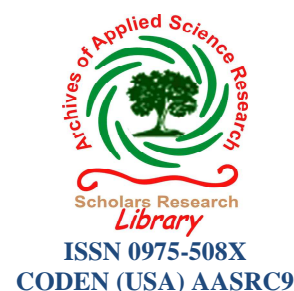




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Biosorption of Ferrous Ion from Aqueous Solutions by using Activated carbon prepared from *Thespesia Populnea* Bark

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ABSTRACT

Thespesia Populnea Bark Carbon (TPC) was synthesized and employed for the removal of ferrous ions from aqueous solutions. The effects of pH, temperature and initial concentration of metal ion on the biosorption capacity were investigated. Two adsorption kinetic models were applied for analyzing the data. Langmuir and Freundlich isotherms from aqueous solution of ferrous ion on TPC were determined. The sorption follows pseudo-second-order kinetics. The results indicate that the highest percentage of ferrous ion adsorption was obtained for the smallest size of the sorbent particles. The thermodynamic parameters of the ferrous ions uptake on to the solid sorbents show that, the process was endothermic and spontaneous from the data stones.

Key words: Activated Carbon, Ferrous ion, Adsorption Isotherm, Thermodynamic Parameters, Equilibrium and Kinetics.

INTRODUCTION

Waste water or effluents coming out from the various industries contains hazardous substances such as phenols, dyes and heavy metal ions like Cd, Fe, Cu, Pb etc. It is well known that the contamination of water, from the industries provides many adverse effects to human health including diarrhoea, liver damage, anaemia and dark urine [1]. Now a days adsorption technique is widely used in environmental management applications throughout the world. Liquid – solid adsorption systems are based on the ability of certain solids to preferentially concentrate specific substances from solutions on to their surfaces. This principle is mainly applicable for the removal of pollutants such as metal ions, dyes and other organic compounds from waste waters [2-5]. Precursor materials for the commercial activated carbons are coal, lignite; nutshells, wood

bark and peat which are transformed in carbonaceous materials by proper carbonization [6]. In this research work, activated carbon prepared from *Thespesia Populnea* bark were employed for the removal of ferrous ion from aqueous solution. *Thespesia Populnea* is a common tree which is distributed in the coastal regions throughout India. *Thespesia Populnea* tree is popularly known as Puvarasamkallal, Cilanti in Tamil and Portia tree in English, which belongs to Malvaceae family. The bark and fruits possess more curative properties. The main objective of the study was to investigate the adsorption characteristics of *Thespesia Populnea* bark for the sorption of metal ion from aqueous solution with respect to different adsorption isotherm, adsorption kinetics, effects of pH and thermodynamic point of view.

MATERIALS AND METHODS

Activated Carbon was synthesized by treating air-dried *Thespesia Populnea* bark with concentrated sulphuric acid in a weight ratio of 1:1. The resulting product was heated 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 obtained from *Thespesia Populnea* bark was dried for four hours at 100 °C in a hot air oven. The dried material was ground well to fine powder and sieved.

Batch equilibration method:

All experiments were performed at 30, 40, 50 and 60°C temperature in batch process. Batch process was selected because of its simplicity and reliability. The experiments were carried out in different iodine flasks of 100ml capacity. Prior to each experiment, a predetermined amount of adsorbent was added to each flask. The stirring was kept constant (120 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 25 mg/L to 125 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.

Effect of variable parameters

Dosage of adsorbents

Different doses of the adsorbent are mixed with the metal ion and the mixture was agitated in a mechanical shaker. The percentage of different adsorption doses was determined by keeping all other factors constant.

Initial concentration

In order to determine the rate of adsorption, experiments were conducted with different initial concentrations of metal ion ranging from 25 to 125 mg/l. All other factors are kept constant.

Contact time:

The effect of period of contact linking the adsorbent and adsorbate on the removal of the metal ion in a single cycle was determined by keeping initial concentration, particle size, pH, dosage, and temperature constant.

