. Physico–chemical characterisation of Adsorbents.

Properties		RFR	MI3	MC3	PG3
Absolute Density (g mL^{-1})	Dry	2.52	1.59	1.74	1.78
	Wet	2.64	1.28	1.72	1.74
% of Gravimetric swelling		88.08	67.64	67.54	66.29
% of Attritional breaking		9.45	20.78	21.26	18.45
pH		6.5	6.1	5.8	5.8
Conductivity (ohm/cm)$\times10^{-3}$		0.94	0.70	0.62	0.60
% of Moisture		0.30	0.40	0.40	0.40
Surface Area m^2 g^{-1}		432	390	370	362
Description		Brown powder	Black powder	Black powder	Black powder

The absolute density in both hydrated (wet) and dehydrated (dry) of all adsorbents are presented in Table 6.1.It is found that the order of decreasing absolute density in both wet (hydrated) and dry (dehydrated) are as follows

RFR > PG3 > MC3> MI3

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

RFR > PG3 > MC3> MI3

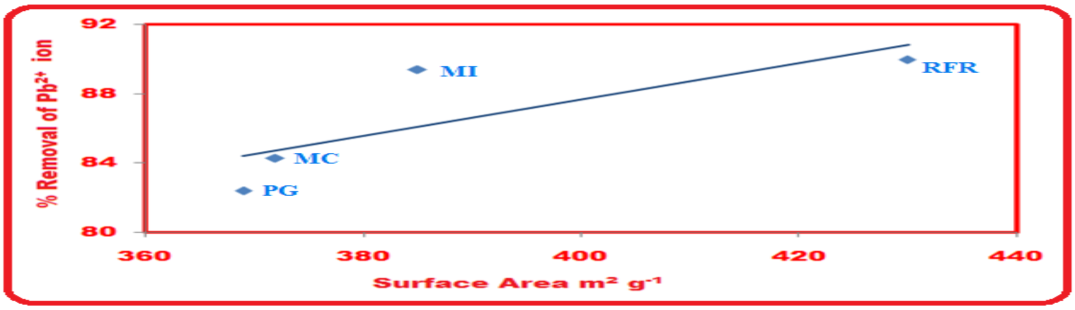


Fig. 1. % of Removal Versus Surface Area

Table 1 indicates that all adsorbents are acidic in nature. Electrical conductivity of all adsorbents are very low and in the order of (0.53-0.94 **)**$\times 10^{-3}$ ohm/cm. From the Table 6.1 shown that the lower moisture content of the various adsorbents (range 0.30-0.42%)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 shown that the % removal of Pb (II) ion Vs surface area of adsorbents which indicates that amount of % removal Pb (II) ion increases with increasing surface area of the adsorbents [12-13].

Effect of Initial Concentration

Table.6.2. Effect of initial concentration of Pb^{2+} ion on the % removal and amount adsorbed by various adsorbents.Contact time-35 min, pH-8.6, Particle size-105-120µ, Dose : 2g/L

Adsorbents	**Parameter**	**Pb^{2+} Concentration in ppm**			
RFR	C_i	10	20	30	40
	C_e	1.35	2.20	2.69	3.52
	% of Removal	86.50	89.00	91.03	91.2
	Amount Adsorbed	2.16	4.45	13.65	9.12
MI3	C_i	10	20	30	40
	C_e	1.65	2.94	3.00	4.72
	% of Removal	83.50	85.30	90.00	88.2
	Amount Adsorbed	4.18	8.53	13.5	17.64
MC3	C_i	10	20	30	40
	C_e	1.72	3.04	3.12	5.88
	% of Removal	82.8	84.8	89.6	85.3
	Amount Adsorbed	4.14	8.48	13.44	17.06
PG3	C_i	10	20	30	40
	C_e	1.90	3.10	3.04	6.22
	% of Removal	81.0	84.5	89.86	84.45
	Amount Adsorbed	4.05	8.45	13.48	16.89

The effect 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.

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.

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

:$\log q_e = \log K + 1/n \log C_e$ ……..….**(8)**

Where,

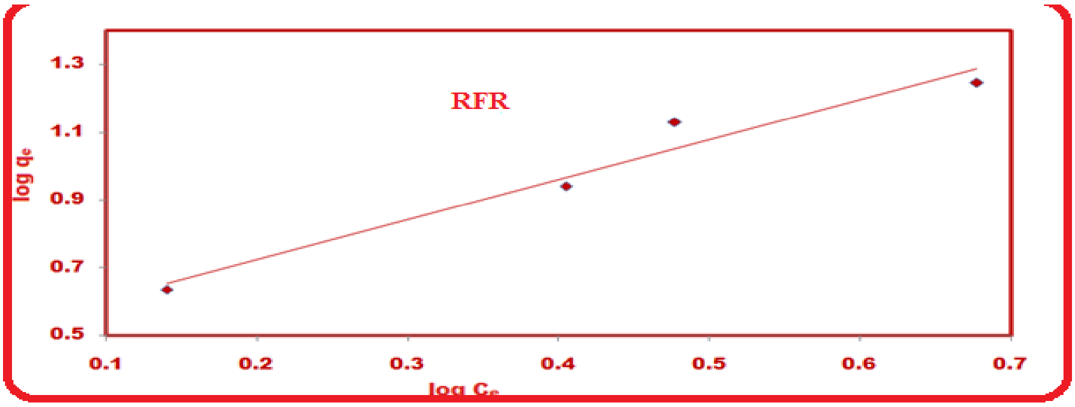
K and n are Freundlich constants indicating sorption capacity (mg g−1) and intensity, respectively.

