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Studies on the adsorption of ferrous ion from aqueous solution by low cost carbon

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ABSTRACT

The influence of adsorbent dose, initial metal ion, pH, other ions, temperature and contact time were studied for the adsorption of ferrous ions on to acid activated carbon prepared from Albizia lebbeck bark. The results were analyzed in the light of Langmuir and Freundlich isotherms From this, the adsorption efficiency, adsorption energy, adsorption capacity, intensity of adsorption and dimensionless separation factor were calculated. From the kinetic studies the rate constant values for the adsorption process was calculated. From the effect of temperature thermodynamic parameters like ΔG°, ΔH°, and ΔS° were calculated. The mechanism of adsorption for that ferrous ion onto carbon have investigated by using the experimental results and confirmed by IR spectra, XRD and SEM images.

Key words: Activated carbon (ALC), Ferrous ion, Adsorption isotherm, Equilibrium, Kinetic and Thermodynamic parameters, Intra-particle diffusion, Regeneration pattern.

INTRODUCTION

Industries are discharging heavy metal pollutants into the environment at an unprecedented and constantly increasing rate. Owing to their mobility in natural water ecosystems and their toxicity, the presence of heavy metals in surface water and ground water poses major inorganic contamination problems. Among those metal ions, iron produces undesirable effects on human and animal life even in low concentrations. In recent years many researchers have studied the removal of different heavy metal ions including chromium, nickel, iron and copper from the water. Wastewaters from industries are released in to nearby land or rivers without any prior treatment, because the conventional treatment methods are not cost effective in the Indian context [1-3]. On the other hand, low cost technologies never allow a wishful metal ion removal and it has certain disadvantages. Adsorption is one of the most effective methods and activated carbon is the preferred adsorbent widely employed to treat wastewater containing different classes of metal ions recognizing the economic drawback of commercial activated carbon. Many investigators have studied the feasibility of using inexpensive alternative materials like pearl millet husk, date pits, saw dust, buffing dust of leather industry, coir pith, crude oil residue, tropical grass, olive stone, almond shells, pine bark, wool waste, coconut shell etc., as carbonaceous precursors for the removal of metal ions from water and wastewater [3,4]. The present study aims at to evaluate the efficiency of an acid activated carbon prepared from *Albizia lebbeck* bark for the removal of metal ions from aqueous solutions. In order to design adsorption treatment systems, knowledge of kinetic and mass transfer processes is essential. In this paper, we have reported the applicability of kinetic and equilibrium models for the adsorption of ferrous ions onto acid activated carbon, ALC.

EXPERIMENTAL SECTION

Adsorbent: Carbon was prepared by treating air-dried *Albizia lebbeck* bark with con sulphuric acid in a weight ratio of 1:1. The resulting black product was kept in a furnace maintained at 500°C for 12 hours followed by washing with water until free from excess acid and dried at 150 ± 5°C. The carbon product thus obtained was ground and the portion retained between 0.035 to 0.040 mm sieves was used in all the experiments. All chemicals used were supplied by SD fine chemicals with high purity.

Batch equilibration method: All experiments were carried out at 35, 40, 45 and 50ºC temperature in batch mode. Batch mode was selected because of its simplicity and reliability. The experiments were carried out in different 100 ml Erlenmeyer glass flasks of 100 ml capacity. Prior to each experiment, a predetermined amount of absorbent was added to each flask. The stirring was kept constant (125 rpm) for each run, throughout the experiment, to ensure equal mixing. Each flask was filled with a known volume of sample before commencing stirring such as metal solutions with an initial concentration of 5 mg/L to 30 mg/L. The flask containing the sample was withdrawn from the shaker at the predetermined time interval, filtered and the residual concentration of the metal ion was measured. The effects of different parameters such as dosage of the adsorbent (10 to 100 mg/50 ml), initial adsorbate concentration (5 to 30 mg/L), initial pH of the adsorbate solution (pH 3-10), adsorption in presence of other ions such as Cl^- and Ca^{2+}, temperature of the system (35 to 50 ºC) and the effect of period of contact between the adsorbent and adsorbate on the removal of the ferrous ions in a single cycle were determined by keeping particle size, initial concentration, dosage, pH and temperature constant.

