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Red Mud as Adsorbent to Remove Lead (II) from Aqueous Solutions

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Abstract

Batch experiments under different experimental conditions have been performed to evaluate the adsorption characteristics of red mud. Freundlich and Langmuir adsorption isotherm models have been used to discuss the data obtained. Kinetics of adsorption have been discussed using Lagergren first-order equation, pseudo-second-order equation and intra-particle diffusion models. Thermodynamic parameters such as change in free energy ΔG, change in enthalpy ΔH and change in entropy ΔS have been evaluated and discussed to know the spontaneity and feasibility of the process.

Keywords: Red mud, adsorption, Pb(II) ion, langmuir isotherm, lagergren first-order equation, pseudo-second-order equation.

Introduction

Lead is used in many industries such as battery, plumbing, painting, petrochemical, smelting etc. The effluents from these industries contain lead which pollute soil and river and cause serious problem to environment and human health.

Adsorption method is effective and economical among various methods to remove heavy metals from aqueous system. Though activated carbon is a very good adsorbent but it is expensive. A large number of substances have been used as adsorbents along with red mud[1-5].

Red mud is a by-product of aluminium industry. It mainly consists of oxides of aluminium, iron, silicon and calcium and has been suggested as a cheap adsorbent to remove heavy metals from aqueous system[6-10].

The aim of this study is to examine the removal characteristics of red mud to remove lead(II) from aqueous solutions. The adsorption of lead(II) ion on red mud has been evaluated as a function of initial lead ion concentration, contact time, temperature, pH and particle size. The equilibrium data has been discussed by Langmuir and Freundlich adsorption isotherm and kinetics have been discussed using Lagergren first order, pseudo second order and intraparticle diffusion model. Besides, some thermodynamic parameters such as change in Gibbs free energy ΔG, change in enthalpy ΔH and change in entropy ΔS have been calculated and discussed.

Material and Methods

Red mud was obtained from BALCO, Korba(C.G). For characterization and morphology of red mud SEM and FTIR were obtained from SAIF-IIT Bombay. Stock solutions of Pb(II) was prepared from A.R. quality $Pb(NO_3)_2$. 1.0 g of red mud was added in 25 ml aqueous solution of Pb(II) of given concentration in different glass bottles. It was then agitated in a shaking machine. After pre-determined time interval, the solutions were centrifused, filtered and analyzed for concentration by spectrophotometer. Initial Pb(II) concentrations used were 100, 150, 200 and 250 mgL^{-1}. Different contact time intervals 20, 40, 60, 80, 100, 120 and 140 min. Various pH values were 2.0, 4.0, 6.5 and 8.0. Different temperatures for adsorption were 303K, 313K and323K and particle size (45μ, 75 μ and 150μ). For equilibrium study, initial Pb(II) concentration used were 25, 50, 75, 100, 125, 150, 175, 200, 225 and 250 mgL^{-1} .

The following mass balance equation[11] was used to calculate the amount of Pb(II)ion adsorbed : $q_e = V (C_i - C_e) /m$

where C_i and C_e are Pb(II) ion concentration in mgL^{-1} before and after adsorption respectively, V is the volume of adsorbate in litre, and m is the weight of the adsorbent in grams. The percentage of removal of Pb(II) ion was calculated from the following equation[11]: Removal % $= 100 (C_i - C_e)/ C_i$

Results and Discussion

Characterization of red mud: Different red mud contain the same basic chemical elements but in different proportions. Different compounds present are Fe_2O_3, Al_2O_3, SiO_2, CaO, Na_2O and TiO_2.

Figure-1(a) is the SEM spectrum of red mud before adsorption and 1(b) after adsorption. It is evident from figure 1(b) that adsorption of lead has taken place between 1.7 to 2.7 keV.
The FTIR spectra of red mud before and after adsorption is shown in figure-2. It shows a broad band around 3500 cm^{-1},

which is attributed to surface -OH group of silanol groups (-Si-OH) and adsorbed water molecules on the surface[12]. A peak around 1400 cm^{-1} –1600 cm^{-1} is attributed to presence of carbonate. A strong peak at 995.22 cm^{-1} is due to stretching vibration of Si(Al)-O group[13]. Figure 2(b) shows new peaks at 2922.94 cm^{-1}, 2262.68 cm^{-1} and 837.69 cm^{-1}. These additional bands and variation in vibrational frequencies indicates the presence of lead on red mud surface.

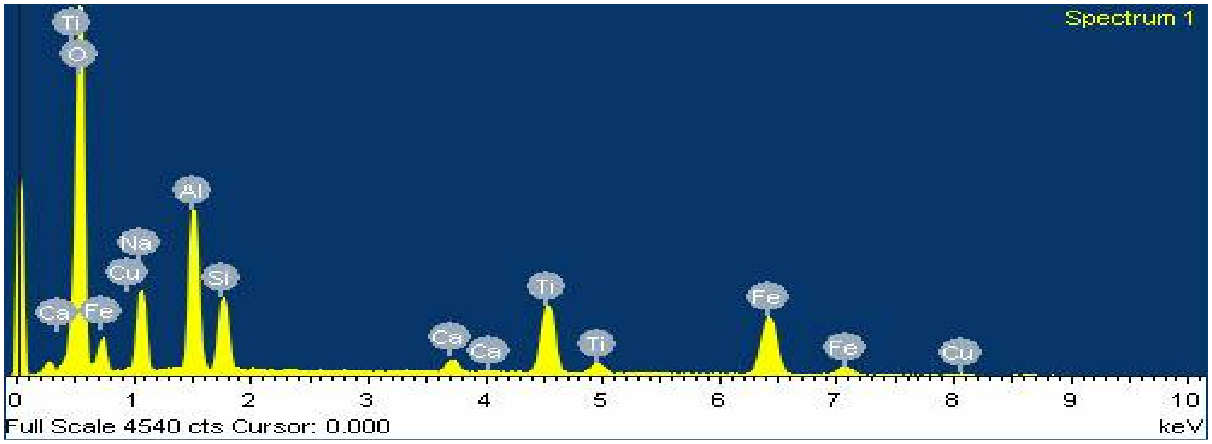

Figure-1
(a) Before adsorption (45µ)