Where ' q_e' is the amount of adsorbate adsorbed, $q_e = (C_i - C_e) / m$

Where

C_i and C_e are initial and equilibrium concentrations; 'm' is mass of adsorbent;

Fig.2.Freundlich isotherm plot for the removal of Pb^{2+} ion by RFR)



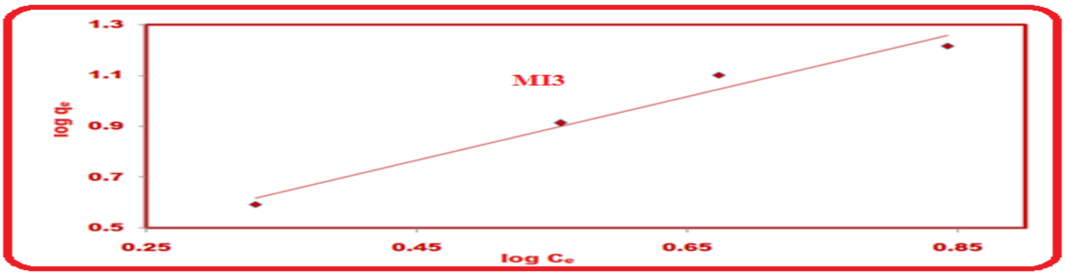


Fig.3.Freundlich isotherm plot for the removal of Pb^{2+} ion by MI3

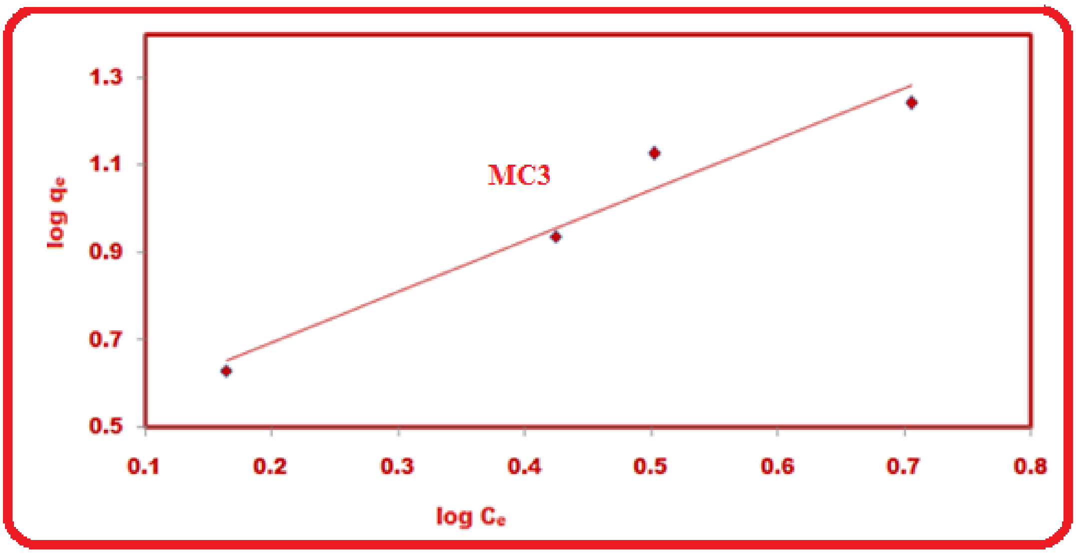


Fig.4.Freundlich isotherm plot for the removal of Pb^{2+} ion by MC3

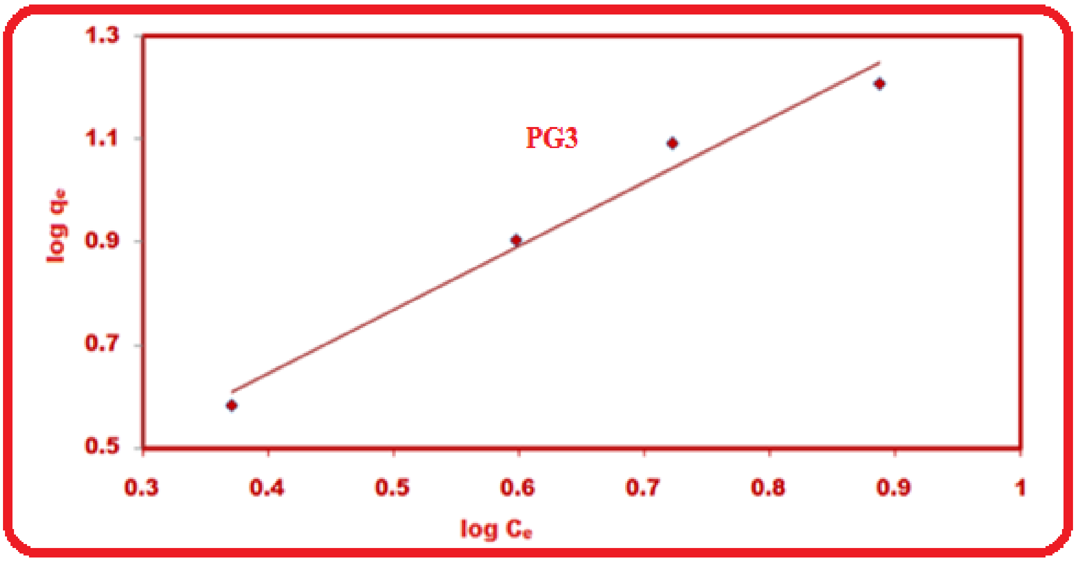


Fig.5.Freundlich isotherm plot for the removal of Pb^{2+} ion by PG3

(2) Langmuir isotherm :

$$1/q_e = (1 / Qb) \times 1/C_e + (1 / Q)) \qquad \ldots\ldots\ldots(9)$$

Where,

K and (1/n) are measures of adsorption capacity and intensity of adsorption, respectively; q_e is the amount adsorbed per unit mass of adsorbent; C_e is the equilibrium concentration (ppm); Q and b are the Langmuir constants, which are the measures of monolayer (saturation) adsorption capacity (in mgg^{-1}) and surface energy (in Lmg^{-1}), respectively. By plotting $1/q_e$ Vs $1/C_e$ one get on Q and b (Figures6-9). 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].