Zero point charge: The pH at the potential of zero charge of the carbon (pH_{zpc}) was measured using the pH drift method. The pH of the solution was adjusted by using 0.01 M sodium hydroxide or hydrochloric acid. Nitrogen was bubbled through the solution at 25 ºC to remove the dissolved carbon dioxide. 50 mg of the activated carbon was added to 50 ml of the solution.

After stabilization, the final pH was recorded. The graph of final pH versus initial pH was used to determine the zero point charge of the activated carbon [4].

Titration studies: According to Boehm [4] only strong acidic carboxylic acid groups are neutralized by sodium bicarbonate, where as those neutralized by sodium carbonate are thought to be lactones, lactol and carboxyl group. The weakly acidic phenolic groups only react with strong alkali, sodium hydroxide. Therefore, by selective neutralization using bases of different strength, the surface acidic functional group in carbon can be characterized both quantitatively and qualitatively. Neutralization with hydrochloric acid characterizes the amount of surface basic groups that are, for example, pyrones and chromenes. The results indicate that the activated carbon used may possesses acidic oxygen functional group on their surface and this is supported well by their respective zero point charge values. The results obtained from the above characterization studies are given in the Table.1

Regeneration studies: The regeneration of the adsorbed carbon is done by using 0.2 M mineral acids and sodium chloride solutions.

RESULTS AND DISCUSSION

Characterization of the adsorbent: Activated carbon is widely used as an adsorbent due to its high adsorption capacity, high surface area, micro porous structure and high degree of surface respectively. The wide usefulness of carbon is a result of its specific surface area, high chemical and mechanical stability. The chemical nature and pore structure usually determines the sorption activity. The physico-chemical properties of the chosen adsorbent are listed in following Table 1.

Table 1 Characteristics of the adsorbent

Properties	ALC
Particle size (mm)	0.035
Density (g/cc)	0.3846
Moisture content (%)	1.95
Loss on ignition (%)	85
Acid insoluble matter (%)	3.8
Water soluble matter (%)	0.72
PH of aqueous solution	6.8
pH_{zpc}	6.25
Surface groups (m equiv/g)	
i) Carboxylic acid	0.228
ii) Lactone, lactol	0.045
iii) Phenolic	0.052
iv) Basic (pyrones and chromenes)	0.034

Effect of carbon concentration:

The adsorption of the metal ion on carbon was studied by varying the carbon concentration (10-100 mg/50ml) for ferrous ion concentrations of 15 mg/L. The percentage of adsorption increased with increase in the carbon concentration (Figure 1). This has attributed to the increased carbon surface area and availability of more adsorption sites [5,6]. Hence the remaining parts of the experiments are carried out with the adsorbent dose of 50 mg/50ml.