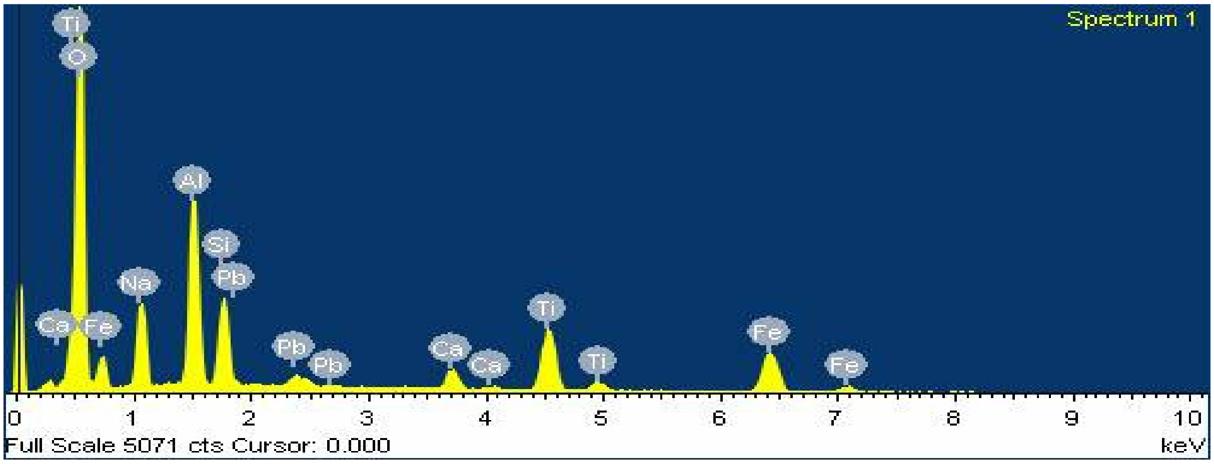

Figure-1
(b) After adsorption (45µ)

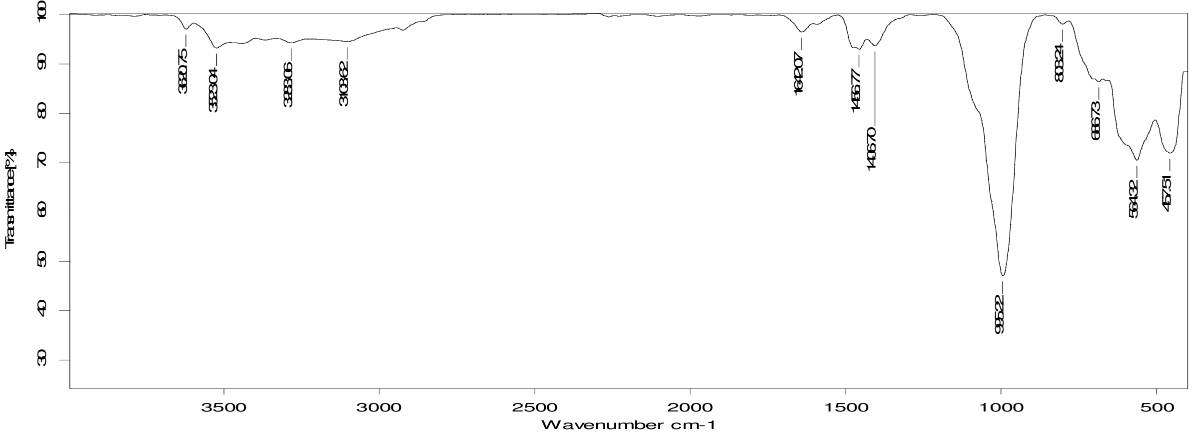

Figure-2
(a) FTIR before adsorption

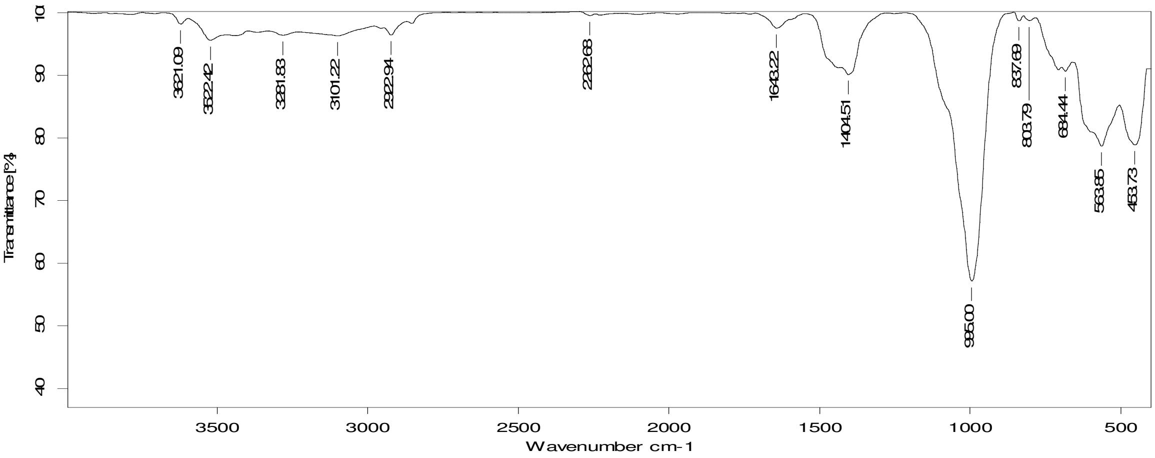

Figure-2
(b) FTIR after adsorption

Effect of initial Pb(II) ion concentration: Percentage removal of Pb(II) ion versus initial concentration has been shown in figure-3. It shows that with increase in initial Pb(II) ion concentration, the percentage removal of Pb(II) ion decreases from 85.20% at 100 mgL^{-1} to 70.08% at 250 mgL^{-1}. The reason may due to the fact that adsorbents possess a limited number of active sites and these sites become saturated at certain concentration.

