Received: 01-02-2014
Accepted: 28-03-2014

ISSN: 2321-4902
Volume 1 Issue 6

Online Available at www.chemijournal.com

International Journal of Chemical Studies

Red Mud as a Low Cost Adsorbent to Remove Cu(II) ion from Aqueous Solutions

Kumar Sujata [1*], Singh D [3], Mishra A.K [3], Upadhyay M [2], Kumar Saroj [3]

1. Department of Chemistry, Kirodimal Institute of Technology Raigarh (C.G), INDIA
   [Email: skumarrgh@rediffmail.com]
2. Department of Chemistry, Dr. C.V. Raman University Bilaspur (C.G), INDIA
3. Department of Chemistry, K. Govt. Arts & Sc. College Raigarh (C.G), INDIA,

In the present study, adsorption characteristics of red mud to remove Cu(II) ion from aqueous solutions have been evaluated under batch mode experiments. To have an idea about the nature of adsorption, Freundlich and Langmuir adsorption isotherm models have been discussed. To know the order of reaction Lagergren pseudo first order and pseudo second order equation have been employed and discussed. Intraparticle diffusion model have been discussed to have an idea of the mechanism of adsorption. Spontaneity and feasibility of the process have been discussed using thermodynamic parameters such as change in free energy, change in enthalpy and change in entropy. Activation energy of the process and sticking probability have been calculated and discussed.

Keyword: Red mud, adsorption, Cu(II) ion, Langmuir isotherm, Lagergren pseudo first-order equation, pseudo-second- order equation.

1. Introduction

Effluents from many industries contain copper and its compounds. These effluents when discharged in nearby river without treatment, they cause pollution to the water and soil which ultimately cause problem to human health as well as environment.

Various methods have been employed and studied to remove heavy metals from aqueous system. However, adsorption method is cheap, easy handling, effective and sludge free. Many substances have been studied as adsorbent along with red mud which is a by-product of aluminium industry. Red mud consists mainly of oxides of Al, Si, Fe, and Ca. These oxides act as active sites for adsorption. Many studies have shown that it can be used as a cheap adsorbent to remove heavy metals from aqueous system [1-5].

In this study, adsorption of Cu(II) ion on red mud has been evaluated as a function of initial copper ion concentration, contact time, temperature , pH and particle size. For equilibrium studies Langmuir and Freundlich adsorption isotherms have been discussed. For kinetics of adsorption Lagergren pseudo first order equation and pseudo second order equation have been discussed. Thermodynamic parameters along with activation energy and sticking probability have been evaluated and discussed.

2. Material and Methods

Red mud was obtained from BALCO, Korba (C.G). As it is alkaline in nature, it was washed with water till nearly neutral, dried at 105 ^{o}C and sieved to get desired particle size. For its characterization and morphology XRF, SEM and FTIR were obtained from SAIF-IIT Bombay. A.R. quality $CuSO_4$ was used to prepare stock solutions.

In 25 ml of aqueous solution of Cu(II) of given concentration 1.0 g of red mud of desired size was added. It was then agitated in a shaking

machine at desired temperature and pH. After pre-determined time interval, the solution was centrifused, filtered and analyzed for remaining concentration of metal ion by spectrophotometer. Different parameters were: initial metal ion concentration as 25, 50, 75, 100, 125, 150, 175, 200, 225 and 250 mgL^{-1} for equilibrium study and 100, 150, 200 and 250 mgL^{-1} for rate study; temperature as 303K, 313K and 323K; pH as 2.0, 4.0, 6.5 and 8.0 and particle sizes as 45 µ, 75 µ and 150 µ.