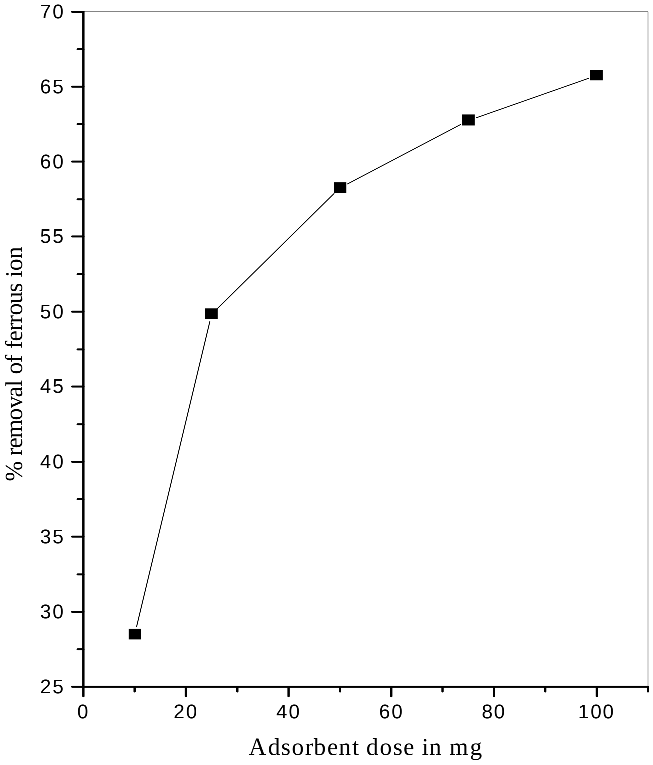

Fig.1-Effect adsorbent dose on the adsorption ferrous ion

[Fe]=15 mg/L;Contact time=60 min;Temp=35^{0}C

Effect of contact time and initial metal ion concentration:

The experimental results for the adsorption of ferrous ions on the activated carbon at various concentrations (5, 10, 15, 20, 25 and 30 mg/L) with contact time are shown in Figure 2. The equilibrium data presented in Table 2 reveals that, the percent adsorption decreased with increase in initial metal ion concentration, but the actual amount of metal ion adsorbed per unit mass of carbon increased with increase in metal ion concentration. It means that the adsorption is highly dependent on initial concentration of metal ion. It is because of that at lower concentration, the ratio of the initial number of metal ion to the available surface area is low, subsequently the fractional adsorption becomes independent of initial concentration. However, at high concentration the available sites of adsorption becomes fewer and hence the percentage removal of metal ion is dependent upon initial concentration. An equilibrium is established at 40 minutes for all concentrations. Figure 2 reveals that the curve is single, smooth, and continuous, leading to saturation, suggesting the possible monolayer coverage of the metal ion on the carbon surface [5,6].

Table 2- Equilibrium parameters for the adsorption of ferrous ion onto activated carbon

Initial [Fe(II)] in mg/L	**Ce, mg/ L**				**Qm, mg/g**				**% Removal of Fe(II) ions**			
	Temp., °C											
	35	**40**	**45**	**50**	**35**	**40**	**45**	**50**	**35**	**40**	**45**	**50**
5	1.480	1.335	1.1250	1.084	3.520	3.661	3.825	3.916	70.39	73.21	76.50	78.38
10	3.379	3.187	3.023	2.887	6.622	6.813	6.977	7.113	66.21	68.13	69.77	71.13
15	6.281	6.097	5.824	5.614	8.718	8.903	9.176	9.386	58.12	59.35	61.17	62.57
20	9.487	9.282	9.087	8.878	10.513	10.718	10.913	11.122	52.56	53.59	54.56	55.60
25	12.437	12.378	12.078	11.879	12.563	12.622	12.922	13.124	50.25	50.48	51.68	52.49
30	14.989	14.884	14.628	14.487	15.011	15.116	15.372	15.513	50.00	50.38	51.23	51.70

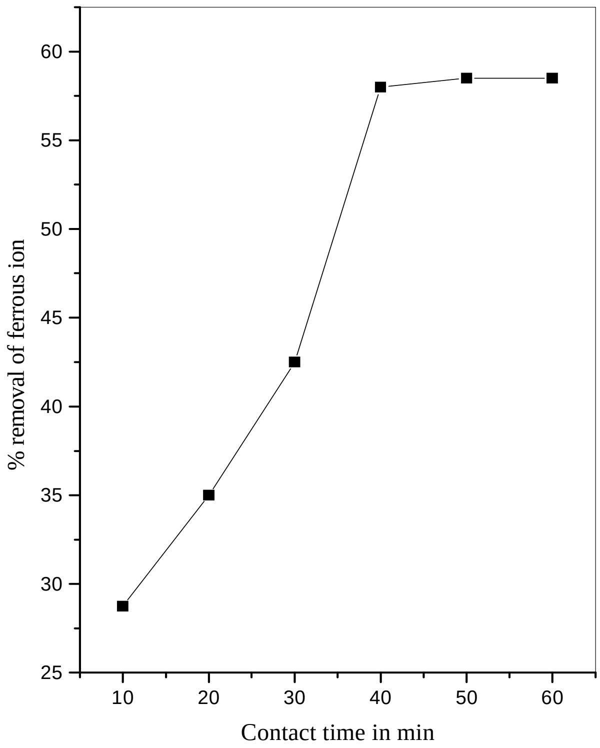

Fig.2-Effect of contact time on the adsorption of ferrous ion

[Fe]=15 mg/L;Adsorbent dose=50 mg/50 ml;Temp=35^{0}C

Adsorption isotherm:

The experimental data were analyzed by using linear form of the Langmuir and Freundlich isotherms [7,8].

