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Adsorption kinetics of ferrous ions in aqueous solution by acid activated carbon prepared from *Samanea Saman*

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ABSTRACT

Samanea saman barks which have been chemically modified in acidic condition were used as adsorbent for the removal of ferrous ions from aqueous solution. The adsorbent was characterized by SEM images, FT-IR and XRD analysis. Effecting parameters like initial pH, initial concentrations of metal ions and contact time were investigated. The adsorption data were well fitted by Langmuir and Freundlich isotherm model. Kinetic data were best described by Reversible First - order model. Thermodynamic studies showed spontaneous and endothermic nature in the adsorption of Fe (II) ions by the modified acid activated Samanea saman barks.

Key words: Activated *Samanea saman* carbon (SSC), ferrous ion, adsorption isotherm, equilibrium, kinetic and thermodynamic parameters, intraparticle diffusion, regeneration pattern.

INTRODUCTION

The need to protect the environment from further contamination by transition and heavy metal ions is well established and universally reinforced by legislation which sets limits on the levels in effluents which may be discharged into sewers and local waters. All chemical plants, factories and other facilities employing solutions of such metals should therefore be treating their wastewater before discharge. Electrochemical methods compete with a number of other technologies including evaporation, precipitation, ion exchange and solvent extraction to offer solutions to the needs of the many industries involved. Electrochemical methods, however, are uniquely capable of recovering pure metal for recycle. Although electrochemical technology for metal ion removal has been available for some time [1-3], it continues to develop to meet the challenges of lower consent levels and more complex effluent compositions. However, there is a requirement to remove the final traces of metal species after these treatment procedures. At very low concentrations, such pollutants can be removed by adsorption on activated carbon. Activated carbons have well-developed porous structures with specific surface chemical properties and are widely used in industry for the removal of many organic compounds from both liquid and gas phases. Activated carbons contain hydrophobic graphene layers and various hydrophilic functional groups. Organic compounds are adsorbed on the former, whereas polar species are adsorbed on the latter. Surface chemistry plays an important role in the adsorption of aqueous heavy metals on activated carbons [4-6], Chemical oxidation, which incorporates both oxygen and nitrogen functional groups on the surface of activated carbon, enhances the adsorption of aqueous metal cation species and modifies the selectivity of the activated carbon for these species [7,8], Oxygen functional groups are involved in the formation of surface complexes with aqueous metal species and ion exchange with the displacement of protons [9], Nitrogen functional groups coordinate with aqueous metal species, but the metal ions are displaced at pH 4.1[8]. Aqueous metal ions have different affinities for various functional groups such as carboxylic groups and phenolic groups on the carbon surface. Metal anionic species are adsorbed by a different mechanism; for example, the auro cyanide ion is mainly adsorbed on the graphene layers [10]. Redox reactions involving the aqueous metal species have also been proposed [11-13]. Several factors affect the adsorption of aqueous metal species on activated carbon, and these include the surface charge of activated carbon and the speciation of metal ions in solution. This leads to a dependence of the amount adsorbed on the point of zero charge (pH_{PZC}), isoelectric point, and experimental conditions, such as ionic strength, pH, and concentrations of species in solution. The adsorption of aqueous metal ions is also strongly influenced by competition of different aqueous metal ions to occupy the limited number of surface sites, which decreases the removal efficiency of activated carbon for the metals of interest [14]. Quantitative modeling of the adsorption of aqueous metal species has been investigated to interpret adsorption in relation to electrostatic effects, ion exchange, and coordination with functional groups on the amphoteric carbon surface [15]. These models suggest that the adsorption of aqueous species onto a hydrated solid surface must overcome an extra energy barrier to complete the exchange.

EXPERIMENTAL SECTION

Treatment of Samanea saman

All the chemicals used were of analytical grade and were used without further purification. *Samanea saman* was treated with conc. Sulphuric acid in a weight ratio 1:1, to increase the adsorption properly of the adsorbent. The resulting mixture was kept in a furnace maintained at 600°C for 12 hours. After this, the contents were extensively washed with doubly distilled water to remove excess acid and filtered through a Whatman filter paper. Then it was dried for 5 hours at 125 ± 5°C. By a sieving process, the carbon product as ground and the portion retained between 0.040 – 0.045 mm sieves were separated and stored in a pyrex glass bottle.

Chemical and reagents

Chemicals used for all the experiments are of analytical and lab reagents grades and distilled water was used in throughout the experiments.

Batch Adsorption Studies

Batch adsorption experiments were conducted using known weight of adsorbent material was added to 50 ml of the dye solutions with an initial concentration of 10 mg/l to 60 mg/l at various temperatures were 35, 40, 45, and 50°C. The flasks were shaken vigorously using a mechanical shaker rotating with a speed of 125 rpm. The solution was then filtered through Whatmann filter paper (No, 42) at preset time intervals and the residual dye concentration was measured. The percent adsorption (%) and distribution ratio (K_d) were calculated using the equation.

$$\% \text{ Adsorption} = C_i - C_r / C_r \times 100 \text{ -------------------------------[1]}$$

Where C_i and C_r are the concentrations of the metal ion in initial and final solutions and respectively, and

$$K_d = \text{amount of metal in adsorbent /amount of metal in solution} \times V/m \text{ ml/g -----[2]}$$

Where V is the volume of the solution (ml) and m is the weight of the adsorbent (g). The percent adsorption and K_d (ml/g) can be correlated by the following equation.

$$\% \text{ Adsorption} = 100\, K_d / K_d + V/m \text{ ---------------------[3]}$$

Ferrous ion stock solution

Stock solution of ferrous ion ranging from 10 mg to 60 mg was dissolved in one litre of distilled water.

Buffer preparation

Different pH buffers had been used a range of 3 - 10 to study the effect of pH on the removal efficiency of the adsorbent. For maximum range of pH solution of dilute nitric acid and sodium hydroxide are used for maintaining the pH of the solution.

Effect of Variable Parameters

Dosage of Adsorbent

10 to 100 mg/50 ml of the adsorbent was taken and the fixed concentration of ferrous ion was added and the mixture was agitated in a mechanical shaker. Keeping all other factors constant, we determined the percentage adsorption.

Initial concentration of ferrous ion

Initial concentration of ferrous ion ranging from 10 to 60 mg/l as taken and other factors was kept constant. From this, the rate of adsorption was determined.

Contact time

The removal of ferrous ion in a single cycle was determined by keeping particle size, initial concentration, dosage, pH and temperature constant.

Initial pH

For entire experiments the pH range was maintained in between 3 – 10. If the pH range increased or decreased should be maintained by adding required amounts of dilute nitric acid and sodium hydroxide solutions. During this experiment, particle size of the adsorbents and temperature were kept constant.

Other ions

While the determination of ferrous ions in the presence of chloride, nitrate and calcium ions were experimentally verified by using the adsorbent *Samanea saman*. From this, the percentage of metal ion adsorbed was determined from 30 mg/l of initial concentration of the ferrous ion solution with varying concentration of the added ion keeping all other factors constant.

Temperature

For this experiments, thermostatic shaker machine (Remi, India) was used to maintain the four different temperatures *viz,* 35, 40, 45 and 50°C. During the adsorption studies, the constancy of the temperature was maintained with an accuracy of ±0.5°C.