The amount of Cu(II) ion adsorbed was calculated using following mass balance equation [6]:

$$q_e = V (C_i – C_e) /m$$

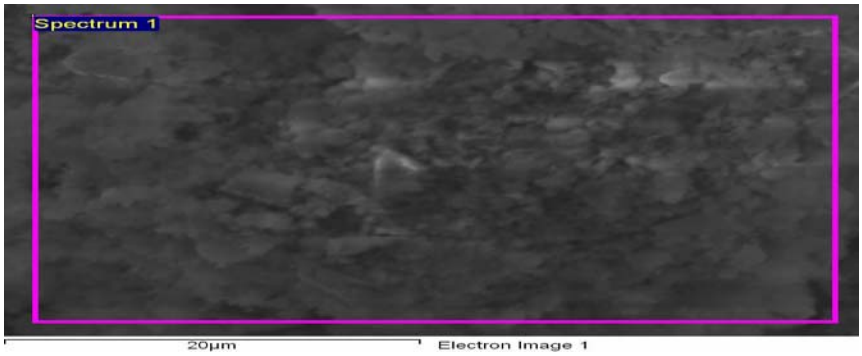
Where, C_i and C_e are Cu(II) ion concentration in mgL^{-1} before and after adsorption respectively, V is the volume of adsorbate in litre, and m is the weight of the adsorbent in grams. The percentage of removal of Cu(II) ion was calculated from the following equation [11]:

$$\text{Removal } \% = 100 (C_i – C_e)/C_i$$

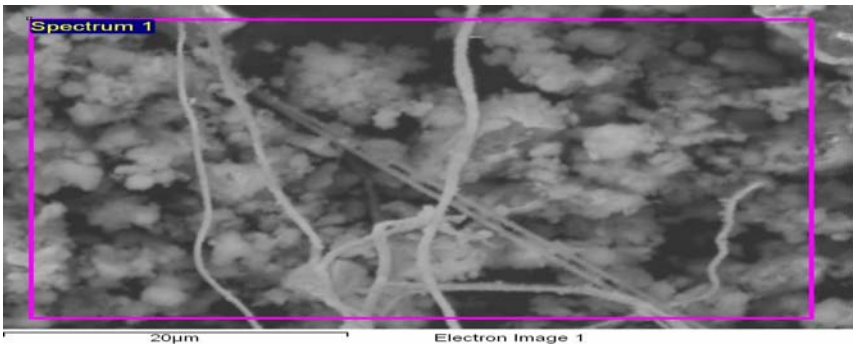
3. Results and Discussion

3.1 Characterisation of red mud

Different red mud contain the same basic chemical elements, but in different proportions. Chemical composition of the present red mud obtained from XRF studies are: SiO_2 (43.17%), Al_2O_3 (13.25%), Fe_2O_3 (41.20%), CaO (1.09%), MgO (0.73%) and TiO_2 (1.26%).



(a) Before adsorption (45 µ)



(b) After adsorption (45 µ)

Fig 1: (a) is the SEM image of red mud before adsorption and 1(b) after adsorption.

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 [7]. A peak around 1400–1600 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 [8]. Figure 2(b) shows some new peaks. These additional peaks and variation in vibrational frequencies indicates that adsorption has taken place on red mud surface.