The Langmuir [7] isotherm is

$$C_e/Q_e = 1/Q_m b + C_e /Q_m$$

Where C_e is the equilibrium concentration (mg/L), Q_e is the amount adsorbed at equilibrium (mg/g) and Q_m and b are Langmuir constants related to adsorption efficiency and energy of adsorption, respectively. The plots of C_e/Q_e versus C_e suggest linearity and the applicability of the Langmuir isotherm to the Fe^{2+}- ALC adsorption system (Figure 3). Values of Q_m and b were determined from slope and intercepts of the plots and are presented in Table 3. From the results, it is clear that the value of adsorption efficiency, Q_m, and adsorption energy, b, of the carbon increases on increasing the temperature. From the values we can conclude that the maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on adsorbent surface with constant energy and no transmission of adsorbate in the plane of the adsorbent surface. Further, it confirms the exothermic nature of the adsorption process involved in the system. To confirm the favorability of the adsorption process, the separation factor (R_L) was calculated and presented in Table 4. The R_L values lie between 0 and 1, which confirm the ongoing adsorption process is favourable [9-11].

Table 3- Langmuir constants and statistical parameter

S.No.	Temp., °C	Q_m	b	R^2
1	35	21.83	0.1050	0.972
2	40	20.34	0.1267	0.976
3	45	19.59	0.1472	0.979
4	50	19.54	0.1597	0.976

The Freundlich equation was also employed for the adsorption of ferrous ions on ALC. The Freundlich isotherm is:

$$\log Q_e = \log K_F + 1/n \log C_e$$

Where Q_e is the amount of ferrous ions adsorbed (mg/ g), C_e is the equilibrium concentration of metal ion in solution (mg/L) and K_F and n are constants incorporating all factors affecting the adsorption capacity and intensity of adsorption, respectively. Linear plot of log Q_e versus log C_e shows that the adsorption of ferrous ion follows the Freundlich isotherm (Figure 4). Values of K_F and n are given in the Table 5, show the increase of negative charge on the surface that enhances the electrostatic force like van der Waal’s between the carbon surface and metal ion, which increases the adsorption of ferrous ion. The values clearly show that there is dominance in adsorption capacity. The intensity of adsorption is an indication of the bond energies between metal ion and adsorbent and the possibility of slight chemisorptions rather than physisorption. The possibility of multilayer adsorption of metal ion through the percolation process cannot be ruled out. However, the values of n are greater than one indicating the adsorption is much more favourable [10-12].

Table 4- Freundlich constants and statistical parameter

S.No.	Temp., °C	K_F	n	R^2
1	35	1.8036	1.6954	0.994
2	40	1.7381	1.8089	0.994
3	45	1.6837	1.9193	0.995
4	50	1.6689	1.9523	0.998

Table 5 Dimensionless separation factor, R_L

$[Fe(II)]_{initial}$, mg/L	Temp., °C			
	35	40	45	50
5	0.655	0.613	0.576	0.557
10	0.487	0.442	0.414	0.386
15	0.389	0.346	0.303	0.295
20	0.322	0.284	0.253	0.235
25	0.276	0.240	0.214	0.201
30	0.240	0.209	0.184	0.173