$$R_L = 1/(1 + b\,C_i) \qquad \text{--------} \quad (10)$$

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

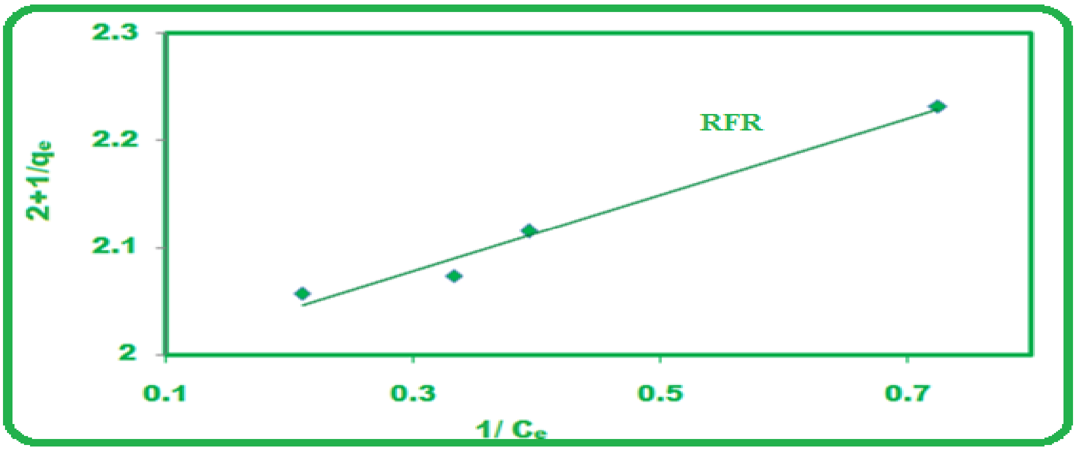


Fig 6 Langmuir isotherm plot for the removal of Pb^{2+} ion by RFR

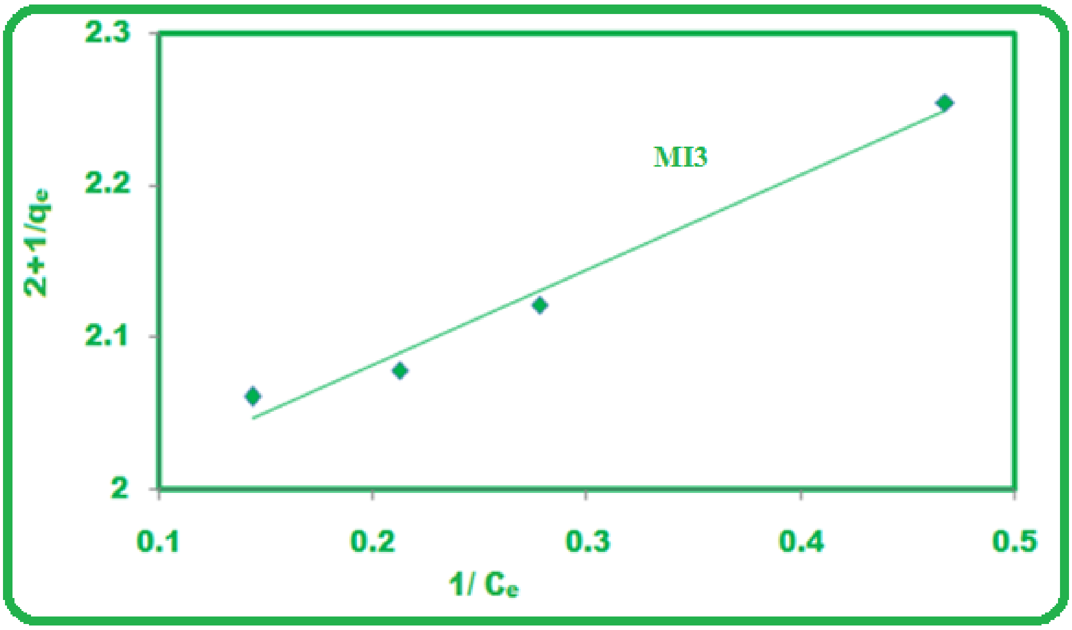


Fig 7 Langmuir isotherm plot for the removal of Pb^{2+} ion by MI3

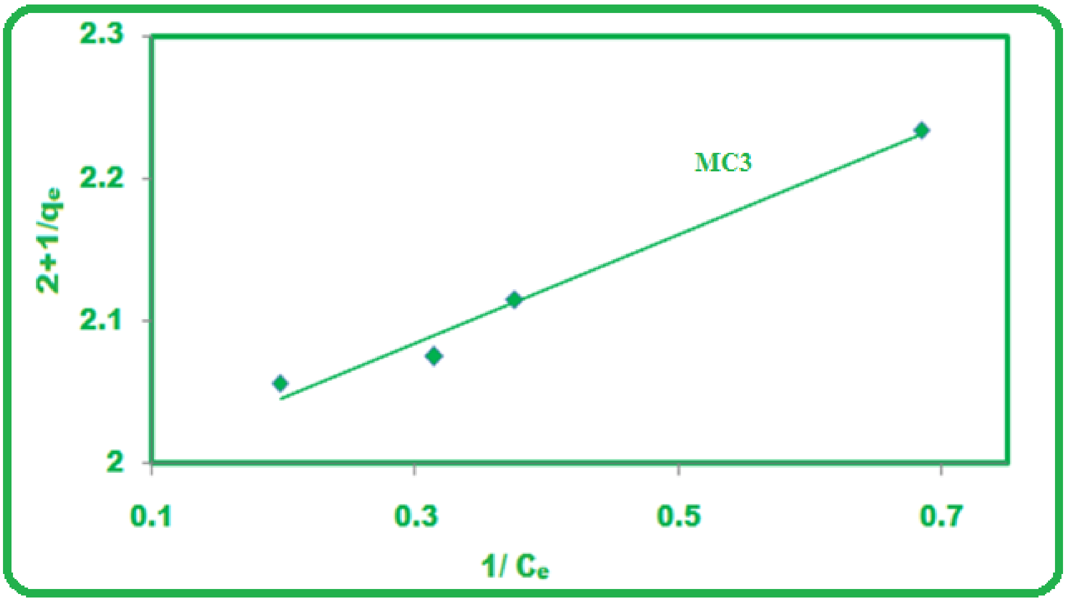