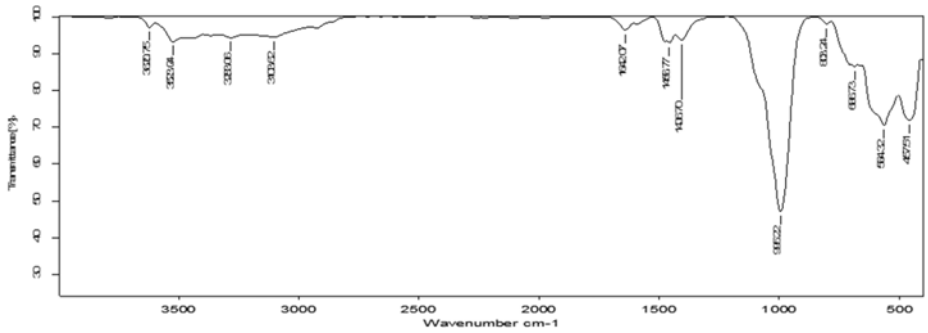


Fig 2(a): FTIR before adsorption

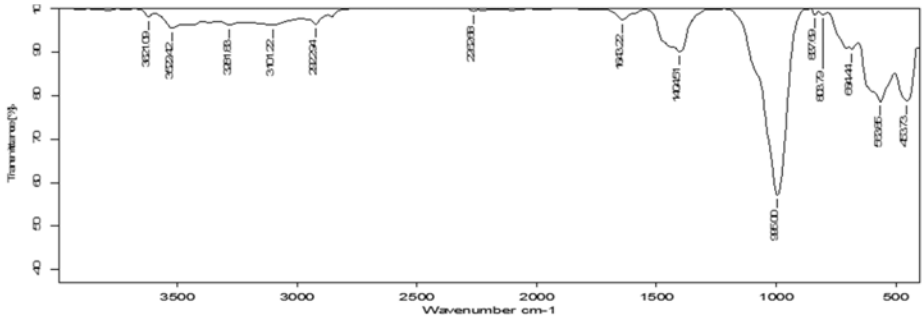


Fig 2(b): FTIR after adsorption

3.2 Effect of initial Cu(II) ion concentration

Figure-3 represents percentage removal of Cu(II) ion versus initial metal ion concentration. It is evident that as initial Cu(II) ion concentration increases from 100 mgL^{-1} to 250 mgL^{-1}, the percentage removal of Cu(II) ion decreases from 79.2% to 70.08%. This may be explained by the fact that adsorbents possess a limited number of active sites and these active sites become saturated at certain concentration.

Figure-4 represents the amount adsorbed at equilibrium q_e (mgg^{-1}) increases with increase in initial metal ion concentration. As initial metal ion concentration increases from 100 mgL^{-1} to 250 mgL^{-1}, the amount adsorbed increases from 1.98 mgg^{-1} to 4.38 mgg^{-1}. The reason might be due to the fact that mass transfer resistance of Cu(II) ion between aqueous phase and the solid phase is possibly overcome by the initial metal ion concentration.

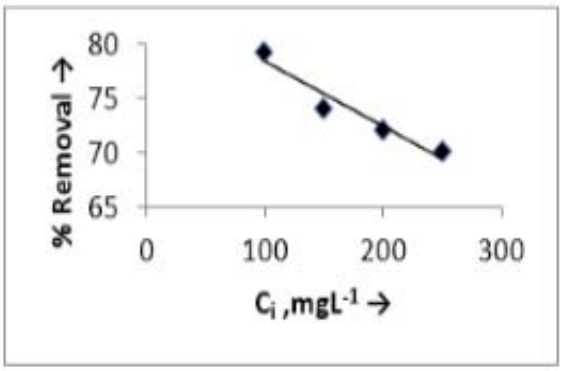


Fig 3: Effect of initial conc. on Cu(II) adsorption

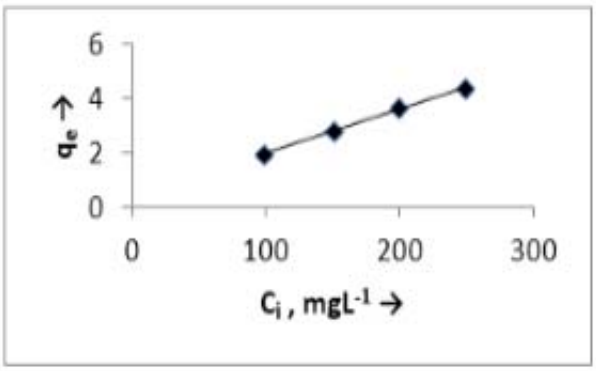


Fig 4: Effect of initial conc. on Cu(II) adsorption

3.3 Effect of contact time

Figure-5 represents the effect of contact time on the adsorption of Cu(II) ion on red mud. It is evident that amount adsorbed increases with time and after 120 minutes equilibrium is reached. Initially the rate of adsorption is fast which gradually slows down till equilibrium is reached. The reason might be the fact that initially more number of active sites are present in the red mud and so the rate of adsorption is fast. With increase in time as adsorption progresses, number of active sites decreases and therefore, the rate of adsorption decreases [10].