However, q_e(adsorbed amount at equilibrium in mgg^{-1}) increases with initial concentration of lead(II) ion which is evident from figure-4. It increases from 2.13 mgg^{-1}at 100 mgL^{-1} to 4.38 mgg^{-1} at 250 mgL^{-1}. The necessary driving force to overcome the mass transfer resistance of Pb(II) ion between the aqueous and the solid phase is possibly provided by the initial concentration of metal ion. The increase in Pb(II) ion concentration also increases the interaction between Pb(II) ions in the aqueous phase and the red mud surface resulting in higher adsorption of Pb(II) for the given mass of red mud[14].

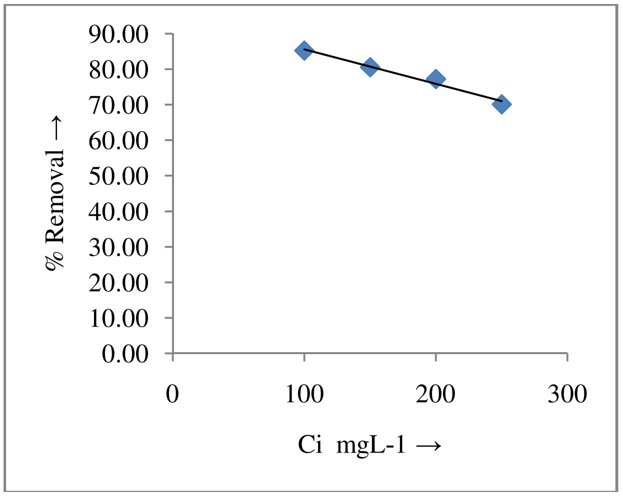

Figure-3
Effect of initial conc. on Pb(II) adsorption

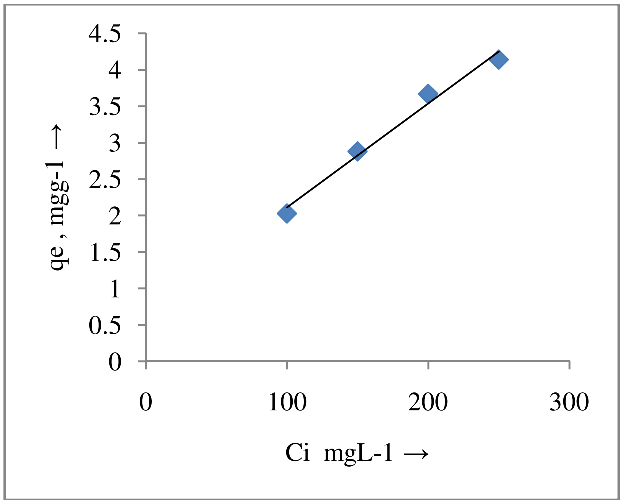

Figure-4
Effect of initial conc. on Pb(II) adsorption

Effect of contact time: Removal of Pb(II) ion by red mud has been shown in figure-5. Adsorption increases with time and equilibrium is reached in 120 min. Adsorption rate is fast initially which may be due to more number of active sites on adsorbent surface. As adsorption progresses, number of active sites decreases and the rate of adsorption slows down[15-16].

Effect of pH: Figure-6 shows the effect of pH on adsorption of Pb(II) ion on red mud. The amount of Pb(II) adsorbed on red mud increased from 1.88 mgg^{-1} (75.2 %) to 2.41 mgg^{-1} (96.4 %) by increasing pH of solution from 2.0 to 8.0.

Speciation studies[17] have shown that at low pH lead remains in the form of Pb^{++} and at higher pH in the form of $Pb(OH)^+$. It is probable that in acidic medium positively charged surface of adsorbent does not favour the association of cationic adsorbate species. In alkaline medium negatively charged surface offers the suitable sites for the adsorption of Pb^{++} and $Pb(OH)^+$.

Effect of temperature: Figure-7 shows the effect of temperature on adsorption. It is evident that adsorption of Pb(II) ion on red mud increases from 2.13 mgg^{-1} (85.20 %) to 2.39mgg^{-1} (95.6 %) by increasing temperature from 303K to 323K indicating the process to be endothermic The rate constant of adsorption are 2.09 x 10^{-2}, 3.74 x 10-^{2} and 4.11 x 10^{-2} per min at 303K, 313K and 323K respectively which indicate that the rate of adsorption also increases with temperature.