Initial pH:

Adsorption experiments were carried out at a range of pH of the solution 3-11. The acidic and alkaline pH of the medium has been maintained by adding the necessary amounts of hydrochloric acid and sodium hydroxide solutions. The parameters like particle size of the adsorbents, and temperature were kept constant while carrying out the experiments.

Other ions:

Adsorption studies of a specific metal ion in the presence of magnesium, calcium, sulphate and chloride ions were experimentally determined using the adsorbents. This involved the determination of the percentage of metal ion adsorbed from 25 mg/L of initial concentration of the metal ion solution with varying concentration of the added ion keeping all other factors constant.

Temperature:

The adsorption experiments were carried out at four different temperatures viz., 30, 40 50 and 60°C in a thermostated shaker machine (Remi, India). The constancy of the temperature was maintained with an accuracy of $\pm 0.5^\circ \text{C}$.

Desorption studies

The studies help to elucidate the nature of adsorption and recycling of the spent adsorbent and the metal ion. The effects of different reagents were employed for desorption studies.

RESULTS AND DISCUSSION

Characteristics of the adsorbent

The wide usefulness of activated carbon is a result of their specific surface area, high chemical and mechanical stability. The chemical nature and pore structure generally determines the sorption activity. The physico chemical properties of the adsorbent are listed in Table 1.

Effect of contact time and initial Fe (II) ion concentration

The experimental data for adsorption of ferrous ion on the activated carbon (TPC) at different concentrations (25, 50, 75, 100 and 125 mg/L) and contact times are shown in fig (1). It is observed that at 25 mg/l of Fe (II) concentration the amount of Fe (II) adsorbed is about 82%. The percentage of Fe (II) ions removed at 25, 50, 75, 100 and 125 mg/L levels are 82, 81.5, 81, 80 and 70 respectively. It is therefore evident that at low concentration ranges the percentage of adsorption is high because of the availability of more active sites on the surface of the adsorbent. As the concentration of metal ion increases, more and more surface sites are covered and hence at higher concentrations of metal ions the capacity of the adsorbent get exhausted due to non-availability of the surface sites [7]. The effect of contact time on Fe (II) adsorption on TPC was investigated to study the rate of Fe (II) removal. Fig (1) shows the percentage removal of Fe (II) for various values of initial Fe (II) concentration ranging from 25 to 125 mg/L⁻¹. It is evident from fig (1) that the time varies in parameter for the adsorption of Fe (II) on TPC

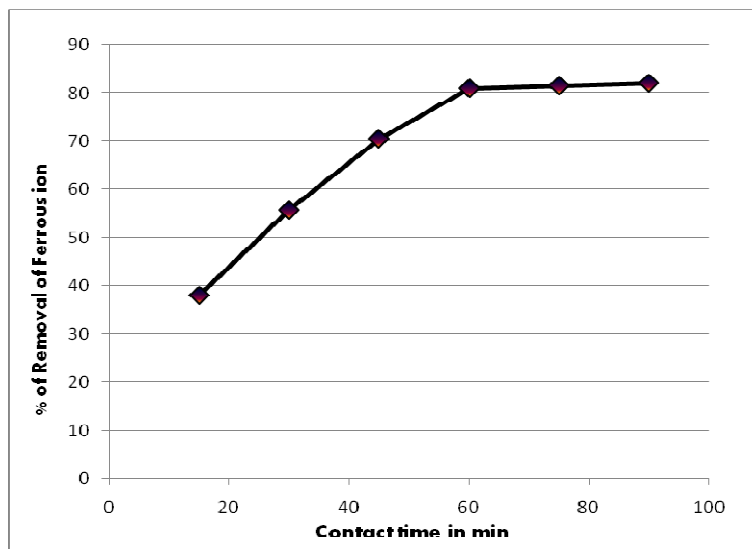


Fig. 1- Effect of contact time on the adsorption of ferrous ion onto TPC
[Fe]= 50 mg/L: Adsorbent dose = 25mg/ 50ml: pH=6.5