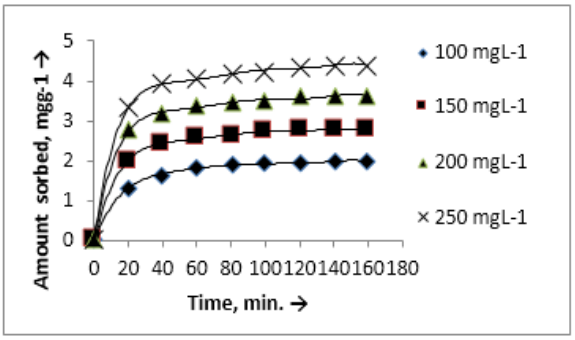


Fig 5: Effect of contact time on adsorption of Cu(II)

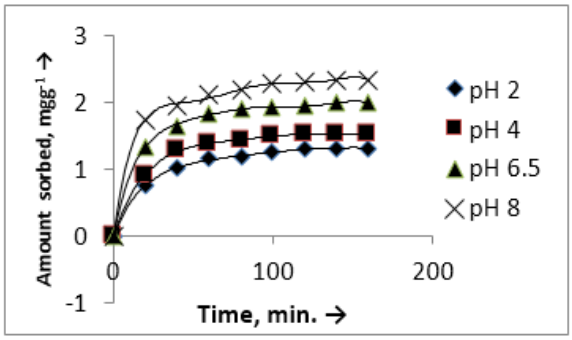


Fig 6: Effect of pH on adsorption of Cu(II) ion

3.4 Effect of pH

Figure-6 represents the effect of pH on adsorption. By increasing pH from 2.0 to 8.0 the amount adsorbed increases from 1.31 mgg^{-1} (52.4%) to 2.33 mgg^{-1} (93.2%). The reason might be due to the fact that at low pH red mud surface acquires positive charge which does not attract Cu^{+2} much. At high pH the surface becomes negatively charged and Cu^{+2} is adsorbed easily, thereby increasing the amount of adsorption [11].

3.5 Effect of temperature

Figure-7 represents the amount of Cu(II) ion adsorbed with temperature. It is evident that with increase in temperature, the amount adsorbed increases. It increases from 1.98 mgg^{-1} (79.20%) at 303K to 2.28 mgg^{-1} (91.2%) at 323K. It indicates the endothermic nature of adsorption. The rate constant of adsorption are $4.03x10^{-2}$, $5.02x10^{-2}$ and $6.63x10^{-2}$ per minute at 303K, 313K and 323K respectively indicating that the rate of adsorption increases with increase in temperature. Increase in adsorption with temperature might be due to increase in mobility of ions as well as increase in pore size of the adsorbent.

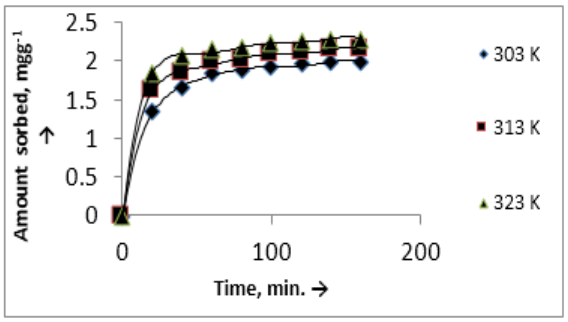


Fig 7: Effect of temperature on adsorption of Cu(II)

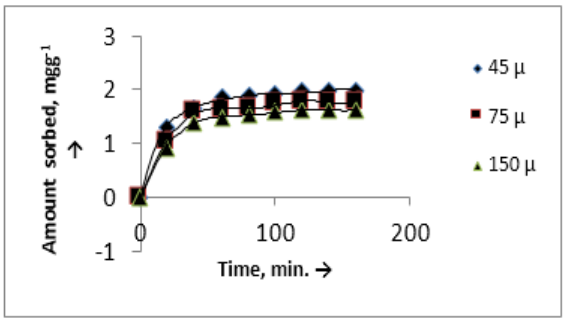


Fig 8: Effect of particle size on adsorption of Cu(II) ion

3.6 Effect of particle size

Figure-8 represents the amount of Cu(II) ion adsorbed with particle size. It is evident that as particle size decreases the amount adsorbed increases. The amount adsorbed at 150 µ is 1.87 mgg^{-1} (65.20%) which increases upto 1.98 mgg^{-1} (79.20%) at 45 µ. The reason might be the fact that as particle size decreases, surface area increases and number of active sites increases thereby increasing adsorption.