Fig8 Langmuir isotherm plot for the removal of Pb^{2+} ion by MC3

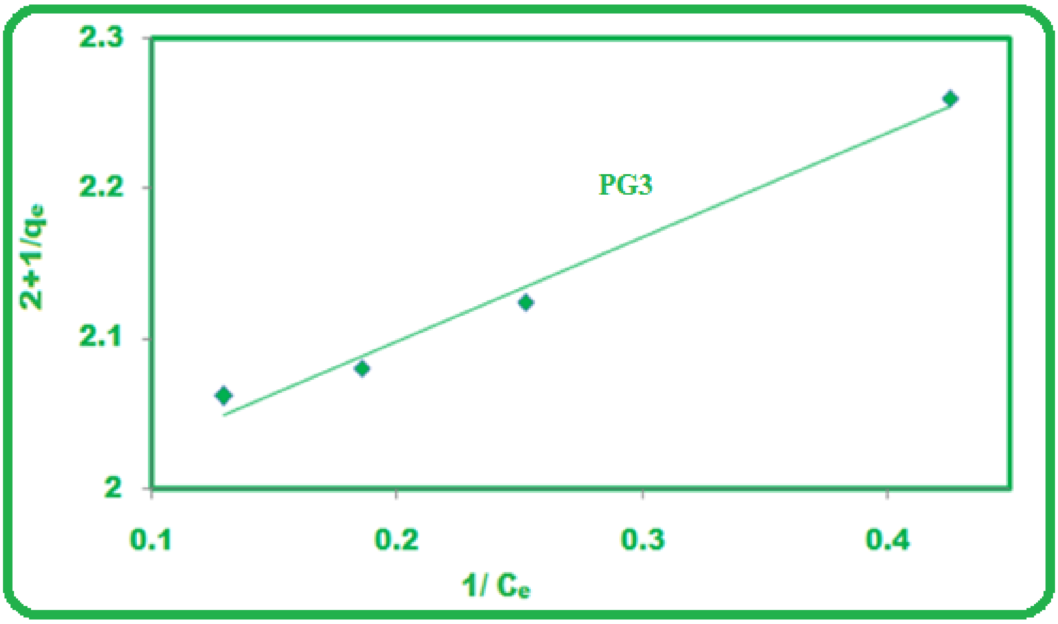


Fig .9 Langmuir isotherm plot for the removal of Pb^{2+} ion by PG3

(3) BET isotherm

$$C_e / (C_i - C_e) q_e = 1/ b Q + (b-1) / b Q (C_e / C_i) \qquad \ldots\ldots\ldots(11)$$

Where
Q is the maximum adsorption at monolayer (mg g−1),
C_e is the equilibrium concentration of Pb(II) ion in ppm.