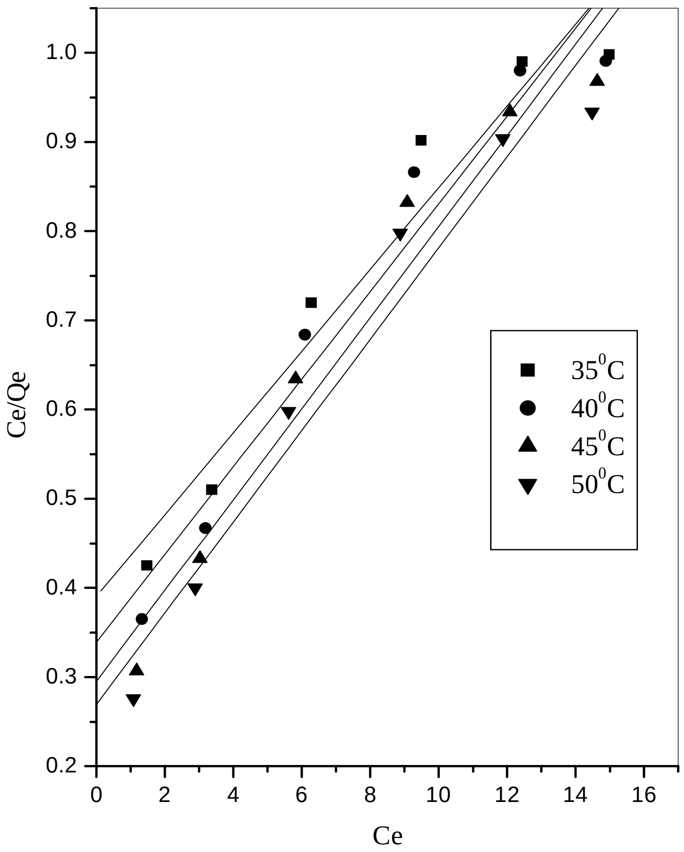

Fig.3-Linear Langmuir isotherm for the adsorption of ferrous ion

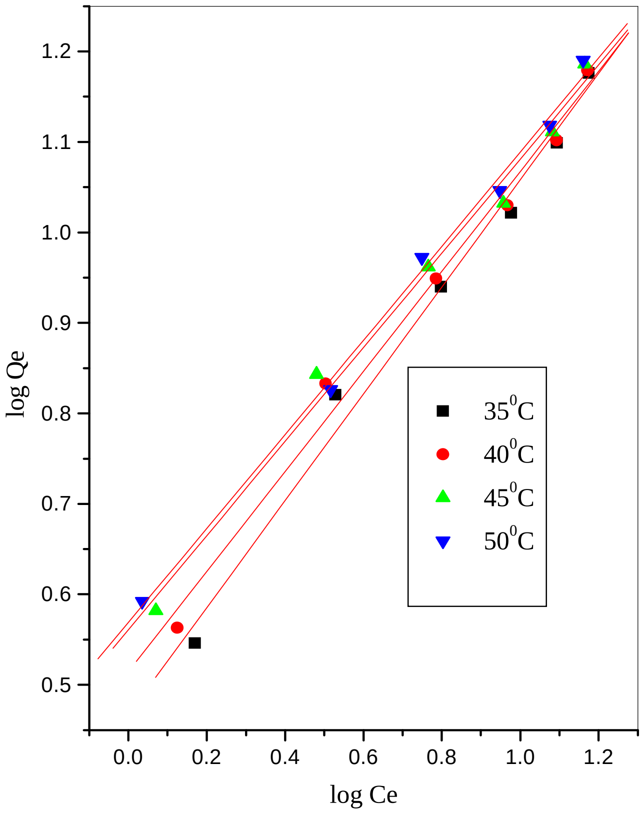

Fig.4-Linear Freundlich isotherm for the adsorption of ferrous ion

Kinetics of adsorption: Kinetics of sorption describes the solute uptake rate, which in turn governs the residence time of sorption reaction. It is one of the important characteristics in defining the efficiency of sorption. In the present study, the kinetics of the ferrous ion removal has been carried out to understand the behavior of this low cost carbon adsorbent. The adsorption of ferrous ions from an aqueous solution follows reversible first order kinetics, when a single species is considered on a heterogeneous surface. The heterogeneous equilibrium between the ferrous ion solution and the activated carbon is expressed as:

$$A \underset{k_2}{\overset{k_1}{\rightleftarrows}} B$$

Where k_1 is the forward rate constant and k_2 is the backward rate constant. A represents ferrous ion remaining in the aqueous solution and B represents ferrous ions adsorbed on the surface of activated carbon. The rate constants [11-13] were calculated and are presented in Table 6 is evident that the forward rate constant is much higher than the backward rate constant suggesting that the rate of adsorption is clearly dominant. At equilibrium, the rate is the ratio of the concentration of adsorbate in adsorbent and concentration of adsorbate in aqueous solution given by K_0. The calculated values are presented in the Table 7. The results indicate that K_o values decrease with increase in the concentration of the ferrous ions and increases with increase in temperature