Zero point charge

The pH drift method was very useful to measure the potential of zero charge of the carbon (pH Zpc) while using 0.01 M NaOH or nitric acid, the pH of the solution was adjusted. To remove the dissolved oxygen, Nitrogen was bubbled through the solution at 25°C. In 50 ml of the solution, 50 mg of the activated carbon was added. The final pH was recorded while it undergoes stabilization. The graph was plotted between pH and initial pH which was used to determine the zero point charge of the activated carbon [16].

Titration Studies

The compounds which are neutralized by using sodium carbonate are strong acidic carboxylic acid groups on the basis of Boehm [17]. Where neutralization takes place in the presence of sodium carbonate, the product obtained are considered as lactones, lactol and carboxylic group. The weakly acidic phenolic groups only react with strong alkali, sodium hydroxide. The surface acidic functional group in carbon can be characterized both quantitatively and qualitatively, by selective neutralization using bases of different strength. The amount of surface basic groups like pyrones and chromones and characterized by neutralization with hydrochloric acid. The basic properties have described to surface basic properties have described to surface basic groups and the pi electron system of carbon basal planes. The activated carbon possesses acidic oxygen functional group on their surface and it is supported well by their respective zero point charge values. These results are obtained from the above characterization studies that indicated in Table1.

Regeneration Studies

0.2 M mineral acids and sodium chloride solutions are taken for the regeneration of the adsorbed carbon.

Analytical Measurements

The adsorbents before and after adsorption were recorded at the CECRI, Karaikudi, South India for FT-IR, SEM and XRD patterns.

RESULTS AND DISCUSSION

Properties of the Adsorbent

The chemical nature and pure structure usually determines the sorption activity. The physical and chemical property of the *Samanea saman* was listed in Table 1.

Table 1 Physico -Chemical Properties of the *Samanea saman* adsorbent

Properties	*Samanea saman* (SSC)
Particle size (mm)	0.040
Density (g/cc)	0.4548
Moisture content (%)	2.56
Loss on ignition (%)	89
Acid insoluble matter (%)	2.75
Water soluble matter (%)	0.68
pH of aqueous solution	6.6
pH_{zpc}	5.9
Surface groups (m equiv/g)	
(i) Carboxylic acid	0.326
(ii) Lactone, lactol	0.052
(iii) Phenolic	0.043
(iv) Basic (pyrones and chromenes)	0.029

Effect of adsorbent dosage

The adsorption of adsorbate on adsorbent was studied by changing the adsorbent (10 – 100 mg/50 ml) for adsorbate concentration of 30 mg/l. If the dosage of adsorbent increase the percentage of adsorption of adsorbate also increases, and then the surface area of the adsorbent increases and availability of more adsorption sites were produced [17-19] (Figure 1). For entire adsorption studies 50mg/50 ml of dosage of adsorbent was enough.

Effect of contact time and initial ferrous ion concentration

The effect of contact time and different initial concentration was also studied. It was observed that percentage removal of dye decreases with increase in ferrous ion initial concentration. Equilibrium had established at 40 minutes for all concentrations. From this, it means that the adsorption was highly dependent on initial concentration of ferrous ion. Table 2 and figure 2 reveals that the curves are single, smooth and continuous, leading to saturation, suggesting the possible monolayer coverage of the ions on the carbon surface [17, 18].

Adsorption Isotherms

The adsorption isotherms were studied using initial concentration of ions between 15 mg to 75 mg/l at an adsorbent dose 25mg/l. The data obtained is fitted into the Langmuir isotherm which is the most popular and is a two parameters equation described as [20]

$$C_e/Q_e = 1/Q_m b + C_e/Q_m \text{ ---------------------------[4]}$$

Where constants b and Q_m relate to the energy of adsorption and adsorption capacity and their values are obtained from the slope and intercept of the plot of C_e/Q_e versus C_e as shown in figure 3, and Table 3. The observed values shows that the adsorbent prefers to bind acidic ions and that speciation predominates on sorbent characteristics, when ion exchange is the predominant mechanism takes place in the adsorption of *Samanea saman*, it confirms the endothermic nature of the process involved in the system [21,25,26]. The value of b, which is a measure of heat of adsorption, is utilized to calculate dimensionless separation parameter R_L [23]. The values found to be in between 0 to 1 and confirm that the ongoing adsorption process is favorable [24] shown in Table 4. The adsorption data obtained are also fitted to the Freundlich isotherm which is the earliest known relationship known as described by the following equation [25].

$$\log Q_e = \log K_f + 1/n \log C_e \text{ ----------------------------[5]}$$

Where K_f is adsorption capacity and n is adsorption intensity. The slope (1/n) and intercept (K_f) 0f a log – log plot of Q_e vs C_e are determined. The results of both regressed isotherms are tabulated in Table 5 and figure 4. The intensity of adsorption is an indicative of the bond energies between dye and adsorbent and the possibility of slight chemisorptions rather than physisorption [16, 22]. However, the multilayer of adsorption of *Samanea saman* through the percolation process may be possible. The values of n are greater than one indicating the adsorption is much more favorable [24].

Effect of Temperature

Effect of temperature on adsorption of ferrous ion was studied by conducting different sets of experiments at initial concentration of 45 mg/l at different temperature *i.e.*, 35, 45, 55 and 65°C. It is observed that adsorption of ferrous ion increases with increase in the temperature.

Thermodynamic parameters

The thermodynamic equilibrium constant K_0 is obtained by calculating the difference between solid phase concentration and liquid phase concentration.

$$K_0 = C_{solid} / C_{liquid} \text{ ---[6]}$$

And extrapolating to zero[26] 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 thermodynamic constants like Gibbs's free energy (ΔG^o), enthalpy change (ΔH^o), and entropy change (ΔS^o), are calculated to evaluate the thermodynamic feasibility of the process and to confirm the nature of the adsorption process. The Gibb's free energy change of the process is related to equilibrium constant (K_0) by equation

$$\mathbf{\Delta G^o = - RT\ln K_0} \text{ ---[7]}$$

The Gibb's free energy change is related to the enthalpy change (ΔH^o) and entropy change (ΔS^o) as

$$\mathbf{\log K_0 = \Delta S^o/(2.303\ RT) - \Delta H^o/(2.303\ RT)} \text{ ------------------[8]}$$

The ΔH° and .ΔS° values obtained from the slope and intercept of Van't Hoff plots (representative Fig.5) have presented in Table 6. The values ΔH° is within the range of 1 to 93 KJ/mol indicates the physisorption. From the results we could make out that physisorption is much more favorable for the adsorption of ferrous ion. The positive value of ΔH° show the endothermic nature of adsorption and it governs the possibility of physical adsorption [22.,27]. Because in the case of physical adsorption, while increasing the temperature of the system, the extent of dye adsorption increases, this rules out the possibility of chemisorptions [27]. The low ΔH° value depicts dye is physisorbed onto adsorbent *Samanea saman*. The negative values of ΔG° (Table 6) shows the adsorption is highly favorable and spontaneous. The positive values of ΔS° (Table 6) show the increased disorder and randomness at the solid solution interface of ferrous ion with *Samanea saman* adsorbent, while the adsorption there are some structural changes in the dye and the adsorbent occur. The adsorbed water molecules, which have 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. The enhancement of adsorption capacity of the activated carbon at higher temperatures was attributed to the enlargement of pore size and activation of the adsorbent surface [20, 27, 24].