C_i 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.

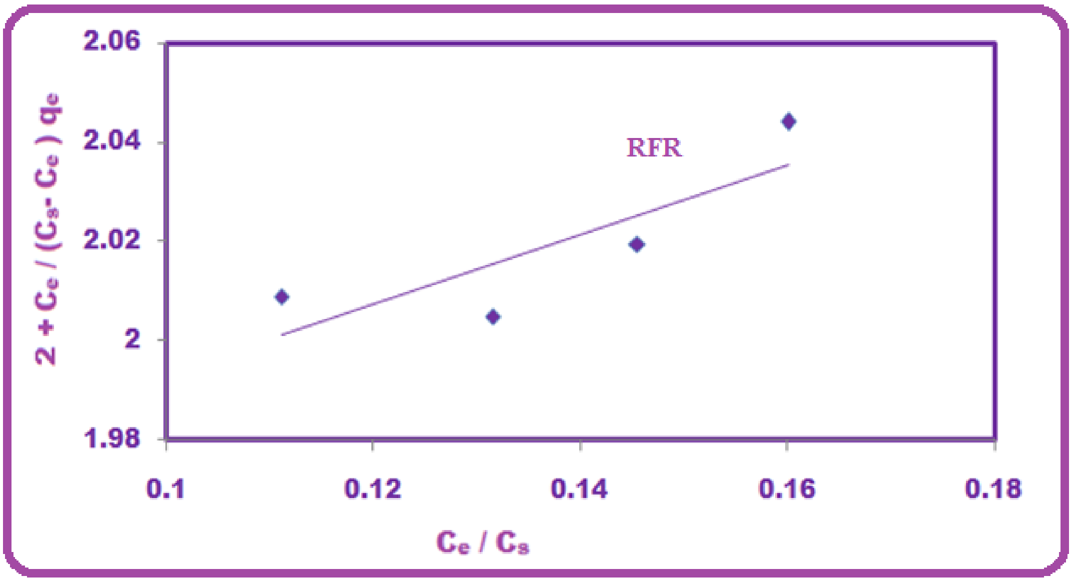


Fig 10 BET isotherm plot for the removal of Pb^{2+} ion by RFR

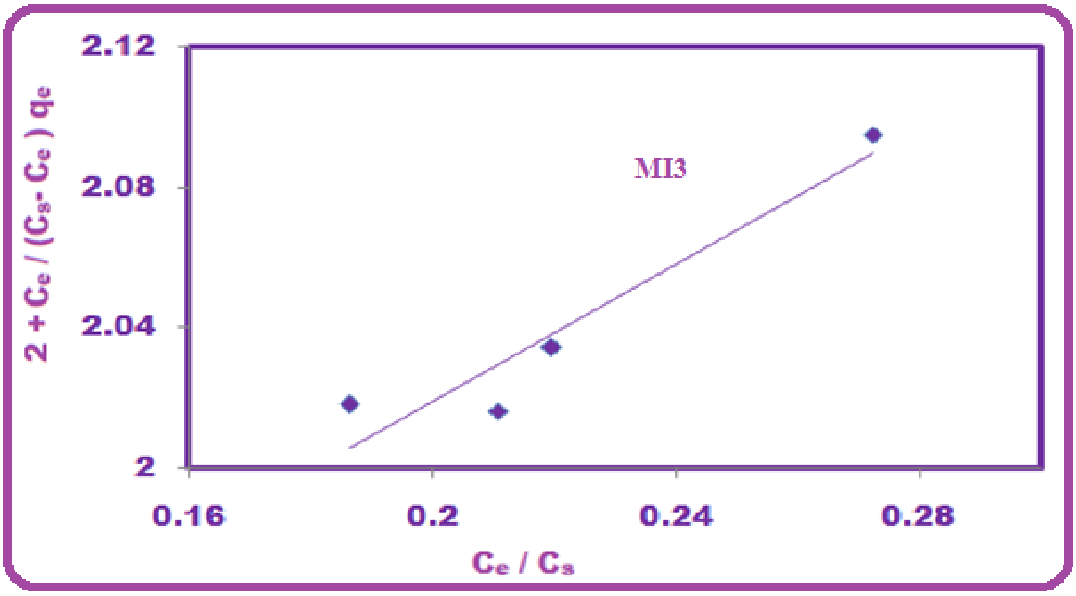


Fig 11 BET isotherm plot for the removal of Pb^{2+} ion by MI3

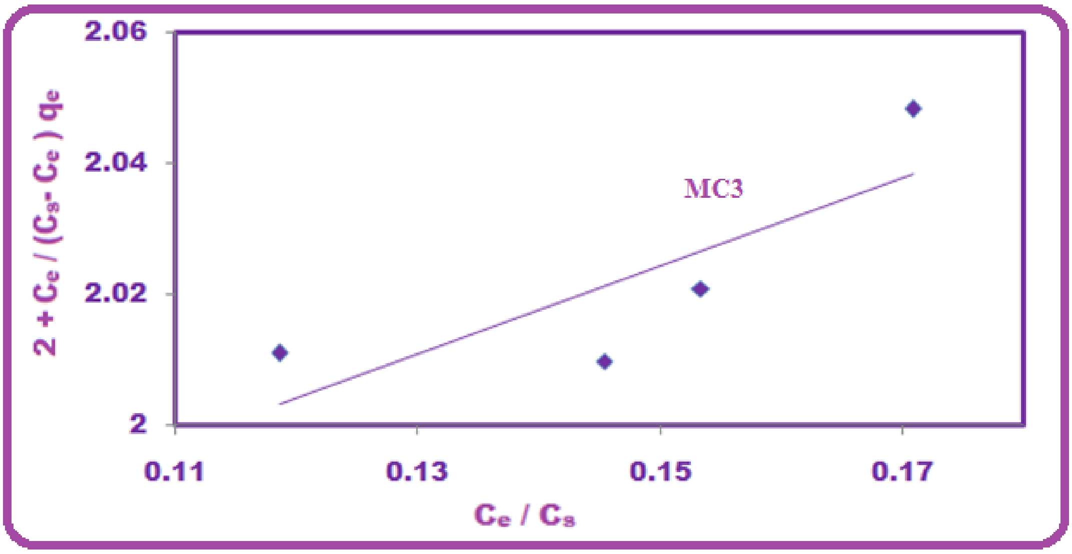


Fig 12 BET isotherm plot for the removal of Pb^{2+} ion by MC3

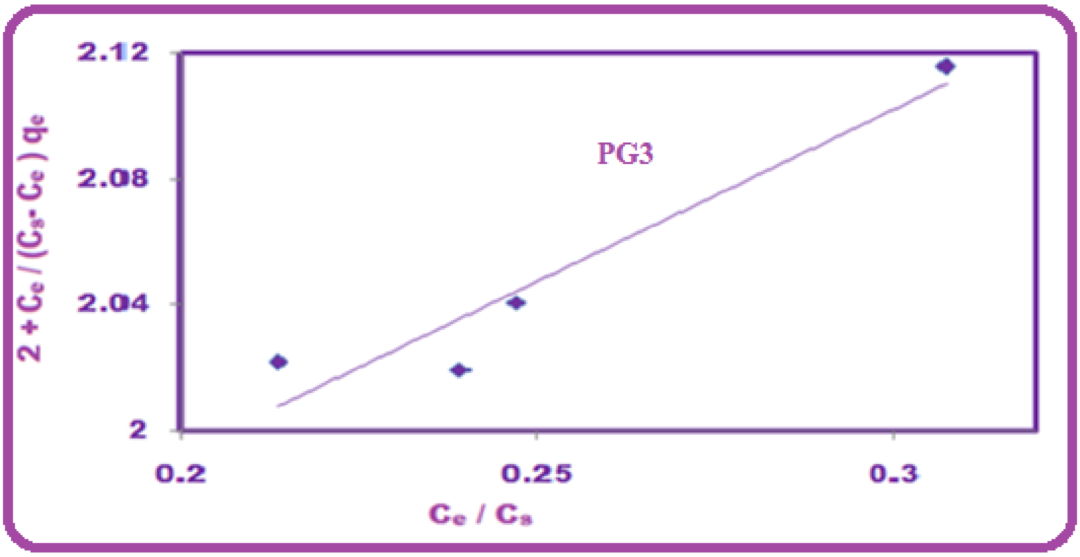


Fig 13 BET isotherm plot for the removal of Pb^{2+} ion by PG3

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.

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 (23.22- 36.01 mg/g) and b (0.0602 - 0.0.0798 L/mg^{-1}) were determined from the slope and intercept of the plot, respectively. The applicability of Langmuir isotherm suggested a 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

Table.3. Results from correlation analysis on testing the applicability of adsorption isotherms for the removal of Pb^{2+} by various adsorbents..

Parameter	**Lead (II) ion**			
	RFR	**MI3**	**MC3**	**PG3**
<u>Freundlich isotherm</u>				
n	0.822	0.843	0.827	0.799
K	3.078	1.945	1.623	1.587
Correlation coefficient (r)	0.9788	0.9993	0.9971	0.9884
<u>Langmuir isotherm</u>				
Q (mgg^{-1})	36.01	32.04	27.88	23.22
b (Lmg^{-1})	0.0798	0.0658	0.0602	0.0698
Correlation coefficient (r)	0.9921	0.9947	0.9923	0.9912
R_L	0.321	0.301	0.321	0.358
<u>BET isotherm</u>				
Q (mgg^{-1})	1.444	1.287	1.124	1.022
b (Lmg^{-1})	9.875	5.022	4.225	4.301
Correlation coefficient (r)	0.8366	0.8154	0.9145	0.8925

.The parameter, R_L indicates the shape of the isotherm. The R_L values obtained were in between 0 and 1 (0.0.301 to 0.358), 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 Table 3 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**

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].