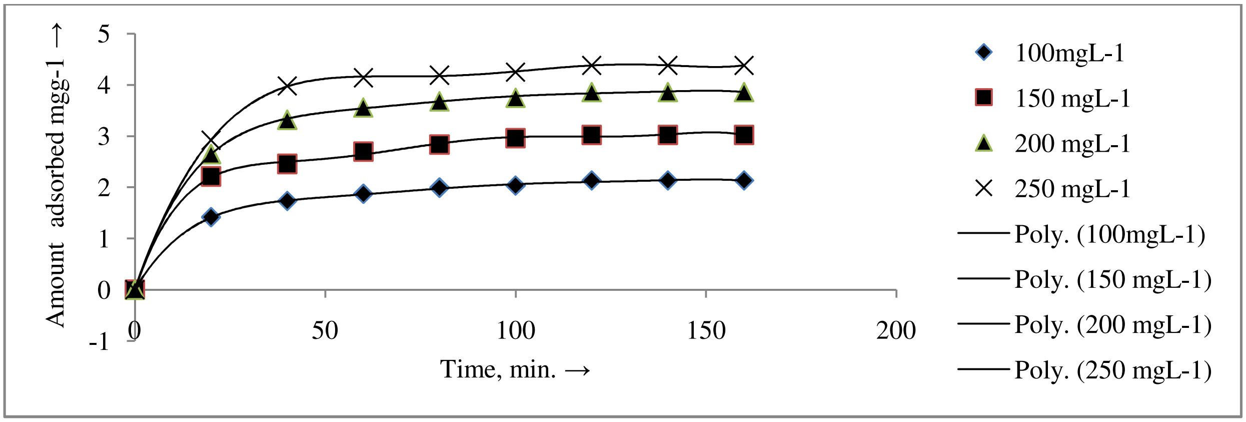

Figure-5
Effect of contact time on adsorption of Pb(II) ion on red mud

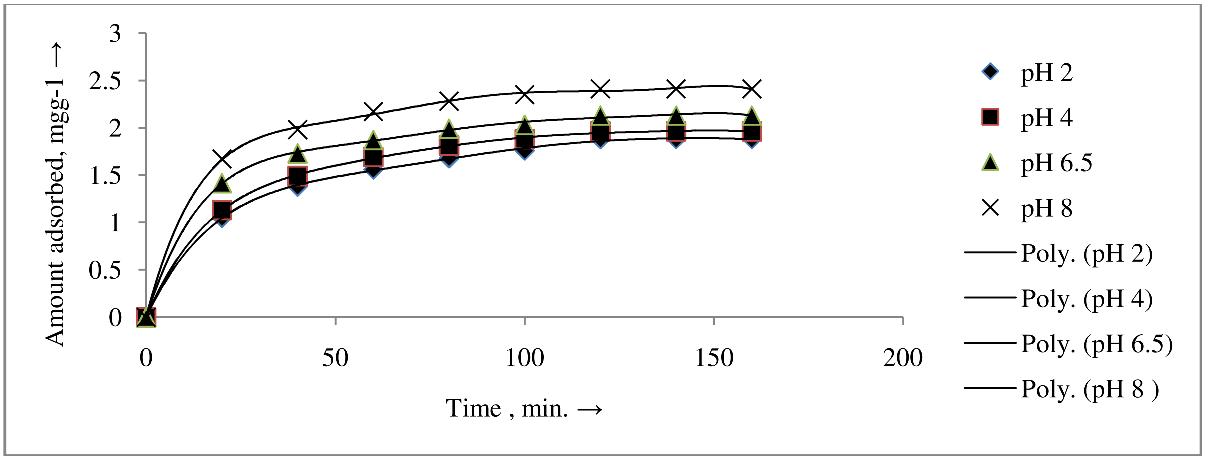

Figure-6
Effect of pH on adsorption of Pb(II) ion on red mud

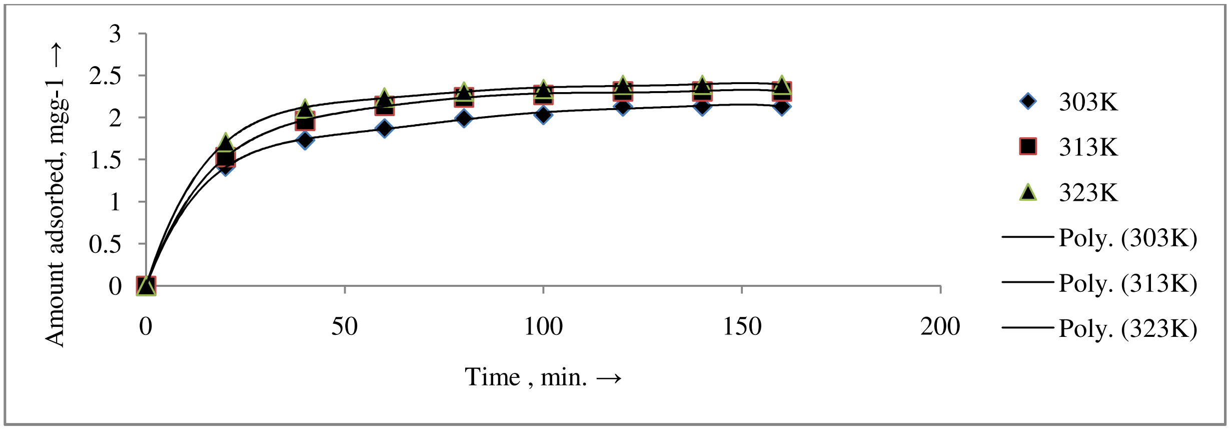

Figure-7
Effect of temperature on adsorption of Pb(II) ion on red mud

Effect of particle size: The effect of particle size of red mud on adsorption of Pb(II) ion has been shown in figure-8. The amount of Pb(II) ion adsorbed on red mud increases from 1.91 mgg^{-1} (76.4%) to 2.13 mgg^{-1} (85.20 %) by decreasing particle size of red mud from 150 µ to 45 µ. This increase in amount of Pb(II) adsorbed on red mud is due to increase in surface area of red mud particles with decreasing particle size.

Adsorption Isotherm: According to the Langmuir adsorption isotherm model, adsorption occurs on a homogeneous surface by monolayer adsorption without interaction between the adsorbed molecules[18]. The linear form of Langmuir isotherm[18] is given as:

$$C_e/q_e = 1/\varphi.b + C_e/\varphi$$

where q_e is the amount of lead adsorbed per gram of the adsorbent at equilibrium, C_e (mgL^{-1}) is equilibrium concentration of Pb(II) and φ and b are Langmuir constants related to adsorption capacity and adsorption energy respectively. The plot of C_e/q_e versus C_e has been shown in figure-9. It is linear which shows that Langmuir isotherm is applicable. The value of φ and b have been calculated from slope and intercept of the straight lines obtained and are given in table-1. The result shows that the values of φ and b increase on increasing the temperature.