3.7 Adsorption Isotherm

Langmuir isotherm model assumes adsorption on a homogeneous surface by monolayer adsorption without interaction between the adsorbed molecules [18]. The linear form of Langmuir isotherm [12] is given as:

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

Where, q_e is the amount of copper adsorbed per gram of the adsorbent at equilibrium, C_e (mgL^{-1}) is equilibrium concentration of Cu(II) ion in the solution and φ and b are Langmuir constants related to adsorption capacity and adsorption energy respectively. Figure-9 shows the relationship between C_e/q_e versus C_e. The plot is linear, indicating the applicability of Langmuir isotherm. Slope and intercept of the straight lines obtained give the value of φ and b respectively and are given in Table- 1. The result shows that the values of φ and b increase on increasing the temperature.

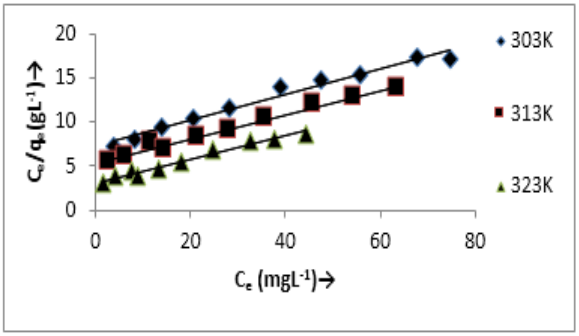


Fig 9: Langmuir isotherm for adsorption of Cu(II)

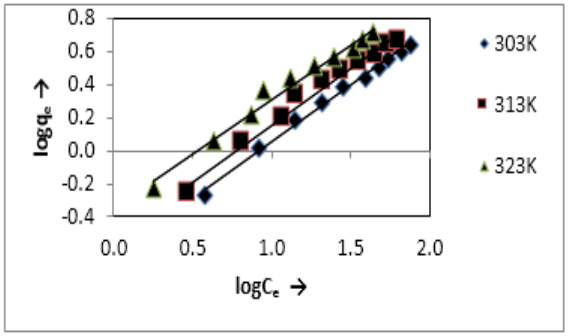


Fig 10: Freundlich isotherm for adsorption of Cu(II)

Table 1: Adsorption isotherm constants for adsorption of Cu(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	0.971	6.89	0.019	0.993	0.235	1.47
313	0.987	7.25	0.027	0.984	0.296	1.47
323	0.979	7.58	0.42	0.980	0.444	1.51

To heterogeneous surfaces involving multilayer adsorption, Freundlich adsorption isotherm model can be applied. The linearized Freundlich equation is represented as [13]:

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

Where, q_e is the amount of Cu(II) ion adsorbed (mgg^{-1}), C_e is the equilibrium concentration of Cu(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. The value of K_f and n increases with increase in temperature. Comparing R^2 value shows that both isotherms are applicable. However, experimental data fits better in Freundlich equation.

3.8 The Lagergren first order kinetic model

The Lagergren pseudo first order rate equation is represented as [14]:

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

Where, q_e and q_t are the amounts of Cu(II) adsorbed (mgg^{-1}) at equilibrium and at time t, respectively. k_1 is the Lagergren rate constant (min^{-1}). Figure-11 represents the plot of $\log(q_e - q_t)$ *versus* t. 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- 2.