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

First order kinetics model takes the form,

$$\log(q_e - q_t) = \log qe - k_1 t / 2.303 \qquad \text{--------(12)}$$

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^{-1})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

Pseudo second order kinetics model takes the form

$$t / q_t = 1 / k_2 q_e^2 + t / q_e \qquad \text{-----------(13)}$$

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 (min^{-1})is the second order rate constant. Values of k_2 can be obtained from linear plots of t /q_t versus‘t’

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

Adsorbents	Correlation coefficient (R)	
	pseudo First order	pseudo Second order
RFR	0.9921	0.8542

MI3	0.9904	0.8123
MC3	0.9823	0.8532
PG3	0.9992	0.9002

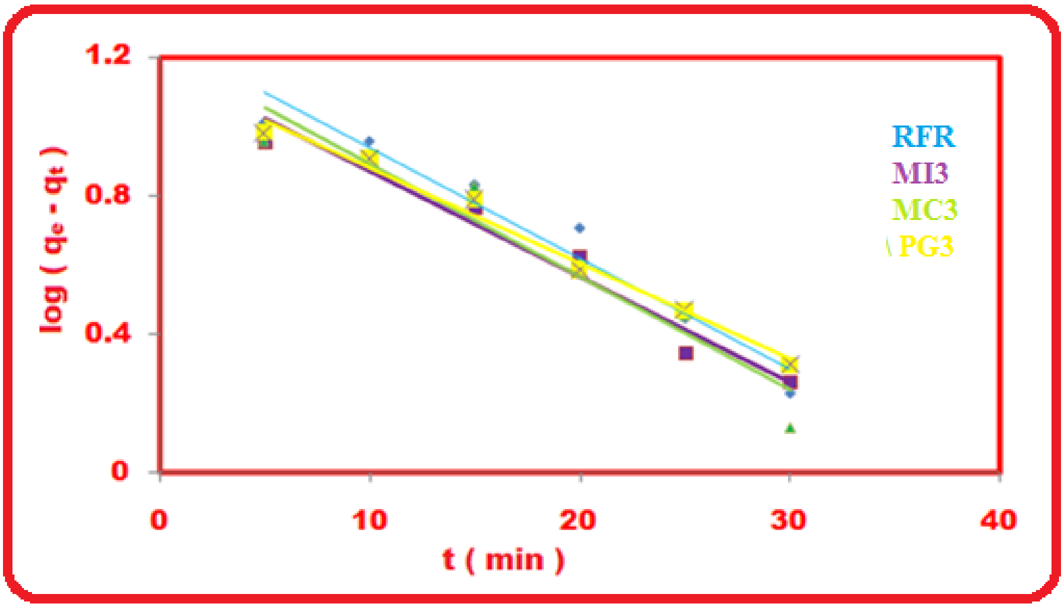


Fig 14. Test of pseudo first order equation for adsorption of Pb^{2+} ion by various adsorbents

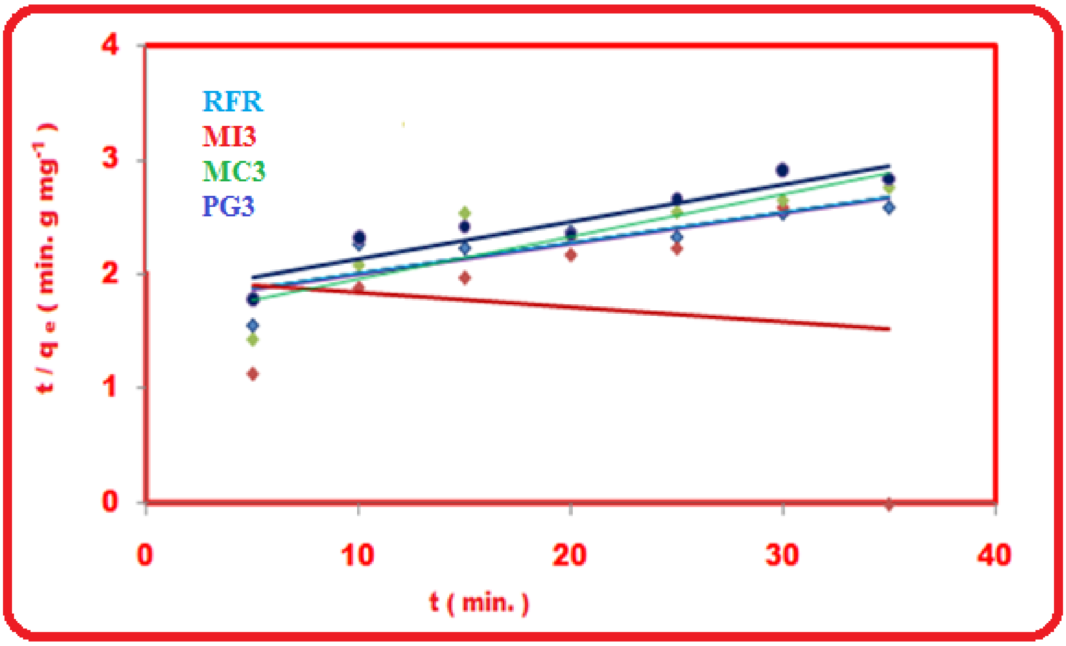


Fig 15. Test of pseudo second order equation for adsorption of Pb^{2+} ion by various adsorbents