Kinetics of adsorption

The kinetics of sorption describes the solute uptake rate, which in turn governs residence time or sorption reaction. It is one of the important characteristics in defining the efficiency or sorption. In the present study, the kinetics of the dye removal was carried out to understand the behavior of these low cost carbon adsorbents. The adsorption of dye from an aqueous follows reversible first order kinetics, when a single species are considered on a heterogeneous surface. The heterogeneous equilibrium between the dye solutions and the activated carbon are 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 dyes remaining in the aqueous solution and B represent dye adsorbed the surface of activated carbon. The equilibrium constant (K_0) is the ratio of the concentration adsorbate in adsorbent and in aqueous solution ($K_0= k_1/ k_2$).

In order to study the kinetics of the adsorption process under consideration the following kinetic equation proposed by Natarajan and Khalaf as cited in literature has been employed [25].

$$\log C_0/C_t=(K_{ad}/2.303)t \text{ ----------------------------------}[9]$$

Where t = 0, t = t, C_0 and C_t are the concentration of the dye in (in mg/l) respectively. The rate constants (K_{ad}) for the adsorption processes have been calculated from the slope of the linear plots of log C_0/C_t versus t for different concentrations and temperatures (representative Fig.6). The determination of rate constants as described in literature given by C_0/C_t versus t for different concentrations and temperatures (representative Fig.6). The determination of rate constants as described in literature given by

$$K_{ad}=k_1+k_2=k_1+ (k_1/K_0)=k_1 [1+1/K_0] \text{ ----------------}[10]$$

The overall rate constant K_{ad} for the adsorption of dye at different temperatures are calculated from the slopes of the linear Natarajan-Khalaf plots. The rate constant values are collected in Table 7 shows that the rate constant (K_{ad}) increases with increases in temperature suggesting that the adsorption process in endothermic in nature. Further, K_{ad} values decrease with increase in initial concentration of the dye. 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 dye concentration and rate of reaction will not be linear. Thus, in the present study pore diffusion limits the overall rate of dye adsorption. The overall rate of adsorption is separated into the rate of forward and reverse reactions using the above equation. The rate constants for the forward and reverse processes are also collected in Table 7 indicate that, at all initial concentrations and temperatures, the forward rate constant is much higher than the reverse rate constant suggesting that the rate of adsorption is clearly dominant [22,27,29].

Intraparticle diffusion

The most commonly used technique for identifying the mechanism involved in the sorption process is by fitting the experimental data in an intraparticle diffusion plot. Previous studies by various researchers showed that the plot of Qt versus $t^{0.5}$ represents multi linearity, which characterizes the two or more steps involved in the sorption process. According to Weber and Morris, an intraparticle diffusion coefficient K_p is defined by the equation 10.

$$K_p=Q/t^{0.5} + C \text{ --------------------------------[10]}$$

Thus the K_p (mg/g $min^{0.5}$) value can be obtained from the slope of the plot of Qt (mg/g) versus $t^{0.5}$ for ferrous ion. From figure 7, it was noted that the sorption process tends to be followed by two phases. The two phases in the intraparticle diffusion plot suggest that the sorption process proceeds by surface sorption and intraparticle diffusion [30,31]. The initial curved portion of the plot indicates a boundary layer effect while the second linear portion is due to intraparticle or pore diffusion. The slope of the second linear portion of the plot has been defined as the intraparticle diffusion parameter K_p(mg/g $min^{0.5}$). On the other hand, the intercept of the plot reflects the boundary layer effect. The larger the intercept the greater would be the contribution of the surface sorption in the rate limiting step. The calculated intraparticle diffusion coefficient K_p value was given by 0.096, 0.144, 0.192, 0.247 and 0.292 mg/g $min^{0.5}$ for initial dye concentration of 15, 30, 45, 60 and 75 mg/l at 35^0C.

Effect of pH

The solution pH plays major role in determining the amount of ferrous ions adsorbed [32]. Adsorption was studied over the range pH – 3-10 and the results are shown in Figure 6. The initial metal ion concentrations were kept constant. Adsorption of Ferrous ions increased appreciably (1-2 times) with increase of pH from 3 to 10 and consistent with results obtained by others. The increase is partly attributed to the formation of different hydroxo species with rise in solution pH. Based on the hydrolysis constants of metal ions as defined in

$$M^{2+} + n\,H_2O \rightleftharpoons M\,(OH)n^{2+} + n\,H^+$$

And taking only primary metal species expected to be formed in the working pH range into consideration, the species distribution diagrams for Ferrous ion is constructed are given in Figure 8, it is evident that Fe^{2+} and its mono hydro species are the predominating species up to pH ~5.9, while di hydro species are also formed to a significant extent above pH ~ 9 for Ferrous ion. Since maximum adsorption ferrous ion was achieved at pH ~ 5.9, it may safely be stated that the removal of ferrous ion was mostly due to adsorption and not precipitation. However, precipitation of small fractions of Fe^{2+} even at pH ~ 9 on the surface by nucleation cannot be neglected. At still higher pH (>9), however, part of Fe^{2+} may be precipitated as di hydroxo species, which also depend upon the initial metal ion concentration. The other important factor, which might contribute to the higher adsorption of metal ions with increased pH, is the pH_{zpc} of *Samanea saman.* At any pH below pH_{zpc} the surface of metal oxides / oxyhydroxides is positively charged and at pH above pH_{zpc} the surface is negative. When the solution pH exceeded pH_{zpc}, the metal species are more easily attracted by the negatively charged surface of adsorbent, favoring accumulation of metal species on the surface and thus promoting adsorption [33,34].

Effect of other ions

Till now all the adsorption results discussed above were obtained by taking a single cation as adsorbate (e.g. Fe^{2+}), however, in reality the contaminated water contains heavy metals, Therefore, it was thought worthwhile to study the effect of some commonly occurring ions on adsorption behavior of Ferrous ion under present study. A typical water sample containing Chloride ions and Calcium ions were doped with known quantities of adsorbate metal ions and they were used as the stimulated water matrix for adsorption. A fixed amount *Samanea saman* was dispersed in this water matrix containing adsorbate. The other adsorption parameters were kept constant, as stated earlier. The results are collected in Figure 9. It is evident that the presence of the above ferrous ion in the adsorbate solution practically did not affect the extent of adsorption. It may be noted that almost the whole ferrous ion content in the adsorbate solution is removed after adsorption. The concentration of other ions, however, marginally decreased (with ion 10% of initial concentration) after adsorption. A higher concentration level of interfering ions may, however, adversely affect the adsorption capacity of *Samanea saman.* Adsorption of different heavy metal from a stimulated water matrix containing a high back ground level of different ions is being carried out to assess its future applicability to removal of toxic metals from industrial effluents [33-35]·

Desorption studies

The nature of adsorption, recycling of the spent adsorbent and the ferrous ion was studied by using desorption studies. If neutral pH water was taken, the adsorbed ferrous ion can be desorbed, and then the binding of the ferrous ion of the adsorbent is by weak bonds. During ion exchange, the adsorption between adsorbent and sulphuric acid or alkaline water desorp the ferrous ion. If chemisorptions taken places, organic acids like acetic acid can desorp the ferrous ion, then the metal ion has held by the adsorbent. Hydrochloric acid is a better reagent for desorption studies compared to various reagents used for desorption studies, because we could get more than 81 % removal of adsorbed Ferrous ion. The rate of sorption was highly pH dependent. The desorption of ferrous ion by mineral acids and the alkaline medium indicates that the ferrous ion was adsorbed onto activated *Samanea saman* through the physisorption mechanism [22, 24, 27, 36].