Table 1-Characteristics of the Adsorbent

Properties	TPC
Particle size(mm)	0.041
Density (g/cc)	0.3243
Moisture content (%)	0.3255
Loss in ignition (%)	0.273
pH of aqueous solution	6.5

Effect of carbon concentration

The adsorption of ferrous ion on carbon was studied by varying the carbon concentration from 25 to 125mg/L while keeping the ferrous ion concentration as 100mg /L⁻¹. In fig (2), the increase in adsorbent dosage from 25 to 125 mg/L⁻¹ resulted in an increase from 81.5to 94% in adsorption of ferrous ion. It is due to the availability of high binding sites for complexation of ferrous ions [8]. The equilibrium values obtained from the studies are depicted in Table.2.

Adsorption isotherms

Adsorption isotherms are used to evaluate the effect of the adsorption process. The analysis of the isotherm data is essential to develop an equation, which accurately represents the results and could be used for design purposes. In order to investigate the sorption isotherm, two equilibrium models were employed: the Langmuir and Freundlich isotherm equations [9-10].

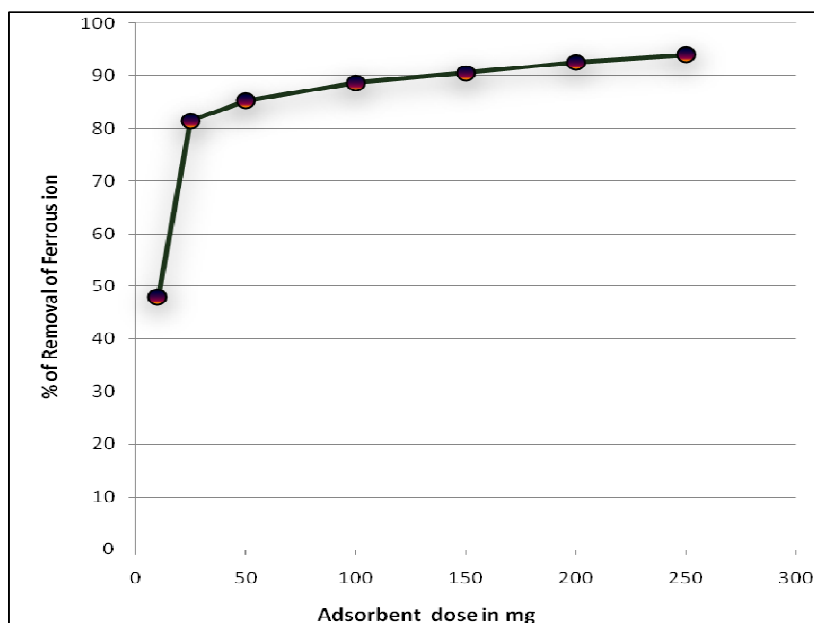


Fig. 2- Effect of adsorbent dose on the adsorption of ferrous ion onto TPC [Fe] = 50mg/L: contact time = 60min: pH=6.5

Table 2 – Equilibrium parameters for the adsorption of metal ions onto activated carbon

Ferrous ion, mg/L	C _e (mg/L)				Q _e (mg/g)				Metal ions removed (%)			
	Temperature ° C											
	30	40	50	60	30	40	50	60	30	40	50	60
25	2.357	2.114	1.906	1.777	45.28	45.77	46.18	46.44	90.57	91.54	92.37	92.89
50	9.293	8.262	6.873	5.878	81.41	83.47	86.25	88.24	81.41	83.47	86.25	88.24
75	20.1745	17.877	15.67	13.722	109.6	114.2	118.6	122.5	73.10	76.16	79.10	81.70
100	38.773	35.860	15.67	29.762	122.4	128.2	168.6	140.4	61.22	64.13	84.32	70.23
125	60.222	56.536	32.79	49.467	129.5	136.9	184.4	151.0	51.82	54.77	73.76	60.42