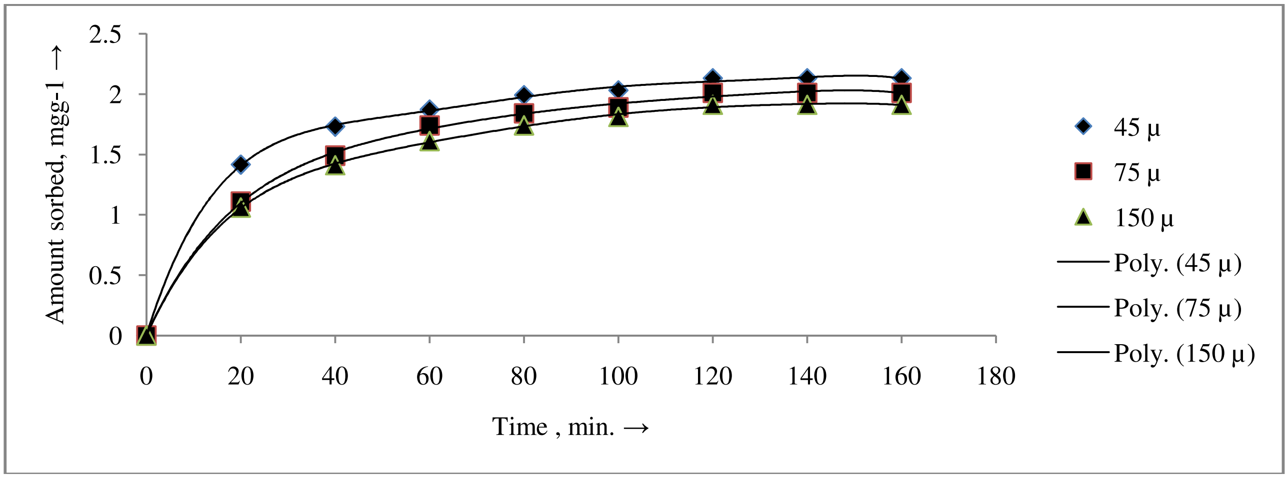

Figure-8
Effect of particle size on adsorption of Pb(II) ion on red mud

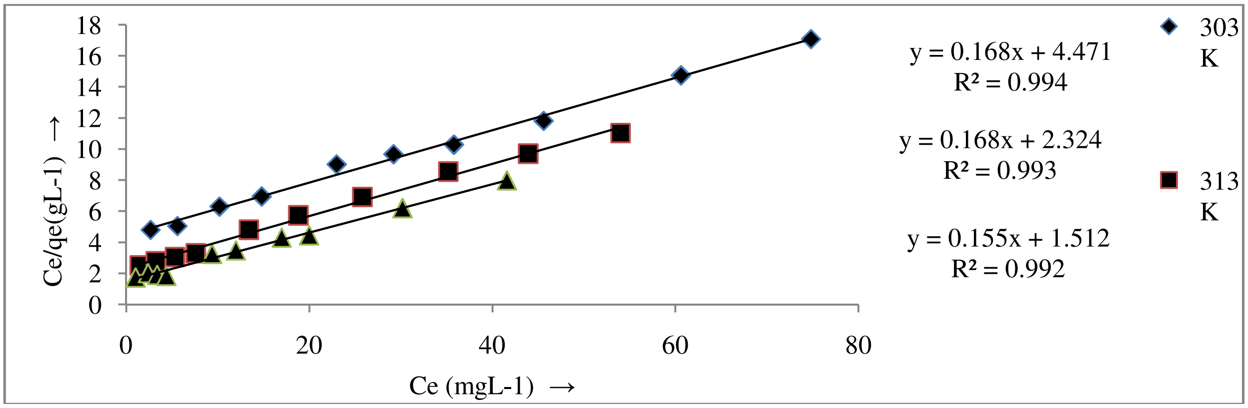

Figure-9
Langmuir adsorption isotherm for the adsorption of Pb(II) ion on red mud

Table-1
Adsorption isotherm constants for adsorption of Pb(II) on red mud

Langmuir Isotherm Results				Freundlich Isotherm Results		
Temp.(K)	Correlation coefficient, R^2	φ	b	Correlation coefficient, R^2	K_f	n
303	0.994	5.95	0.038	0.983	0.469	1.86
313	0.993	5.95	0.072	0.973	0.771	2.09
323	0.992	6.45	0.103	0.943	0.971	2.06

Freundlich adsorption isotherm model can be applied to heterogeneous surfaces involving multilayer adsorption[19]. The linearized Freundlich equation is represented as:

$$\log q_e = \log K_f + 1/n \log C_e$$

where q_e is the amount of Pb(II) ion adsorbed (mgg^{-1}), C_e is the equilibrium concentration of Pb(II) ion in solution (mgL^{-1}) and K_f and n are constants for the adsorption capacity and intensity of adsorption respectively. Plots of $\log q_e$ versus $\log C_e$ has been shown in figure-10 and values of K_f , n and R^2 (correlation coefficient) value have been obtained and given in table-1. Comparing R^2 value shows that both isotherms are applicable. However, experimental data fits better in Langmuir equation.

A dimensionless separation factor (R_L) has been calculated using following equation[19]:
$R_L = 1/1+b.C_i$

where C_i is the initial concentration in mgL^{-1} and b is Langmuir constant (L/mg) related to adsorption energy. It gives important information about the nature of adsorption. If $0<R_L<1$, it indicates the adsorption process to be favourable and if $R_L>1$ the process is unfavourable. It can also be explained that when $b>0$, adsorption system is favourable[16]. The calculated values are given in table- 2. The values $0<R_L<1$ and $b>0$ suggest that the process is favourable.

Adsorption kinetics: The Lagergren first order[20], pseudo-second-order[21] and Intraparticle diffusion kinetic models[22] have been used to discuss the adsorption kinetics.