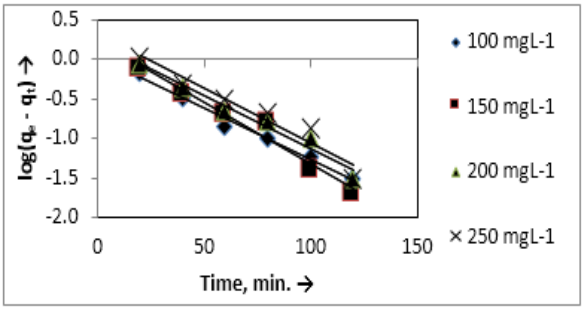


Fig 11: Lagergren pseudo first-order kinetic plot

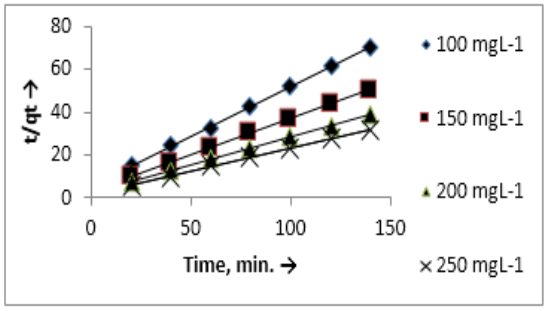


Fig 12: Pseudo-second-order kinetic plot

3.9 The pseudo-second-order kinetic model

The adsorption data have been applied to pseudo-second-order kinetic model also which is represented as [15]:

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

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. Slope and intercept of the graph gives the values of K_2 and q_e respectively, which have been given in Table- 2.

Table 2: Kinetic parameters for adsorption of Cu(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	$2.76x10^{-2}$	1.98	1.06	0.987	$4.03x10^{-2}$	2.146	0.999	0.095	0.995	0.904
150	$3.45x10^{-2}$	2.78	1.67	0.971	$3.60x10^{-2}$	2.976	0.999	0.111	1.627	0.919
200	$2.99x10^{-2}$	3.61	1.57	0.967	$3.36x10^{-2}$	3.817	0.999	0.123	2.316	0.916
250	$2.99x10^{-2}$	4.38	2.03	0.940	$2.75x10^{-2}$	4.630	0.999	0.146	2.835	0.921

3.10 The Intraparticle diffusion model

The Weber and Morris intraparticle diffusion model is expressed as [16]:

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

Where, I is the intercept which reflects the boundary layer effect and K_d is the intra-particle diffusion rate constant. Figure-13 represents plot of q_t versus $t^{1/2}$. The value of K_d and I have been calculated from the slope and intercept and are given in Table - 2. As the linear plots did not pass through the origin, it is evident that intraparticle diffusion is not the only rate limiting step [6].

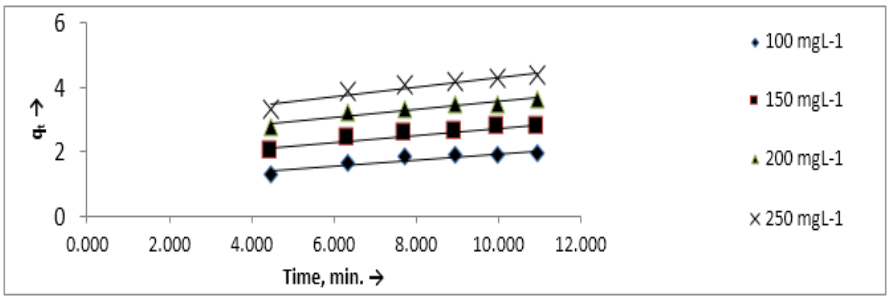


Fig 13: Intraparticle diffusion model for adsorption of Cu(II) ion on red mud

It is evident from Table - 2 that R^2 values are higher in the case of pseudo-second-order equation. Moreover, q_e (cal) values agree better with q_e (exp) in the case of pseudo-second order reaction showing its applicability over other kinetic model. In general the rate constant k_2 decreases with increase in concentration. The reason might be the possibility that at lower concentration less competition for surface active sites whereas at higher concentration, the competition increases thereby rate constant decreases [17].

3.11 Thermodynamic treatment of the adsorption process

Thermodynamic parameters are important in order to determine the feasibility and spontaneity of the process. Different parameters such as free energy, enthalpy and entropy changes have been calculated using the following equations [24].

$$K_c = C_s/C_e$$
$$\Delta G = - RT \ln K_c$$
$$\log K_c = \Delta S/2.303\ R - \Delta H/2.303RT$$

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. Slope and intercept of the plot between $\log K_c$ versus 1/T shown in fig 14 gives the values of ΔH and ΔS. All these values are listed in Table- 3.