Evidences for adsorption

FT – IR spectral studies

FT – IR spectra for the activated *Samanea saman* before and after adsorption of ferrous ion have been recorded a representation spectrum is shown in figures 10a and 10b. From the figure, it could be seen that, the peak position is not changed but the slight reduction of stretching vibration of adsorption bonds takes place. This figure indicates that the adsorption of ferrous ion on the activated *Samanea saman* by physical forces not by chemical combination.

XRD spectral studies

A representative XRD pattern of the activated *Samanea saman* and ferrous ion adsorbed *Samanea saman* is shown in figures 11a and 11b. The intense main peak shows the presence of highly organized crystalline structure of raw activated carbon, after the adsorption of ferrous ion, the intensity of the highly organized peak is slightly disappeared. This has attributed to the adsorption of ferrous ion on the upper layer of the crystalline structure of the carbon surface by means of physisorption rather than chemisorptions.

SEM images

The SEM images of raw activated carbon and a representative image is given in figures 12a and 12b. The bright spots shows the presence of tiny holes on the crystalline of raw activated carbon, after treatment with ferrous ion the bright spots became black shows the adsorption of the ferrous ion on the surface of the activated *Samanea saman* [36,37] .

Table 2 – Equilibrium parameters for the adsorption of ferrous ion by activated carbon (SSC)

Ferrous ion concentration (mg/l)	**C_e (mg/l)**				**Q_e (mg/g)**				**Metal ions removed (%)**			
	Temperature °C											
	35	**40**	**45**	**50**	**35**	**40**	**45**	**50**	**35**	**40**	**45**	**50**
10	1.3271	1.1254	0.9387	0.7239	8.6729	8.8746	9.0613	9.2761	86.72	88.74	90.61	92.76
20	2.8474	2.6326	1.9834	1.6084	17.1526	17.3674	18.0166	18.3916	85.76	86.83	90.08	91.95
30	4.7247	4.3245	3.7482	3.2506	25.2757	25.6755	26.2518	26.7494	84.25	85.58	87.50	89.16
64	7.9783	7.2943	6.9254	6.0235	32.0217	32.7057	33.0746	33.9765	80.05	81.76	82.68	84.94
50	11.2963	10.9214	10.3215	9.8216	38.7037	39.0786	39.6785	40.1789	77.40	78.15	79.35	80.35
60	16.4112	15.8143	14.9281	14.0271	43.5888	44.1857	45.0719	45.9729	72.64	73.64	75.11	76.62

Table 3 - Langmuir isotherm results for the adsorption of ferrous ion by SSC

Temperature	**Statistical parameters/constants**		
°C	**r^2**	**Q_m**	**b**
35	0.9970	66.18	0.1215
40	0.9989	62.89	0.1510
45	0.9978	59.35	0.2016
50	0.9981	56.95	0.2702

Table 4 - Dimensionless Separation factor (R_L) for the adsorption of ferrous ion by SSC

Ferrous ion concentration (mg/l)	**Temperature °C**			
	35	**45**	**55**	**65**
10	0.450	0.398	0.331	0.270
20	0.290	0.248	0.196	0.156
30	0.214	0.181	0.141	0.109
64	0.170	0.142	0.110	0.085
50	0.141	0.116	0.090	0.068
60	0.120	0.099	0.075	0.058

Table 5 – Freundlich isotherm results for the adsorption of ferrous ion by SSC

Temperature	**Statistical parameters/constants**		
°C	**r^2**	**K_f**	**N**
35	0.9852	1.8934	1.5664
40	0.9865	1.8369	1.6444
45	0.9812	1.7399	1.8066
50	0.9882	1.6796	1.9282

Table 6 Equilibrium constant and thermodynamic parameters for the adsorption of ferrous ion by activated carbon (SSC)

Ferrous ion concentration (mg/l)	**K_0**				**ΔG^o**					
	Temperature °C									
	35	**40**	**45**	**50**	**35**	**40**	**45**	**50**	**ΔH^o**	**ΔS^o**
10	1.53	7.88	9.65	12.81	-4.80	-5.37	-5.99	-6.85	32.42	120.66
20	6.02	6.59	9.08	11.43	-4.59	-4.98	-5.83	-6.54	33.29	123.91
30	5.35	5.93	7.00	8.22	-4.29	-4.63	-5.14	-5.65	22.38	86.48
40	4.01	4.48	4.77	5.64	-3.55	-3.90	-4.13	-4.65	18.44	72.52
50	3.42	3.57	3.84	4.09	-3.15	-3.31	-3.56	-3.78	9.56	41.24
60	2.65	2.79	3.02	3.27	-2.50	-2.67	-2.92	-3.18	8.41	35.38

ΔH^o (KJ/mol), ΔS^o(KJ/mol), ΔG^o (KJ/mol)

Table 7 – 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 $^{-1}$) process (SSC)

Ferrous ion concentration (mg/l)	**Temperature (°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**
10	8.38	10.13	11.93	12.75	7.27	1.11	8.99	1.14	10.81	1.12	11.83	0.92
20	6.67	7.36	8.27	9.18	5.72	0.95	6.40	0.96	7.45	0.82	8.45	0.73
30	6.45	6.68	6.99	7.34	5.44	1.01	5.72	0.96	6.03	0.96	6.39	0.95
40	4.84	5.29	5.74	6.05	3.87	0.97	4.33	0.96	4.75	0.99	5.14	0.91
50	4.38	4.60	4.85	5.08	3.39	0.99	3.60	1.00	3.84	1.01	4.09	0.99
60	3.68	3.77	3.90	4.11	2.67	1.01	2.98	0.79	2.93	0.97	3.15	0.96