The Lagergren first order kinetic model: The Lagergren first order rate equation is represented as :

$$\log (q_e - q_t) = \log q_e - k_1.t/2.303$$

where q_e and q_t are the amounts of Pb(II) adsorbed (mgg^{-1}) at equilibrium and at time t , respectively. K_1 is the Lagergren rate constant (min^{-1}). Plots of $\log (q_e - q_t)$ versus t has been shown in figure- 11. Values of q_e and K_1 at different initial concentrations have been calculated from the slope and intercept respectively. These values have been given in table-3.

Table-2
Dimensionless separation factor (R_L)

-----	R_L		
Ci (mgL^{-1})	303 K	313 K	323 K
25	0.515	0.356	0.282
50	0.347	0.217	0.164
75	0.262	0.156	0.116
100	0.210	0.122	0.089
125	0.175	0.100	0.073
150	0.151	0.084	0.061
175	0.132	0.073	0.053
200	0.117	0.065	0.047
225	0.106	0.058	0.042
250	0.096	0.052	0.038

The pseudo-second-order kinetic model: The adsorption data have been applied to pseudo-second-order kinetic model also . The equation is represented as

$$t/q_t = 1/K_2.q_e^2 + t/q_t$$

where K_2 is the rate constant of second order adsorption (g/mg/min.). Plots of t/q_t versus t has been shown in (figure-12). Values of K_2 and q_e have been calculated from the slope and intercept of the graph respectively. These values have been given in table- 3.

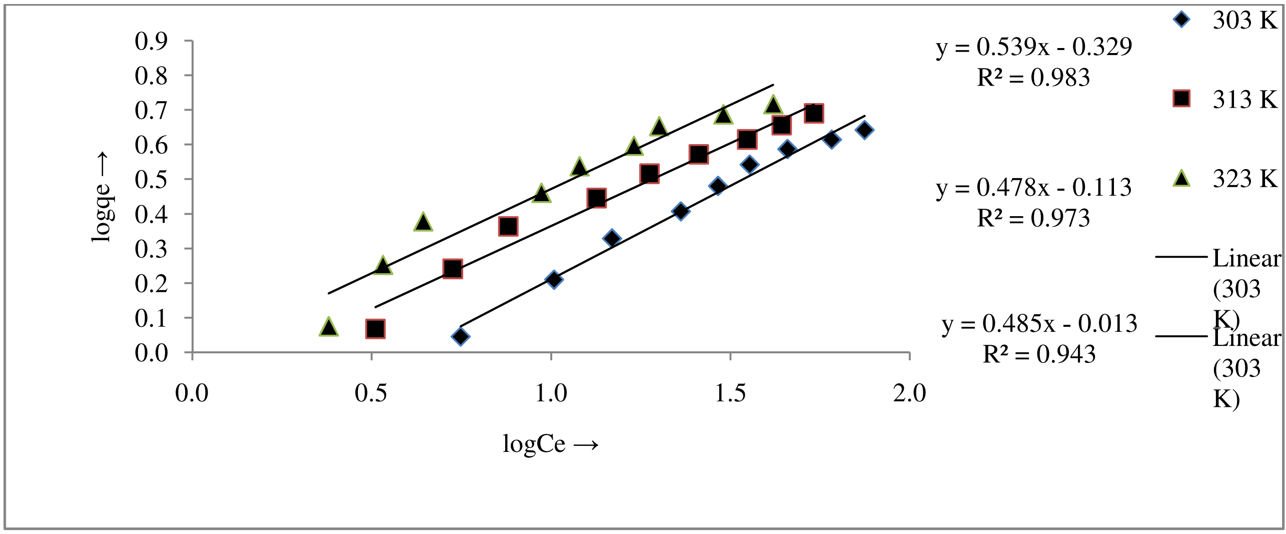

Figure-10
Freundlich adsorption isotherm for adsorption of Pb(II) ion on red mud

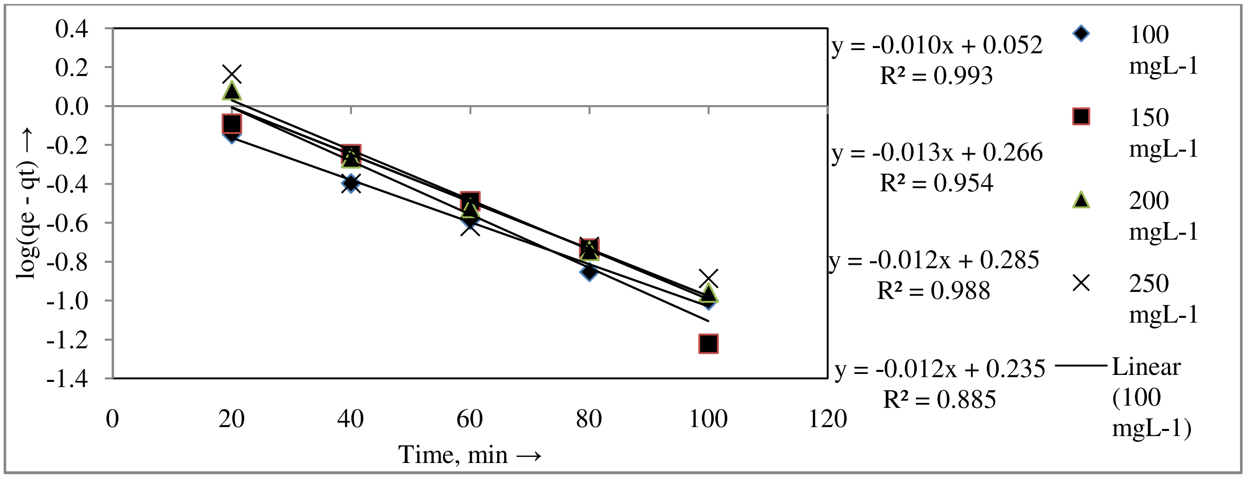

Figure-11
Lagergren first-order kinetic plot for adsorption of Pb(II) ion on red mud