A clear examination of the values in Table 6 helps to describe the mechanism of metal ion removal taking place. In cases of strict surface adsorption, a variation of rate should be proportional to the first power of concentration. However, when pore diffusion limits the adsorption process, the relationship between initial ferrous ion concentration and rate of reaction will not be linear. It shows that pore diffusion limits the overall rate of ferrous ion adsorption [12].

Initial [Fe(II)] in mg/L	Temp., °C											
	k_{ad}				35		40		45		50	
	35	40	45	50	k_1	k_2	k_1	k_2	k_1	k_2	k_1	k_2
5	3.33	3.68	3.94	4.28	2.36	0.97	2.70	0.98	3.01	0.93	3.35	0.93
10	3.06	3.19	3.37	3.55	2.03	1.03	2.18	1.01	2.35	1.02	2.38	1.17
15	2.53	2.60	2.78	2.97	1.47	1.06	1.54	1.06	1.70	1.08	1.88	1.11
20	2.40	2.52	2.65	2.81	1.26	1.14	1.35	1.17	1.45	1.20	1.57	1.24
25	2.27	2.39	2.51	2.72	1.14	1.13	1.20	1.19	1.26	1.25	1.43	1.29
30	2.07	2.14	2.23	2.40	1.04	1.03	1.07	1.07	1.12	1.11	1.25	1.15

Table 6 - Rate constants for the adsorption of ferrous ion (10^3 k_{ad}, min^{-1}) and the constants for forward (10^3 k_1, min^{-1}) and reverse (10^3 k_2, min^{-1}) processes

Table 7 Equilibrium constant and thermodynamic parameters for the adsorption of ferrous ion onto activated carbon

Initial [Fe(II)] in mg/L	Temp., °C									
	35°	40°	45°	50°	35°	40°	45°	50°	ΔH°	ΔS°
	K_0				ΔG°					
5	2.37	2.74	3.25	3.61	-2.22	-2.65	-3.12	-3.44	23.64	83.85
10	1.95	2.13	2.31	2.46	-1.72	-1.97	-2.21	-2.42	13.63	49.76
15	1.38	1.46	1.57	1.67	-0.89	-0.98	-1.20	-1.37	10.56	36.89
20	1.11	1.15	1.20	1.25	-0.26	-0.37	-0.48	-0.60	6.73	22.66
25	1.01	1.02	1.06	1.11	-0.02	0.05	-0.17	-0.26	4.78	15.57
30	1.00	1.01	1.05	1.07	-0.003	-0.04	-0.13	-0.18	3.99	12.96

The contact-time experimental results can be used to study the rate-limiting step in the adsorption process, as reported by Weber and Morris [13,14]. Since the particles are vigorously agitated during the adsorption period, it is probably reasonable to assume that the rate is not limited by mass transfer from the bulk liquid to the particle's external surface. Then we can postulate that the rate-limiting step may be either film or intra-particle diffusion. As they act in series, the slower of the two will be the rate-determining step [13].

The rate constant for intra-particle diffusion is obtained using the equation:

$$Q = K_p t^{½} + C$$

Here, K_p (mg/g/min) is the intra-particle diffusion rate constant. The K_p values obtained from the slope of the linear portions of the curves for different metal ion concentrations at 35^0C are 0.070, 0.129, 0.188, 0.247, 0.364 and 0.470 mg/g/min. The K_p values increased with increase in the ferrous ion concentration, which reveals that the rate of adsorption is governed by the diffusion of adsorbed ferrous ion within the pores of the adsorbent.