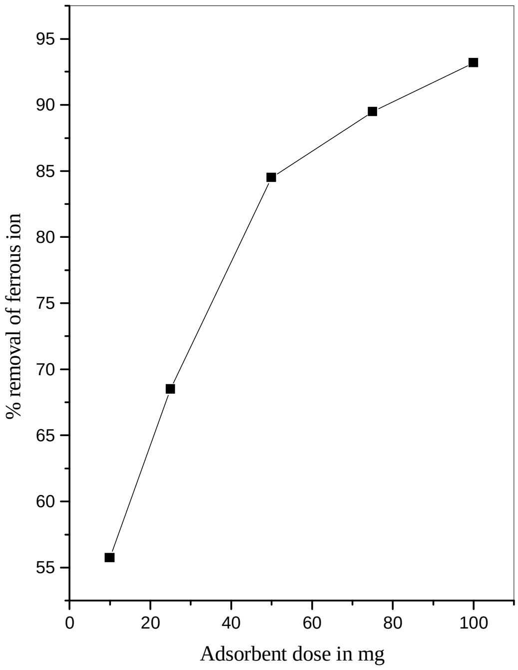


Fig.1-Effect of adsorbent dose on the adsorption of ferrous ion by SSC

[Fe]=30 mg/L;Contact time=60 min;Temp=35^{0}C

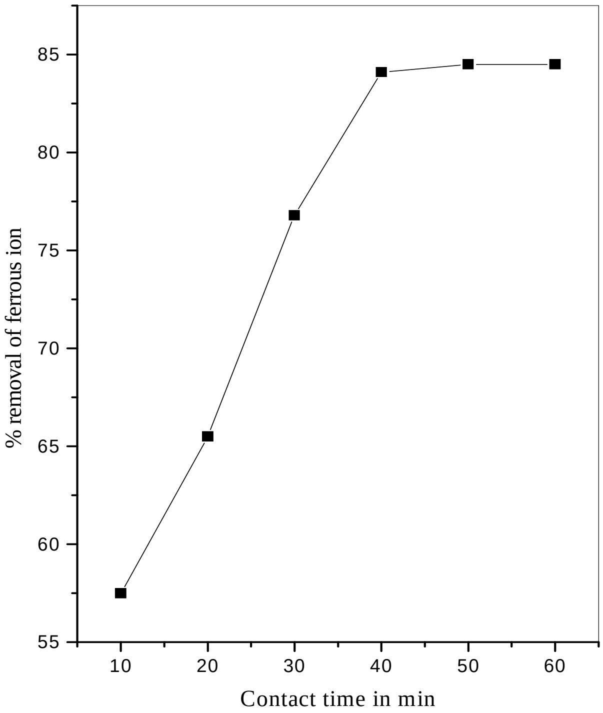


Fig.2-Effect of contact time on the adsorption of ferrous ion by SSC

[Fe]=30 mg/L;Adsorbent dose=50 mg/50 ml;Temp=35^{0}C

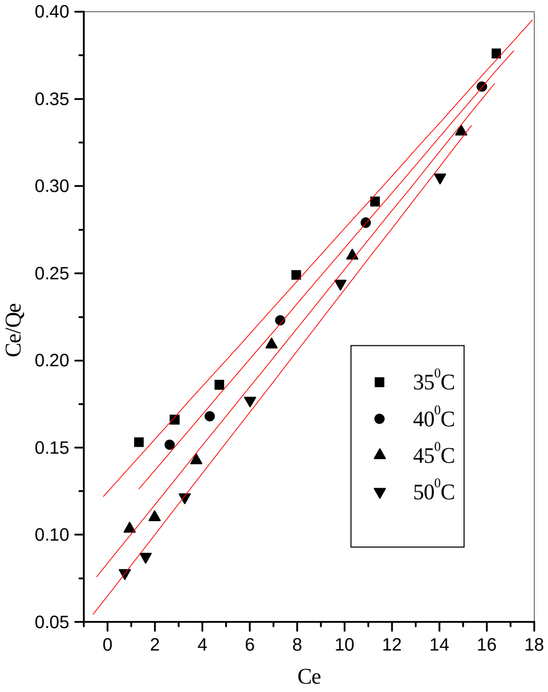


Fig.3-Linear Langmuir isotherm for the adsorption of ferrous ion by SSC

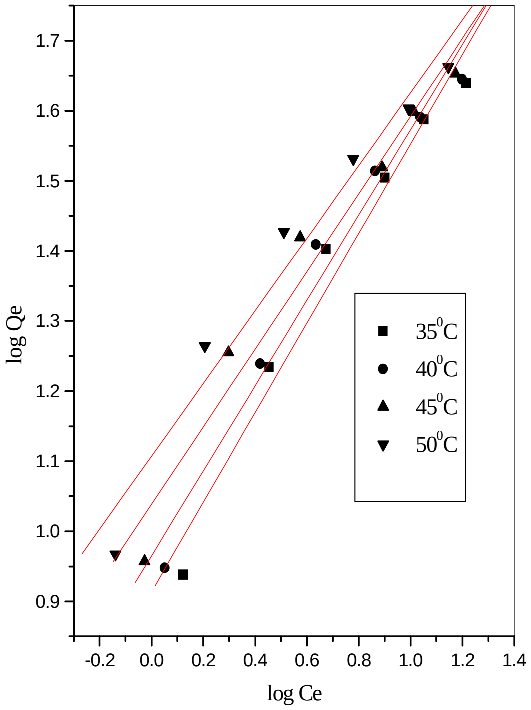


Fig.4-Linear Freundlich isotherm for the adsorption of ferrous ion by SSC

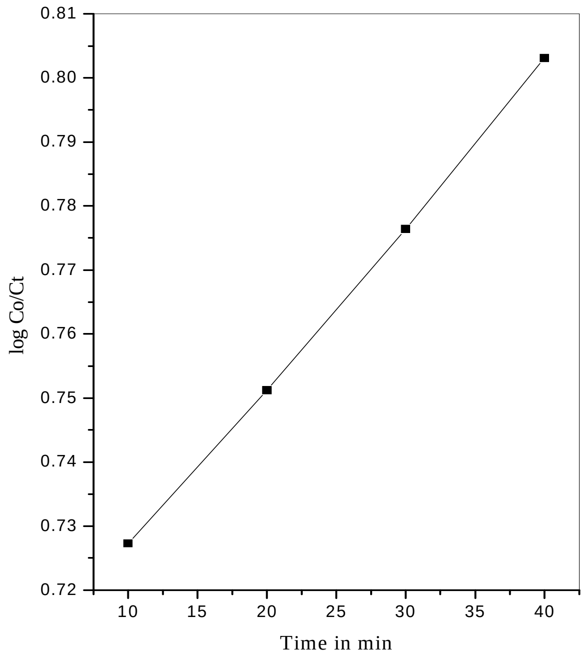


Fig.5-Natarajan-Khalaf plot for the adsorption of ferrous ion
[Fe]=30 mg/L;Adsorbent dose=50 mg/50 ml;Temp=35^{0}C

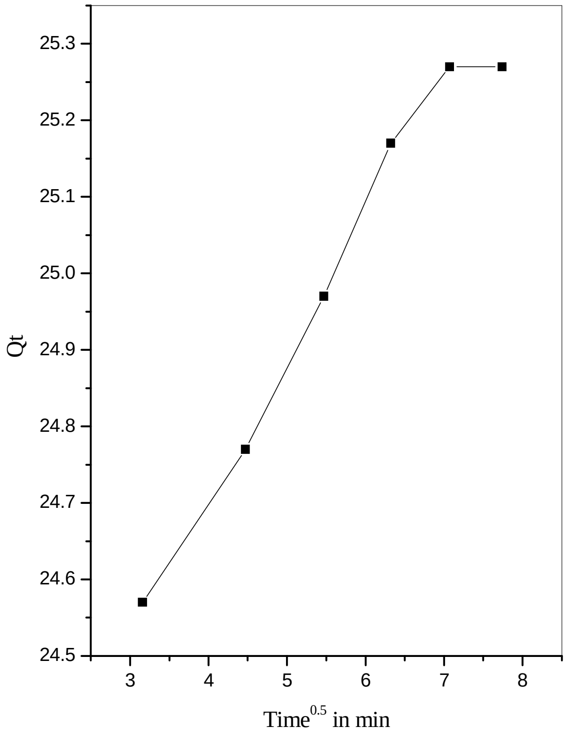


Fig.6-Intra-particle diffusion effect for the adsorption of ferrous ion
[Fe]=30 mg/L;Adsorbent dose=50 mg/50 ml;Temp=35^{0}C