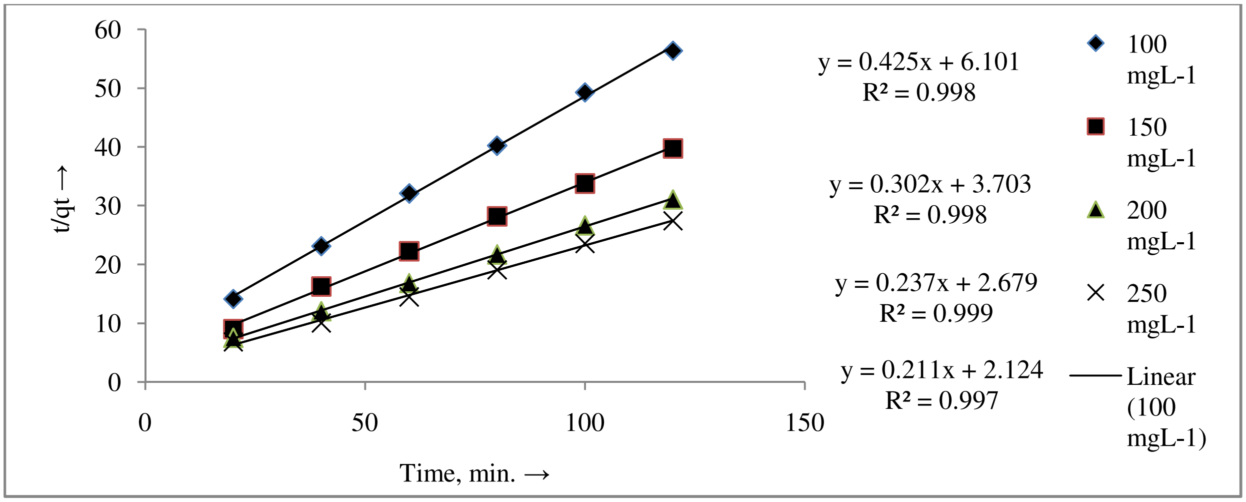

Figure-12
Peudo-second-order kinetic plot for adsorption of Pb(II) ion on red mud

Table-3
Kinetic parameters for adsorption of Pb(II) ion on red mud

	Lagergren first order				**Pseudo- second- order**			**Intraparticle diffusion**		
Conc. mgL^{-1}	**K_1 min^{-1}**	**q_{exp} mgg^{-1}**	**q_{cal} mgg^{-1}**	**R^2**	**K_2 g/mg/min**	**q_{cal} mgg^{-1}**	**R^2**	**K_d $mg/g.min^{1/2}$**	**I**	**R^2**
100	$2.30x10^{-2}$	2.13	1.127	0.993	$2.96x10^{-2}$	2.353	0.998	0.105	1.01	0.961
150	$2.99x10^{-2}$	3.02	1.845	0.954	$2.46x10^{-2}$	3.311	0.998	0.129	1.652	0.988
200	$2.76x10^{-2}$	3.86	1.927	0.988	$2.10x10^{-2}$	4.219	0.999	0.174	2.064	0.896
250	$2.76x10^{-2}$	4.38	1.717	0.885	$2.10x10^{-2}$	4.739	0.997	0.194	2.406	0.766

The Intraparticle diffusion model: The Weber and Morris intraparticle diffusion model is expressed as:

$$q_t = K_d \cdot t^{1/2} + I$$

where I is the intercept which reflects the boundary layer effect and K_d is the intra-particle diffusion rate constant. Plot of q_t versus $t^{1/2}$ has been shown in figure-13. From the slope and intercept the value of K_d and I have been calculated and are given in table- 3. If the plot of q_t versus $t^{1/2}$ is linear and passes through the origin then Intraparticle diffusion is considered to be the sole rate-limiting step[11]. As the linear plots did not pass through the origin, it is evident that intraparticle diffusion is not the only rate limiting step.

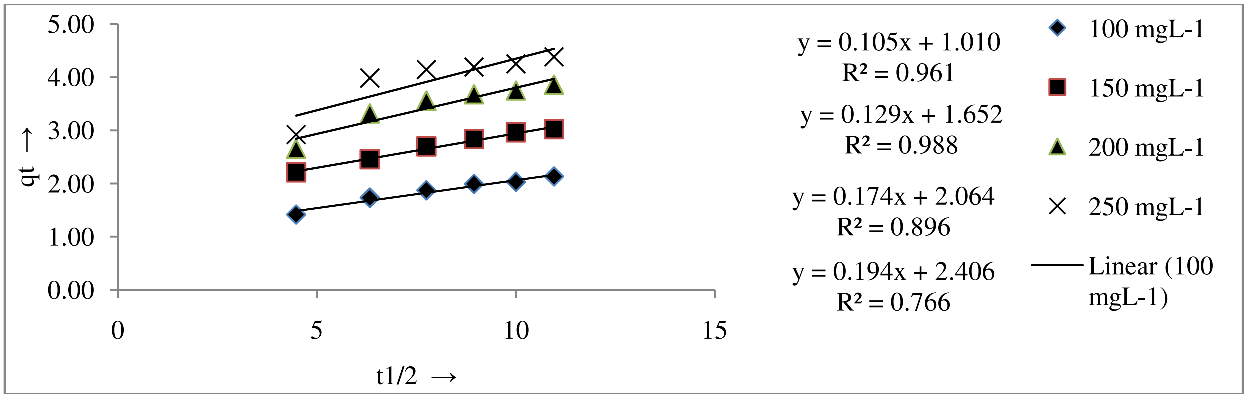

Figure-13
Intraparticle diffusion model for adsorption of Pb(II) ion on red mud

It is evident from table- 3 that pseudo-second-order kinetic model shows high correlation coefficient ($R^2 > 0.99$) at all the studied concentration in comparision to the other kinetic models. Moreover, $q_{e(cal)}$ values agree better with the experimental data in the case of pseudo-second-order kinetic model. In general the rate constant K_2 decreases with increase in concentration. The reason for this may be the possibility of lower competition for surface active sites of adsorbent at lower concentration. As the concentration of the metal ion increases, the competition for the surface active sites increases which decreases the rate[23].