Effect of temperature

The adsorption capacity of the carbon increased with increase in the temperature of the system from 30° to 60°C. Thermodynamic parameters such as change in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were determined using the following equations [9].

$$K_o = Csolid/C_{liquid}$$
$$\Delta G^\circ = -RT \ln K_o$$
$$\log K_o = \Delta S^\circ/(2.303RT) - \Delta H^\circ/(2.303RT)$$

Where K_o is the equilibrium constant, C_{solid} is the solid phase concentration at equilibrium (mg/ L), C_{liquid} is the liquid phase concentration at equilibrium (mg/L), T is the temperature in Kelvin and R is the gas constant. The ΔH° and ΔS° values were obtained from the slope and intercept of van’t Hoff plots and are presented in Table 7. The values are with in the range of 1 to 93 kJ/mol indicating the favorability of physisorption. The positive ΔH° values confirm the endothermic nature of adsorption and it governs the possibility of physical adsorption. Because in the case of physical adsorption, while increasing the temperature of the system, the extent of metal ion adsorption decreases [12-15], which enable the possibility of physisorption rather than chemisorption.

The negative ΔG° values (Table 7) also confirm that the adsorption is highly favorable for ferrous ions. However, it indicates that the metal ion adsorption was spontaneous. The positive values of ΔS° (Table 7) shows the increased disorder and randomness at the solid solution interface of with adsorbent ALC. During the adsorption there are some structural changes in the metal ion and the adsorbent occur. The adsorbed water molecules, which were displaced by the adsorbate species, gain more translational entropy than is lost by the adsorbate molecules, thus allowing the prevalence of randomness in the system [14]. From the results, we could make out that there is more efficient physisorption rather than chemisorption [11-14].

Effect of pH

The experiments carried out at different pH reveal that there is a change in the percent removal of metal ion over the entire pH range of 3 to 10 as shown in the Figure 5. This indicates the strong force of interaction between the metal ion and the activated carbon that, either H^+ or OH^- ions could influence the adsorption capacity. Here the interaction is more at pH 6.25, the competence of acidic H^+ ion with metal ion for the sorption sites. The percentage of sorption increased at the above pH value is due to the presence of ionic COOH, OH and SO_3H groups. The adsorption of metal ion on the activated carbon does involve ion exchange mechanism. Owing to the adsorption of metal ion through ion exchange mechanism by the adsorbent, there should be an influence on the metal ion adsorption while varying the pH. The positive ΔH° value obtained, which indicates irreversible adsorption probably due to polar interaction [16-18].