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

$$SSE = \sum \frac{\left(q_{e(expt.)} - q_{e(cal.)}\right)^2}{q^2_{e(expt.)}} \qquad \text{……..….(14)}$$

Table 5.Fitness of the kinetic models

Adsorbents	Graph	R	K_1	Log q_e	Q_{ecal}.	Q_{eexpt}.	SSE
RFR	$\log(q_e - q_i)$ vs t	0.9921	0.0715	1.183	15.24	13.65	0.01356
MI3		0.9904	0.0724	1.172	14.85	13.50	0.00207
MC3		0.9823	0.0748	1.168	14.52	13.44	0.00645
PG3		0.9992	0.0687	1.153	14.22	13.48	0.00301

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.

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].

$$K_c = q_e / C_e \qquad \text{……..…. (15)}$$

$$\Delta G^\circ = -RT \ln K_c \qquad \text{……..….(16)}$$

$$\log K_c = \Delta S^\circ / (2.303R) - \Delta H^\circ / (2.303RT) \qquad \text{……..….(17)}$$

Where,

Kc is the equilibrium constant, q_e and C_e 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 6.16 and Table 6.6

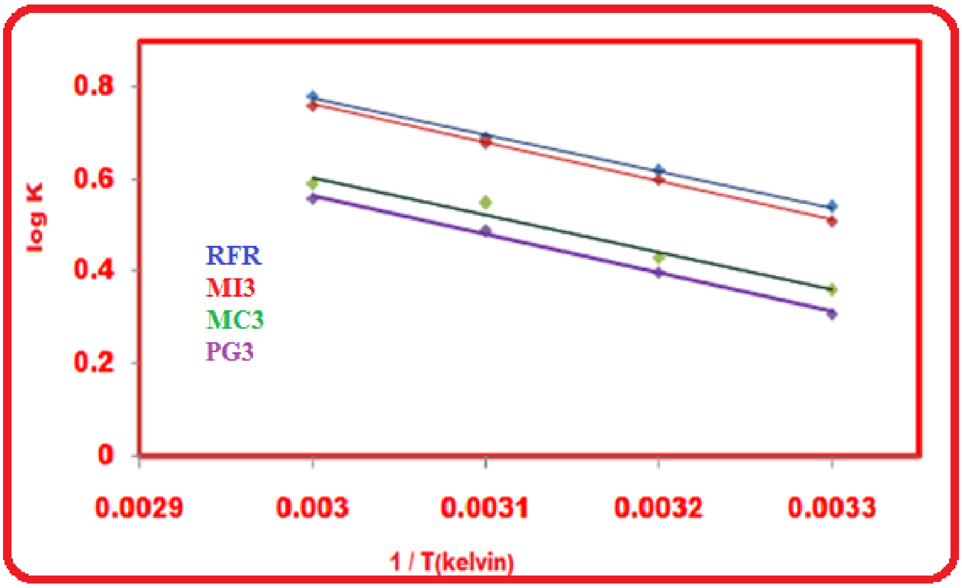


Fig 16 Van’t Hoff plots for the adsorption of Pb (II) ion on various adsorbents

Table.6 Thermodynamic parameters for the removal of Pb^{2+} ion by various adsorbents

Samples	-ΔG KJ. mol^{-1}	ΔH KJ. mol^{-1}	ΔS $KJ.K^{-1}mol^{-1}$
RFR	.4.61	22.54	0.0656
MI3	2.63	19.07	0.0602
MC3	1. 94	17.88	0.0583
PG3	2.57	18.88	0.0597

The thermodynamic parameters can be calculated from Vant Hoff plot (Fig16). The positive value of ΔHº (17.31 to 22.54 KJ/mol.) for the adsorption of Pb^{2+} by all adsorbents showed endothermic nature of the overall process and negative ΔG^0 value (-1.76 to -4.61 KJ/ mol) indicates that the adsorption process is spontaneous [31, 32]. The positive value of ΔS (0.0487 to 0.0592 $KJ.K^{-1}mol^{-1}$) indicates that the increase in randomness adsorption process due to the increase of other eliminated ions into the solution.

CONCLUSION

The conclusions derived from the present studies are:

- The percentage removal of Pb (II) ions increases with the decrease in initial concentration and increase in contact time.
- The adsorption data obeyed the Langmuir isotherms and indicate the formation of unimolecular layer of adsorbents.

- The adsorption process obeys pseudo first order kinetic equations.
- Hence PG3, MI3 and FMC3 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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