Thermodynamic treatment of the adsorption process: The thermodynamic parameters such as free energy, enthalpy and entropy changes have been calculated using the following equations[24].

$K_c = C_s/C_e$

$\Delta G = - RT \ln K_c$

$\log K_c = \Delta S/2.303\ R - \Delta H/2.303\ RT$

where C_e is the equilibrium concentration in solution in mgL^{-1} and C_s is the equilibrium concentration on the adsorbent in mgL^{-1} and K_c is the equilibrium constant. The Gibbs free energy, ΔG was calculated from the above equation. The values of ΔH and ΔS have been calculated from the slope and intercept of the plot between $\log K_c$ versus 1/T shown in figure-14. All these values are listed in table- 4.

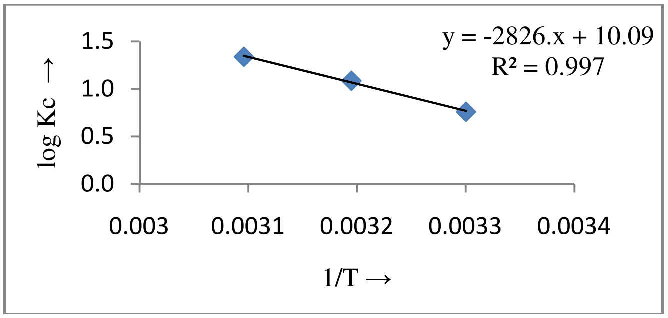

Figure-14
Plot of $\log K_c$ *vs* 1/T

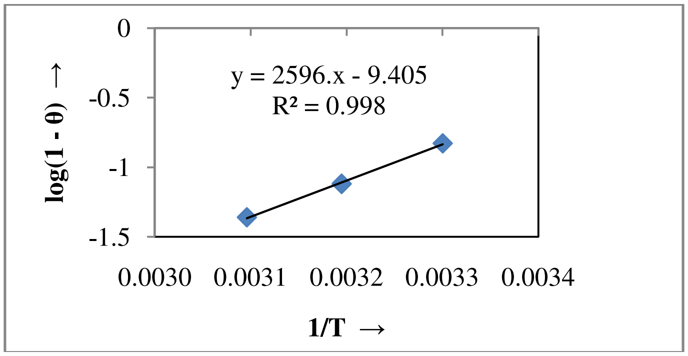

Figure-15
Plot of log(1-θ) *vs* 1/T

The values of activation energy (E_a) and sticking probability (S*) have been calculated from the experimental data. They were calculated using modified Arrhenius type equation related to surface coverage(θ) as follows[25]

$\theta = (1- C_e/C_i)$

$S^* = (1- \theta)e^{-Ea/RT}$

The sticking probability, S*, is a function of the adsorbate/adsorbent system under consideration, depending on temperature and should satisfy the condition $0<S^*<1$ .The values of E_a and S* has been calculated from slope and intercept of the plot of ln(1-θ) versus 1/T shown in figure-15 respectively and have been given in table-4.

Table-4
Thermodynamic parameters for adsorption of Pb(II) ion on red mud

Temp. K	ΔG , kJ/mol	ΔH , kJ/mol	ΔS , J/mol	E_a , kJ/mol	S*, J $K\ mol^{-1}$
303	-4.411	54.11	193.19	49.705	$3.93X10^{-10}$
313	-6.501				
323	-8.268				

It is evident from table-4 that as ΔG values are negative , the process is spontaneous. Endothermic nature of adsorption is indicated by positive ΔH value . The positive value of ΔS shows the affinity of the adsorbent for the Pb(II) ions. The value of E_a has been found to be 46.048 kJ mol^{-1} for the adsorption . The endothermic nature of the adsorption process is supported by positive value of E_a .This is in accordance with the positive values of ΔH. Since S*<<1, it indicates that the probability to stick on surface of red mud is very high[26].

Mechanism: Speciation[17] of Pb(II) with varying pH has been shown in figure-16.

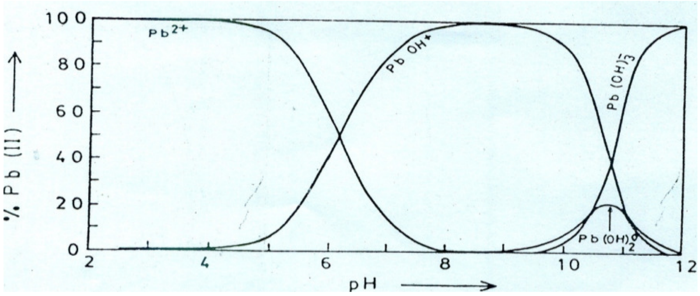

Figure-16
Speciation of Pb(II) with varying pH

It is evident that at lower pH, lead is in the form of Pb^{+2} and at higher pH it is in the form of $Pb(OH)^+$. It is probable that in acidic medium positively charged surface of adsorbent does not favour the association of cationic adsorbate species. In alkaline medium negatively charged surface offers the suitable sites for the adsorption of Pb^{+2} and $Pb(OH)^+$ species[27,28].

$$M-OH \xrightarrow{OH^-} MO^-$$
$$MO^- + Pb^{+2} \longrightarrow MOPb^+$$
$$MO^- + Pb(OH)^+ \longrightarrow MOPb(OH)$$

where M represents the adsorbent surface.

Conclusion

It is evident that initial Pb(II) ion concentration, contact time, pH and temperature have marked effect on adsorption. The equilibrium data are best explained by Langmuir adsorption isotherm. Kinetics of adsorption follows second order rate equation. Thermodynamic parameters also favour the adsorption. It is expected that red mud may be used as an efficient adsorbent under suitable conditions.

Acknowledgement

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