The Langmuir model assumes that the uptake of metal ions occurs on a homogeneous surface by monolayer adsorption without any interactions between adsorbed ions. The Langmuir isotherm model can be commonly expressed in the form of following equations.

$$C_{eq}/Q_{eq} = 1/Q_m b + C_{eq}/Q_m \quad (1)$$

Where C_{eq} is the equilibrium concentration of ferrous ion in solution (mg/L), Q_{eq} is the amount of ferrous ion adsorbed; Q_m and b is Langmuir constants related to adsorption efficiency and energy of adsorption, respectively. The linear plots of C_{eq}/ Q_{eq} vs. C_{eq} suggest the applicability of the Langmuir isotherms fig (3). The values of Q_m and b were calculated from slope and intercepts of the plots are listed 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. The values can conclude that the maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on adsorbent surface with constant energy and no diffusion of

adsorbate in plane of the adsorbent surface. To confirm the favourability of the adsorption process, the separation factor (R_L) was determined and given in Table 2. The values were established to be between 0 and 1 and confirm that the ongoing adsorption process is favorable [11].

Freundlich equation has been widely employed for adsorption isotherm [12]. The Freundlich isotherm describes in multilayer adsorption, which is commonly expressed by the following equation.

$$\log Q_e = \log K_f + 1/n \log C_e \quad (2)$$

Where Q_e is the amount of ferrous ion adsorbed (mg/g), C_e is the equilibrium concentration of ferrous ion in solution (mg/L), and K_f and n are constant integrates, the factors affecting the adsorption capacity and intensity of adsorption, respectively. Linear plots of $\log Q_e$ versus $\log C_e$ shows that the adsorption of ferrous ion obeys the Freundlich adsorption isotherm. In figure (4), the Freundlich adsorption isotherm obtained by plotting C_e/q_e versus C_e for the adsorption of Fe (II) on TPC at the different temperatures investigated, respectively. The K_f and n values are given in Table 3, which indicate that the increase of negative charges on the adsorbent surface makes electrostatic force like Vanderwaal's between the carbon surface and ferrous ion. The values clearly indicate the 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 [13, 14]. However, the multilayer adsorption of ferrous ion through the percolation process may be possible. The values of n are less than one, indicating the physisorption is much more possible [15].

Thermodynamic studies

To study the effect of temperature on the adsorption metal ion by TPC, the experiments were done at different temperatures of 30, 40, 50 and 60°. Thermodynamic parameters such as change in free energy (ΔG°) (kJ/mol), enthalpy (ΔH°) (kJ/mol) and entropy (ΔS°) (J/K/mol) were determined by the following equations.