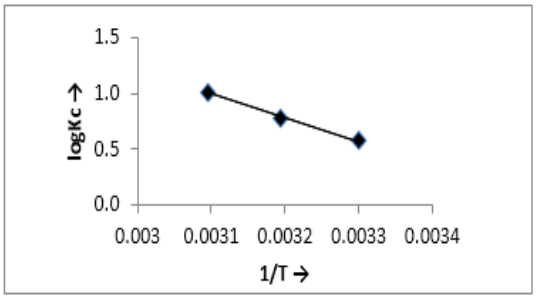


Fig 14: Plot of $\log K_c$ *vs* 1/T

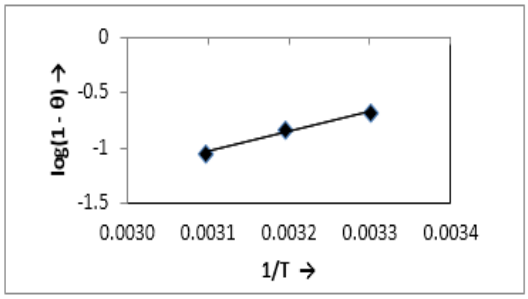


Fig 15: Plot of log (1-θ) *vs* 1/T

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 [19]

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

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-3.

Table 3: Thermodynamic parameters for adsorption of Cu(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	-3.368	40.67	145.17	34.92	2.02X10^{-07}
313	-4.639				
323	-6.280				

Some important conclusions may be withdrawn from the results of Table-3. Negative values of ΔG values indicate that the process is spontaneous. Positive ΔH value indicates the endothermic nature of adsorption. The positive value of ΔS shows the affinity of the adsorbent for the Cu(II) ions. The value of E_a has been found to be 34.92 kJ mol^{-1} for the adsorption. Positive value of E_a supports the endothermic nature of the adsorption process. 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 [20].

4. Mechanism

Speciation [11] of Cu(II) with varying pH has been shown in figure-16.

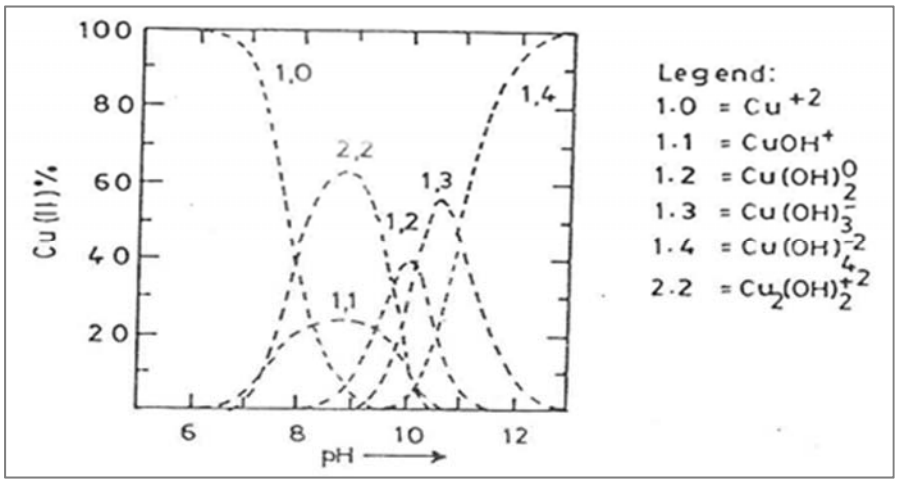


Fig 16: Speciation of Cu(II) with varying pH

It is evident that at lower pH, copper is in the form of Cu^{+2} and at higher pH it is in the form of $Cu(OH)^+$. 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 Cu^{+2} and $Cu(OH)^+$ species [21, 22].

$$M-OH \xrightarrow{OH^-} MO^-$$
$$MO^- + Cu+2 \longrightarrow MOCu^+$$
$$MO^- + Cu(OH)^+ \longrightarrow MOCu(OH)$$

Where, M represents the adsorbent surface.

5. Conclusion

It is evident that initial Cu(II) ion concentration, contact time, pH and temperature have marked effect on adsorption. The equilibrium data are best explained by Freundlich 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.