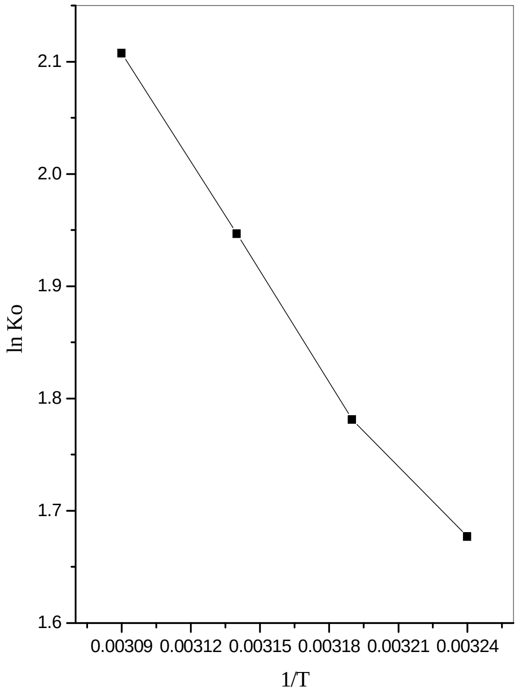


Fig.7-Vant Hoffs plot for the adsorption of ferrous ion
[Fe]=30 mg/L;Adsorbent dose=50 mg/50 ml;Contact time=60 min

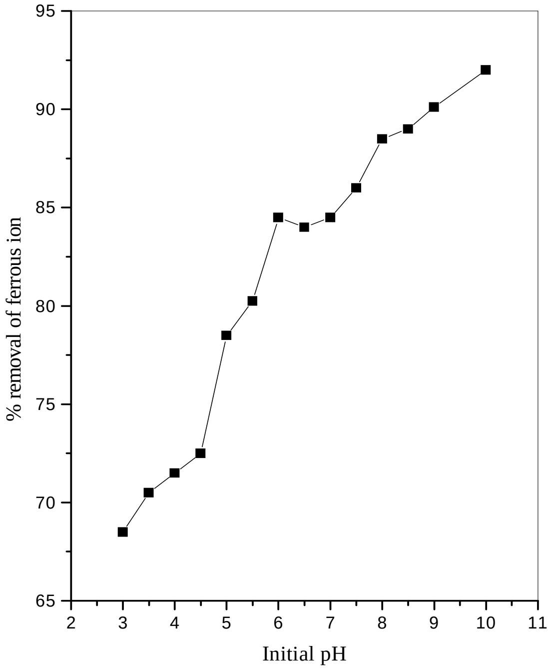


Fig.8-Effect of Initial pH on the adsorption of ferrous ion by SSC
[Fe]=30 mg/L;Adsorbent dose=50 mg/50 ml;
Temp=35^{0}C;Contact time=60 min

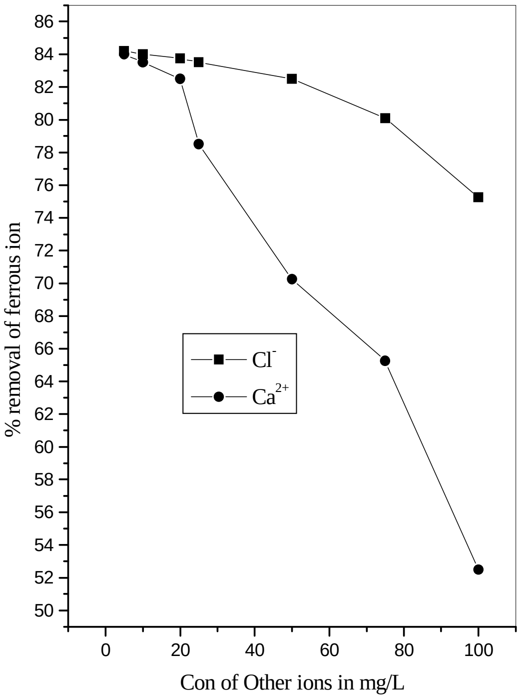


Fig.9-Effect of other ions on the adsorption of ferrous ion by SSC
[Fe]=30 mg/L;Adsorbent dose=50 mg/50 ml;
Temp=35^{0}C;Contact time=60 min