$$K_0 = C_{\text{solid}}/C_{\text{liquid}}$$

$$\Delta G^\circ = -RT \ln K_0$$

$$\log K_0 = \Delta S^\circ / (2.303R) - \Delta H^\circ / (2.303RT)$$

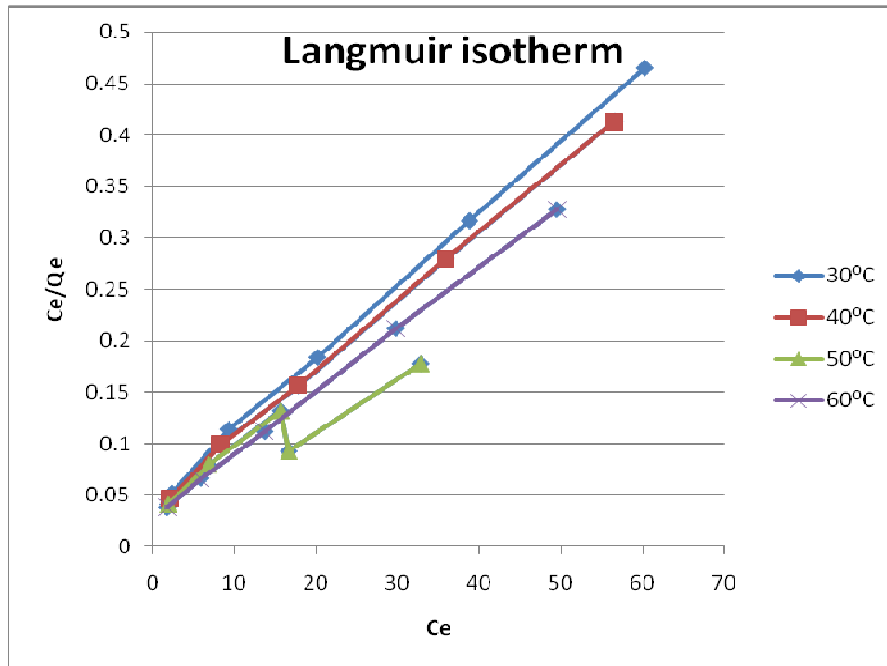


Fig. 3- Langmuir Isotherm for the adsorption of ferrous ion onto TPC

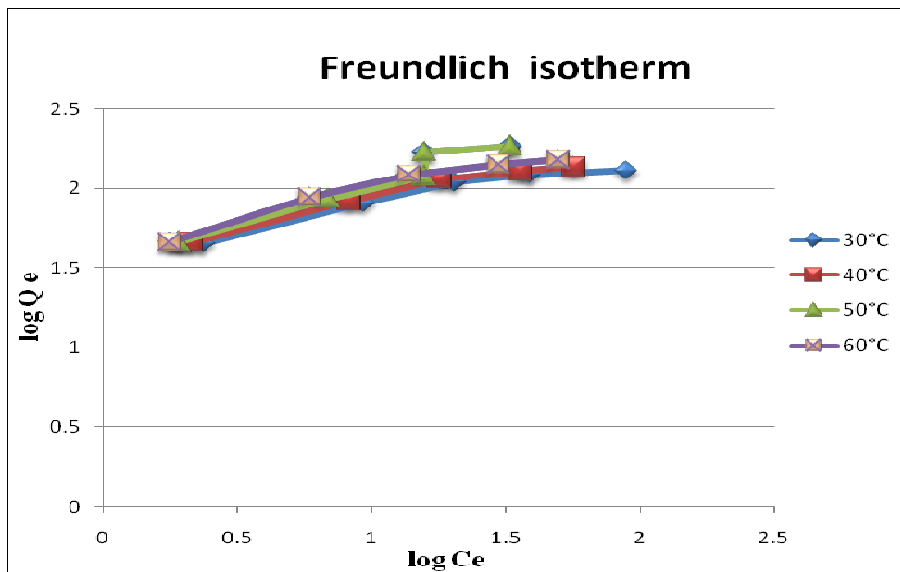


Fig 4- Freundlich Isotherm for the adsorption of ferrous ion onto TPC

Table.3 Langmuir Isotherm, Freundlich Isotherm results and Dimensionless separation factor (R_L)

Ferrous ion, mg/L	Temperature C°	Langmuir Isotherm results			Freundlich Isotherm results			Dimensionless Separation Factor (R_L)				
		Statistical parameters/constants			Statistical parameters/constants			[metal ion]. (mg/L)				
		r^2	Q_m	b	r^2	K_f	n	25	50	75	100	125
30	0.9924	141.81	0.1685	0.9131	4.7735	3.019	0.1918	0.1060	0.0733	0.0560	0.0453	
40	0.9913	149.94	0.1759	0.9162	4.8705	2.947	0.1851	0.1020	0.0704	0.0537	0.0434	
50	0.9922	236.21	0.0984	0.9152	4.6043	1.983	0.2890	0.1689	0.1193	0.0922	0.0751	
60	0.9933	165.26	0.2052	0.9123	5.0982	2.827	0.1630	0.0887	0.0609	0.0464	0.0375	

Table 4 – Equilibrium constant and thermodynamic parameters for the adsorption of metal ions onto activated carbon