6. Acknowledgement
We are thankful to SAIF, IIT Bombay, for SEM and FTIR analysis of red mud.

7. References
1. Bhatnagar A, Minocha AK. Conventional and non-conventional adsorbents for removal of pollutants from water – A review. Indian J Chem Tech 2006; 13:203-217.
2. Karthika C, Sekar M. Removal of Hg(II) ions from aqueous solution by acid acrylic resins: A study through adsorption isotherms analysis. I Res J Environment Sci 2012; 1(1):34-41
3. Singh D, Singh A. Chitosan for the removal of chromium from waste water. I Res J Environment Sci 2012; 1(3):55-57.
4. Nadaroglu H, Kalkan E. Removal of cobalt(II) ions from aqueous solutions by using alternative adsorbent andustrial red mud waste material. Int J Phy Sciences 2012; 7:1386-1394.
5. Mobasherpour I, Salahi E, Asjodi A. Research on the batch and fixed bed column performance of red mud adsorbents for copper removal. Canadian Chemical Transactions 2014; 2(1):83-96
6. Das B, Mondal NK, Roy P and Chatterji S. Equilibrium, Kinetic and Thermodynamic Study on chromium(VI) removal from aqueous solutions using Pistia Stratiotes Biomass. Chem Sci Trans 2013; 2(1):85-104.
7. John C. Interpretation of Infrared Spectra, A Practical Approach, Encyclopedia of Analytical Chemistry, Heyers RA (Ed.), John Wiley & Sons Ltd. Chichester, 2000, 10815–10837.
8. Ekrem K *et al*. Bacteria – Modified Red Mud for Adsorption of Cadmium Ions from Aqueous Solutions. Pol J Environ Stud 2013; 22(2):417-429.
9. Tsai WT, Chen HR. Removal of malachite green from aqueous solution using low-cost chlorella-based biomass. J Hazard Mater 2010; 175(1-3):844-849.
10. Sarin V, Pant KK. Removal of chromium from industrial waste by using eucalyptus bark. Bioresource Technol 2006; 97(1):15-20.
11. Brummer GW. Importance of Chemical Speciation in Environmental Process (Springer Verlag, Berlin), 1986.
12. Bansal M, Singh D, Garg VK, Rose P. Use of agricultural waste for the removal of nickel ions from aqueous solutions: Equilibrium and kinetic studies. World Acad Sci Eng Technol 2009; 51:431-437.
13. Anirudhan TS, Radhakrishnan PG. Thermodynamics and kinetics of adsorption of Cu(II) from aqueous solutions onto a new cation exchanger derived from tamarind fruit shell. J Chem Thermodynamics 2008; 40(4):702-709.
14. Lagergren S. About the theory of so-called adsorption of soluble substsnces, der Sogenannten adsorption geloster stoffe Kungliga Svenska psalka de Miens Handlingar. 1898; 24:1-39.
15. Ho YS, Mckay G. The kinetics of sorption of divalent metal ions onto sphagnum moss peat. Water Res 2000; 34(3):735-742.
16. Weber WJ, Morris JC. Kinetics of adsorption on carbon from solution. J Saint Eng Div Am Soc Eng 1963; 89:31-60.
17. Kumar PS, Ramakrishnan K, Kirupha SD, Sivanesan S. Thermodynamic and Kinetic studies of cadmium adsorption from aqueous solution onto rice husk. Braz J Chem Eng 2010; 27:347.
18. Arivoli S, Hema M, Karuppaiah M, Saravanan S. Adsorption of chromium ion by acid activated low cost carbon-Kinetic, Mechanistic, Thermodynamic and Equilibrium studies. E Journal of Chemistry 2008; 5(4):820- 831.
19. Senthilkumar P, Ramalingam S, Sathyaselvabala V, Kirupha DS, Sivanesan S. Removal of copper (II) ions from aqueous solution by adsorption using cashew nut shell. Desalination. 2011; 266(1-3):63-71.
20. Nevine KA. Removal of direct blue-106 dye from aqueous solution using new activated carbons developed from pomegranate peel: Adsorption equilibrium and kinetics. J Haz Mat 2009; 165(1-3):52-62.
21. Singh D, Rawat NS. Bituminous coal for the Removal of Cd rich water. Ind J Chem Technol 1994; 1:266-270.
22. Singh D, Rawat NS. Sorption of Cu(II) by bituminous coal. Ind J Chem Technol 1995; 2:49-50.