Figure 10a FT – IR Spectra for Raw *Samanea saman carbon*

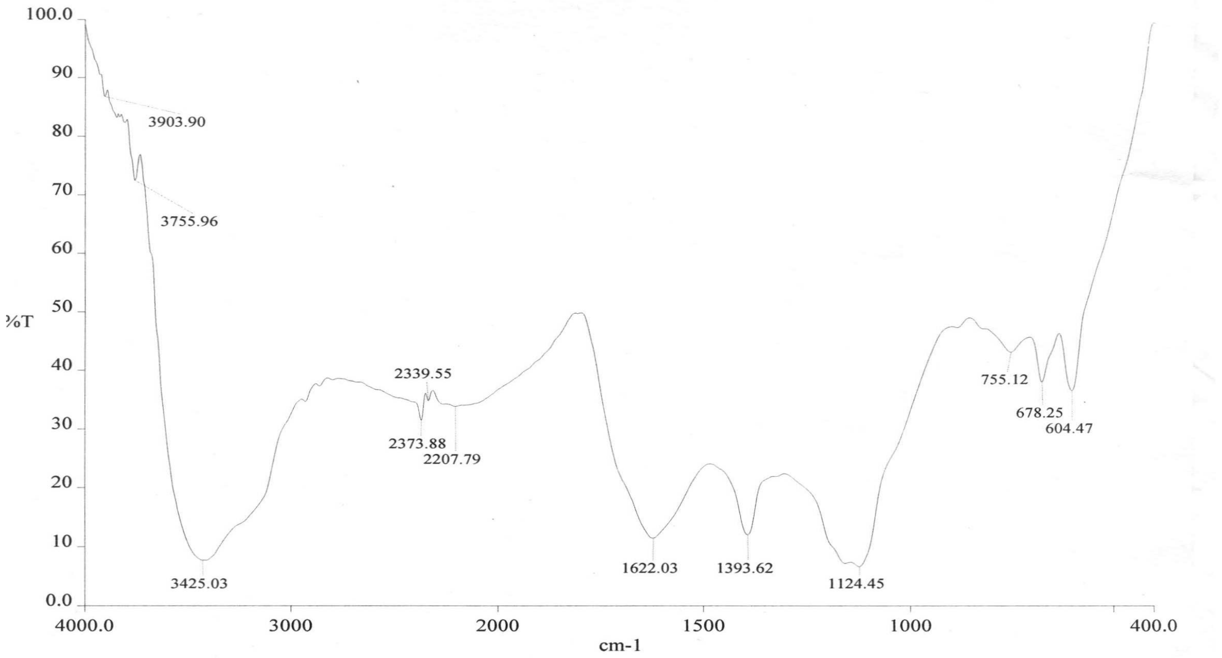


Figure 10b FT – IR Spectra for the adsorption of Ferrous ion by SSC

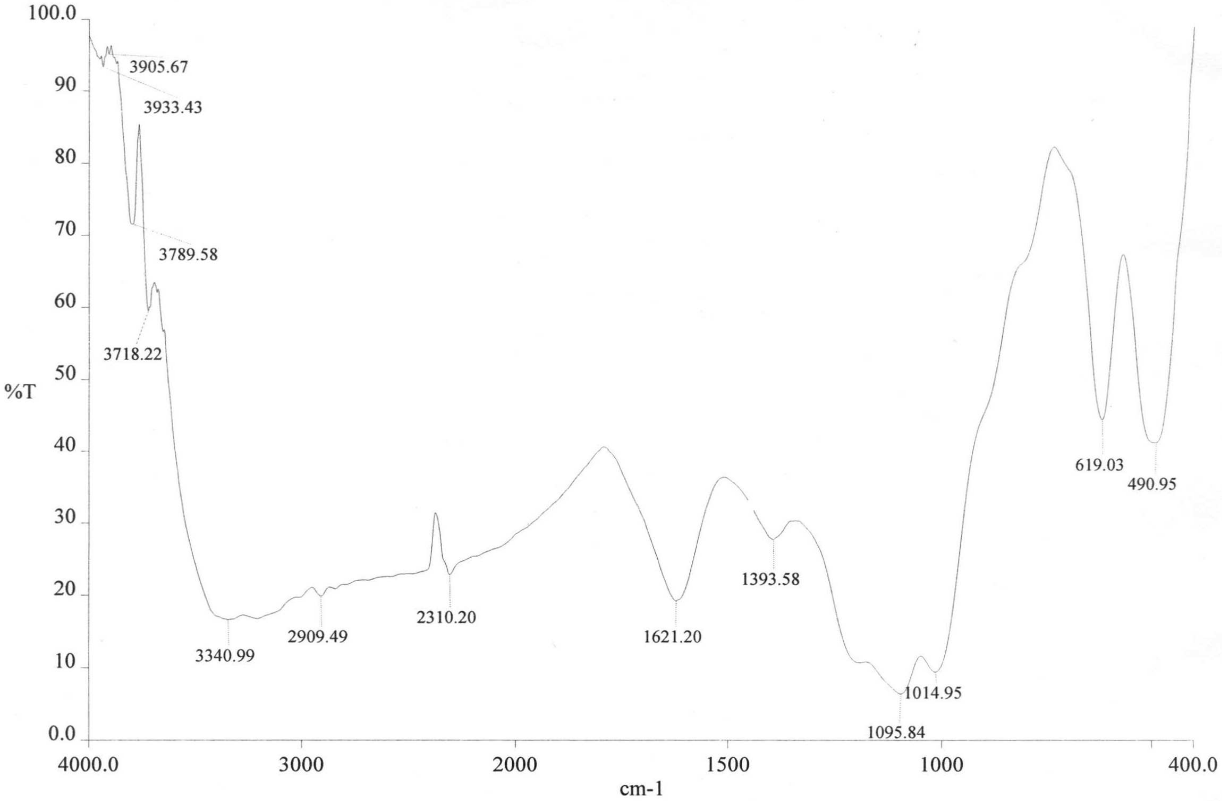


Figure 11a XRD spectra for raw *Samanea saman* carbon

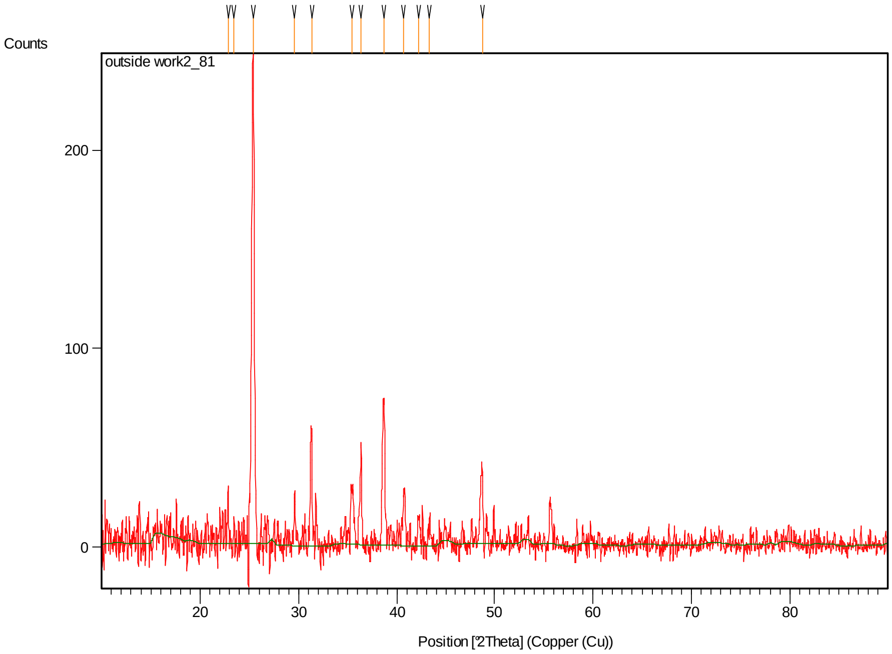


Figure 11b XRD Spectra for the adsorption of ferrous ion by SSC

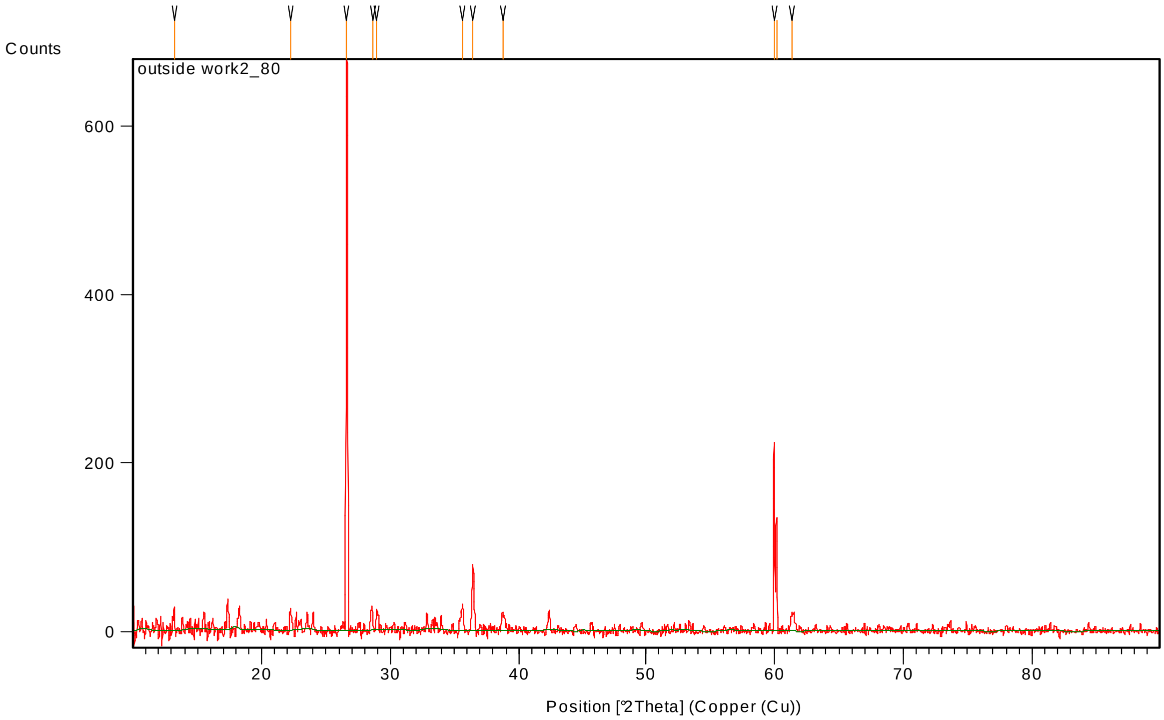


Figure 12a SEM images for raw *Samanea saman* carbon

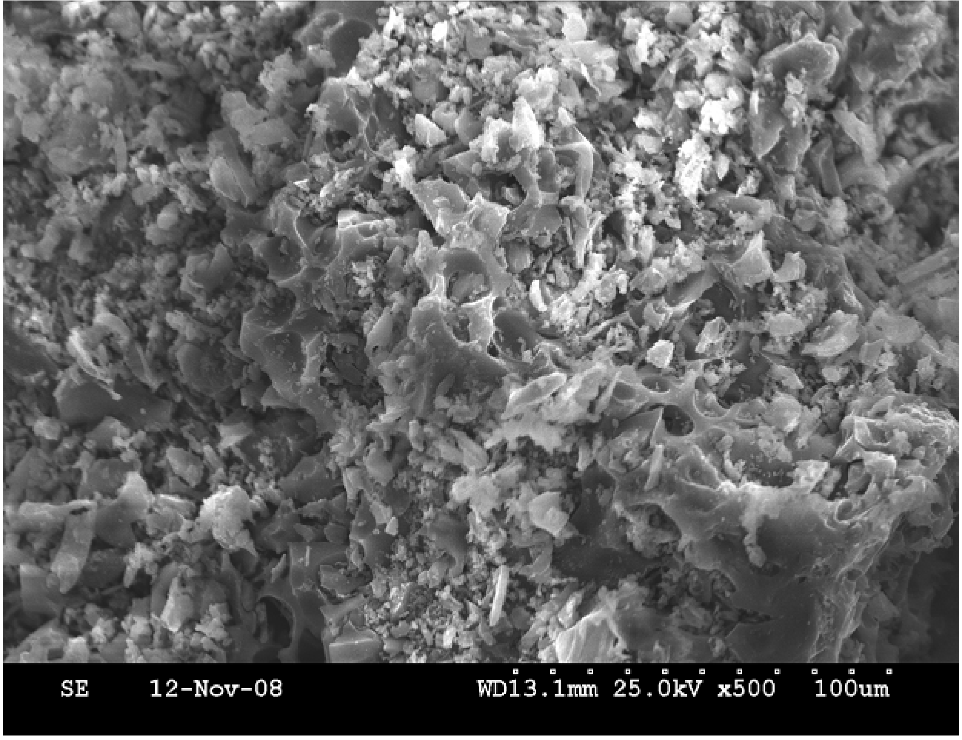
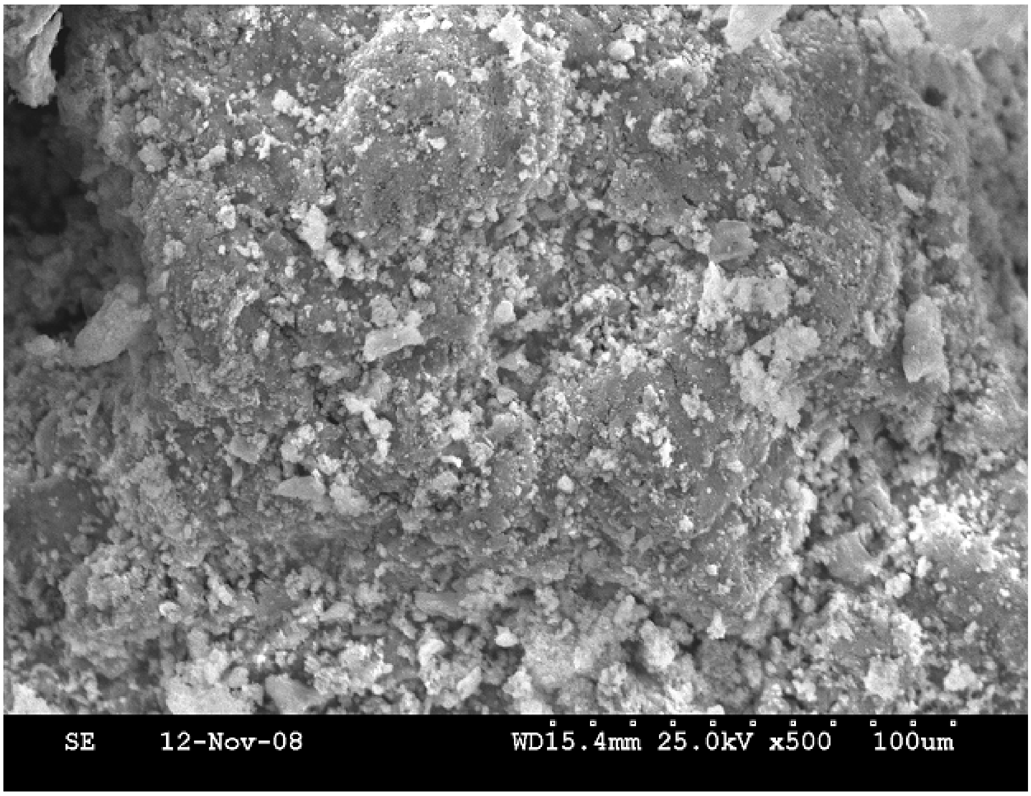


Figure 12b SEM images for the adsorption of ferrous ion by SSC



CONCLUSION

Activated *Samanea saman* has been found to be an economically viable and potential bio sorbent for the removal of ferrous ion. Sorption of ferrous ion onto activated *Samanea saman*, this present work has indicated that the sorbent provide an alternative or adjacent to conventional methods employed to control the level of ferrous pollution. The calculated values of the dimensionless separation factor R_L from the Langmuir and Freundlich isotherm constants confirm favorable sorption of Fe (II) onto *Samanea saman.* The amount of ferrous ion adsorbed increased with increase in pH of the medium. Optimum pH for highest Fe (II) adsorption was 5.9. The amount of ferrous ion adsorbed slightly decreased with increasing ionic strength and increased with increase in temperature. The thermodynamic calculations showed that the Fe (II) adsorption was spontaneous in nature and endothermic nature of the adsorption process. The contact time for the maximum adsorption required was nearly 40 minutes. Adsorption process was found to follow the reversible first order rate kinetics. The values of ΔG^o, ΔH^o and ΔS^o results shows that the carbon employed has a considerable potential as an adsorbent for the removal of ferrous ion.

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