Ferrous ion, mg/L	ΔH°	ΔS°	K.				ΔG°			
			Temperature (C)							
			30°	40°	50°	60°	30°	40°	50°	60°
25	8.7136	47.615	9.6044	10.825	12.116	13.068	-5698.8	-6198.4	-6698.9	-7115.8
50	15.345	62.760	4.380	5.0514	6.274	7.5062	-3720.9	-4214.8	-4931.6	-5580.7
75	13.912	54.174	2.7175	3.1953	3.7860	4.4656	-2518.4	-3023.0	-3576.1	-4142.9
100	19.826	69.865	1.5791	1.7885	5.3814	2.3599	-1150.9	-1513.0	-4519.4	-2377.2
125	16.245	54.726	1.0756	1.2109	2.8110	1.5269	-183.67	-498.15	-2275.5	-1171.7

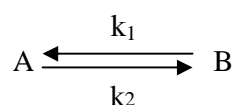
Where K_o is the equilibrium constant, C_{solid} is the solid phase concentration at equilibrium (mg/L), C_{liquid} is the liquid phase concentration at equilibrium (mg/L), T is the temperature in Kelvin, and R is the gas constant. The ΔH° and ΔS° values obtained from the slope and intercept of Van't Hoff plots are given in Table 4. The values ΔH° is the range of 1 to 93 kJ/mol indicates the favorability of physisorption. It is clear that from results that physisorption is much more possible for the adsorption for ferrous ion. The positive values of ΔH° indicate the endothermic nature of adsorption and it governs the possibility of physical adsorption^{15, 16}. Because in the case of physical adsorption, while increasing the temperature of the system, the extent of metal ion adsorption increases, there is no possibility of chemical adsorption. The negative values of ΔG° are given in Table 4 indicate that the adsorption is greatly favorable of ferrous ion. The positive values of ΔS° in Table 4 show the increased disorder and randomness at the solid solution interface of ferrous ion with TPC adsorbent. The results indicate that more efficient physisorption [14 and 17-18].

Adsorption kinetics

Some steps have been used to describe the adsorption mechanism. To find out the mechanism of ferrous adsorption and the potential rate controlling steps, like diffusion mass transport and

chemical reaction process, it is required to characterize the adsorption mechanism. In order to understand the kinetics of removal of Fe (II) using TPC as an adsorbent, pseudo first, pseudo second order are tested with the experimental data. The sorption of ferrous ions on TPC may involve chemical sorption which can control the chemical reaction rate.

The removal of ferrous ion from an aqueous solution obeys the reversible first order kinetics, when a single species considered on a heterogeneous surface. 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 results indicate that K_0 values decreases with increase in the concentration of the ferrous ion and increases with increase in temperature. The calculated values are listed given in the Table 4. The heterogeneous equilibrium between the ferrous ion solution and the activated carbon are represented as



Where k_1 is the forward rate constant and k_2 is the backward rate constant. A indicate that ferrous ion remaining in the aqueous solution and B indicate that ferrous ion adsorbed on the surface of activated carbon. The rate constants calculated as earlier [13, 14 and 19]. The data are specified in Table 5, shows that the forward rate constant is much higher than the backward rate constant suggesting that the rate of adsorption is clearly dominant.

A clear examination of the effect of ferrous ion concentrations on the rate constant K_{ad} (Table 5), the values help to describe the mechanism of metal ion adsorption 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 [15, 20]

Table 5- Rate constants for the adsorption of metal ions (k_{ad}, min^{-1}) and the constants for forward (k_1, min^{-1}) and reverse (k_2, min^{-1}) process.