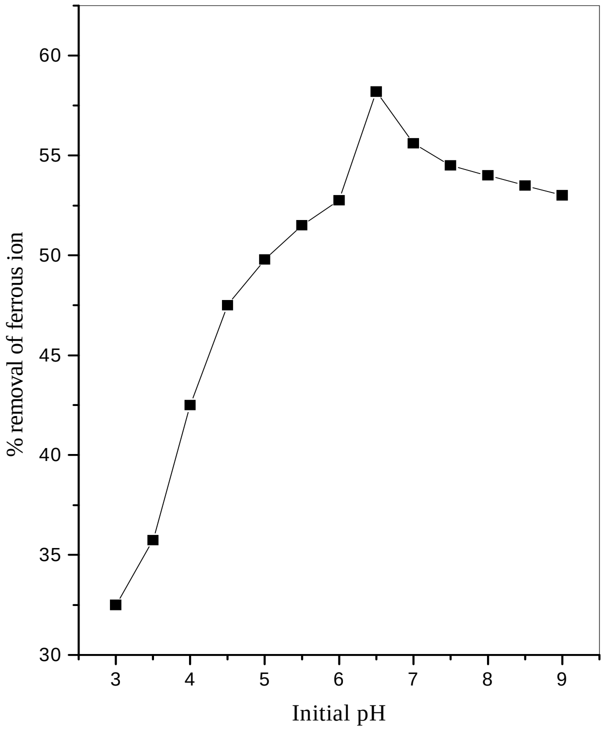

Fig.5-Effect of Initial pH on the adsorption of ferrous ion

[Fe]=15 mg/L;Contact time==60 min;Temp=35^{0}C;
Adsorbent dose=50 mg/50 ml

Effect of other ions

The effect of other ions like Ca^{2+} and Cl^- on the adsorption process was studied at different concentrations. The ions were added to 15 mg/L of metal ion solutions and the contents were agitated for 60 min at 35°C. The results shown in the Figure 6 reveals that low concentration of Cl^- does not affect the percentage of adsorption of metal ion on activated carbon, since the interaction of Cl^- at available sites of adsorbent through competitive adsorption is not so effective. While the concentration of Ca^{2+} ions are increased, the interference of these ions at available surface sites of the sorbent through competitive adsorption also increase, which decreases the percentage of adsorption. The interference was more in the presence of Ca^{2+} compared with Cl^- ion. This is so because ions with smaller hydrated radii, decrease the swelling pressure with in the sorbent and increase the affinity of the sorbent for such ions [1,17,19].

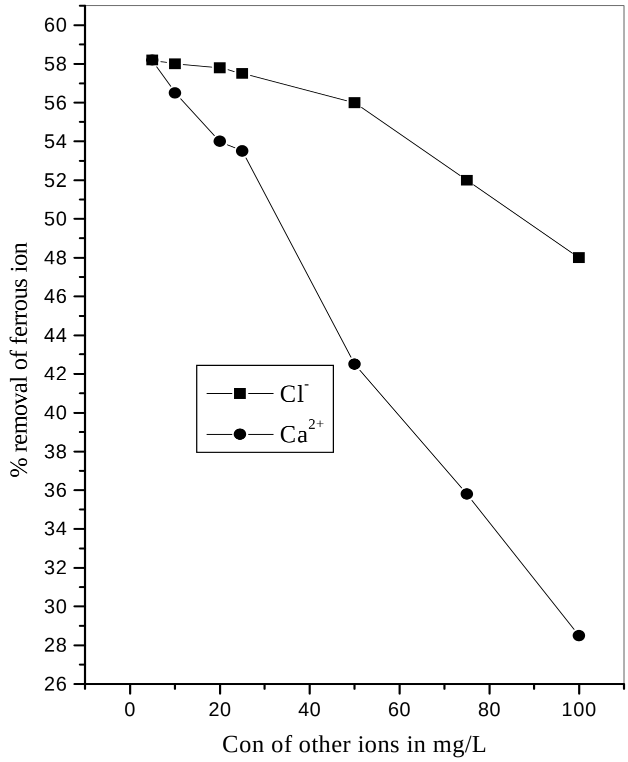

Fig.6-Effect of other ions on the removal of ferrous ion
[Fe]=15 mg/L;Contact time=60 min;
Temp=35^{0}C;Adsorbent dose=50 mg/50 ml

Desorption studies

Desorption studies help to elucidate the nature of adsorption and recycling of the spent adsorbent and the metal ion. If the adsorbed metal ion can be desorbed using neutral pH water or by very dilute acids, then the attachment of the metal ion of the adsorbent is by weak bonds. If sulphuric acid or alkaline water desorbs the metal ion, then the adsorption is by ion exchange. If organic acids, like acetic acid can desorb the metal ion, then the metal ion has held by the adsorbent through chemisorption [18]. The effect of various reagents used for desorption studies reveals that hydrochloric acid is a better reagent for desorption, because we could get more than 78 % removal of adsorbed metal ion. The reversibility of adsorbed metal ion in mineral acid or base is in agreement with the pH dependent results obtained. The desorption of metal ion by dilute mineral acids and alkaline medium indicates that the metal ion was adsorbed onto the activated carbon through by physisorption mechanisms [12,18,19].

CONCLUSION

The experimental data correlated reasonably well by the Langmuir and Freundlich adsorption isotherms. The amount of metal ion adsorbed increased with increase in pH of the medium. The amount of metal ion adsorbed slightly decreased with increasing ionic strength and increased with increase in temperature. The dimensionless separation factor (R_L) showed that the activated carbon can be used for the removal of metal ion from aqueous solution. The values of $\Delta H°$, $\Delta S°$

and ΔG° results show that the carbon employed has a considerable potential as an adsorbent for the removal of metal ions.

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