Ferrous ion, mg/L	Temperature (C)											
	k_{ad}				k_1	k_2	k_1	k_2	k_1	k_2	k_1	k_2
	30°	40°	50°	60°	30°	40°	50°	60°	30°	40°	50°	60°
25	0.0289	0.0299	0.0308	0.0322	0.026	0.002	0.027	0.002	0.028	0.002	0.029	0.002
50	0.0183	0.0197	0.0219	0.0245	0.014	0.003	0.016	0.003	0.018	0.003	0.021	0.002
75	0.0141	0.0152	0.0167	0.0181	0.010	0.003	0.011	0.003	0.013	0.003	0.014	0.003
100	0.0106	0.0113	0.0121	0.0128	0.006	0.004	0.007	0.004	0.010	0.001	0.009	0.003
125	0.0088	0.0094	0.0103	0.0106	0.004	0.004	0.005	0.004	0.007	0.002	0.006	0.004

Effect of pH

It is well known that the pH of a system is an important parameter for the adsorption of Fe (II) [21]. In the research work, effect of pH on the removal of ferrous ion using TPC as an adsorbent was studied with initial pH range from 3-11. The relation between the initial pH of the solution and percentage removal of ferrous ion is depicted in Figure 5. We have observed that the

percentage adsorption ferrous ions increased appreciably (1-2 times) with increase of pH from 3 to 6.5 and consistent with results obtained by others.

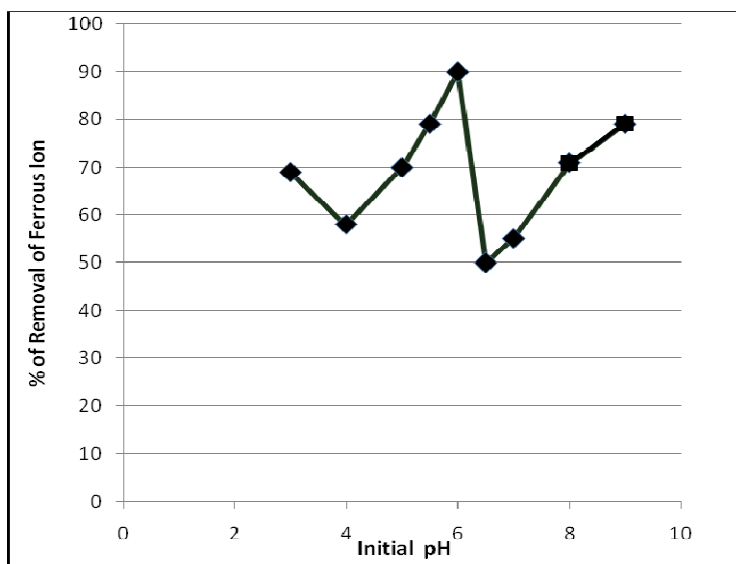


Fig. 5- Effect of pH on the adsorption of ferrous onto TPC
[Fe]= 75mg/L: adsorbent dose = 25 mg / 50ml: contact time = 60min

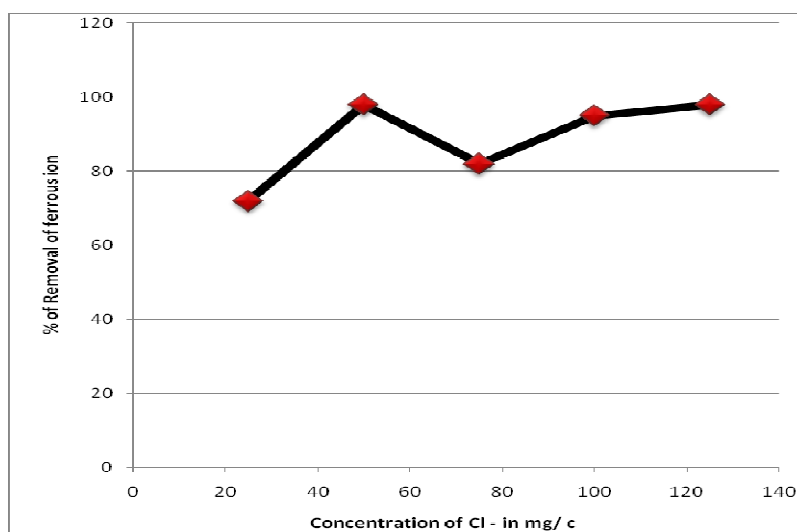


Fig. 6- Effect of other ions on the removal of ferrous ion onto TPC
[MG]= 100mg/L: adsorbent dose = 25 mg / 50ml: contact time = 60mi

Effect of the other ions

The effect of other ion like Cl^- on the adsorption process was studied at various concentrations. The effect of sodium chloride on the adsorption of ferrous ion on TPC is shown in Figure 6. The low concentrate NaCl solutions have slight influence on the adsorption capacity. When the concentration of NaCl increases, the ionic strength is increased.

At higher ionic strength, the adsorption of ferrous ion will be high due to the partial neutralization of the positive charge on the carbon surface and a consequent compression of the

electrical double layer by the Cl^- anion. The chloride ion also enhances adsorption of ferrous ion by pairing their charges, and hence reducing the repulsion between the removal of ferrous ions on the surface. This initiates carbon to adsorb more positive ferrous ions [22- 23].

Evidences for adsorption

The IR spectra of the raw activated carbon before and after adsorption of ferrous ion are shown in Fig. 7.a and Fig. 7.b. It could be seen there is slight reduction of stretching vibration adsorption bands. This clearly indicates the adsorption of ferrous ion on the adsorbent by the physical forces and not by chemical combination.

The XRD diagrams of activated carbon and ferrous ion -adsorbed carbon are shown in Fig.7.1a and Fig. 7.1b. 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 peaks is slightly decreased. 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.

The SEM diagrams of raw activated carbon and ferrous ion -adsorbed activated carbon are shown in 7.2a and Fig. 7.2b. The bright spots, shows the presence of tiny holes on the crystalline structure of raw activated carbon, after treatment with ferrous ion the bright spots become black shows the adsorption of the metal ion on the surface of the carbon.

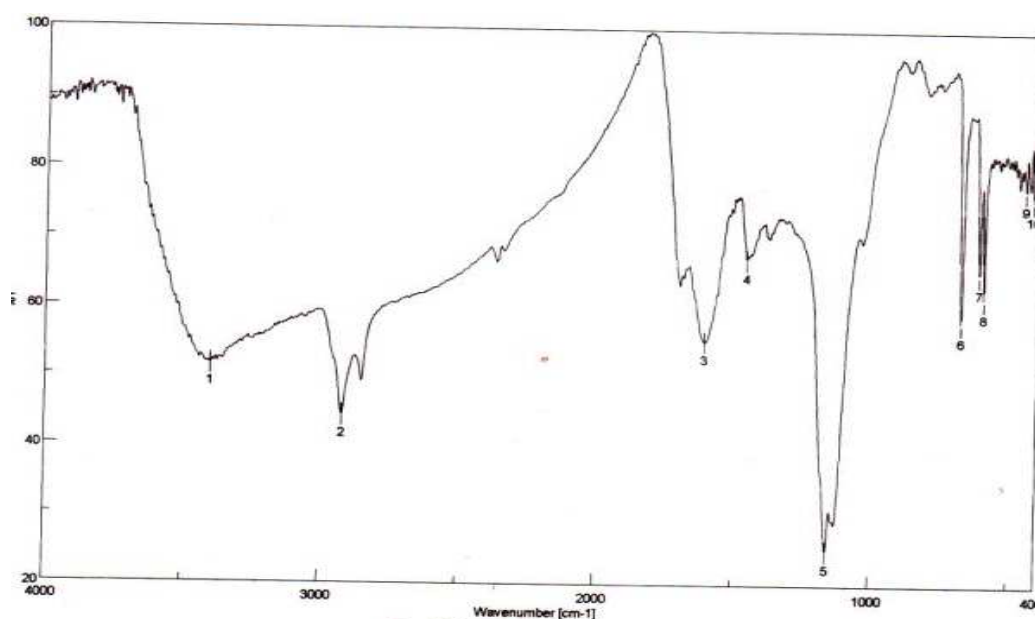
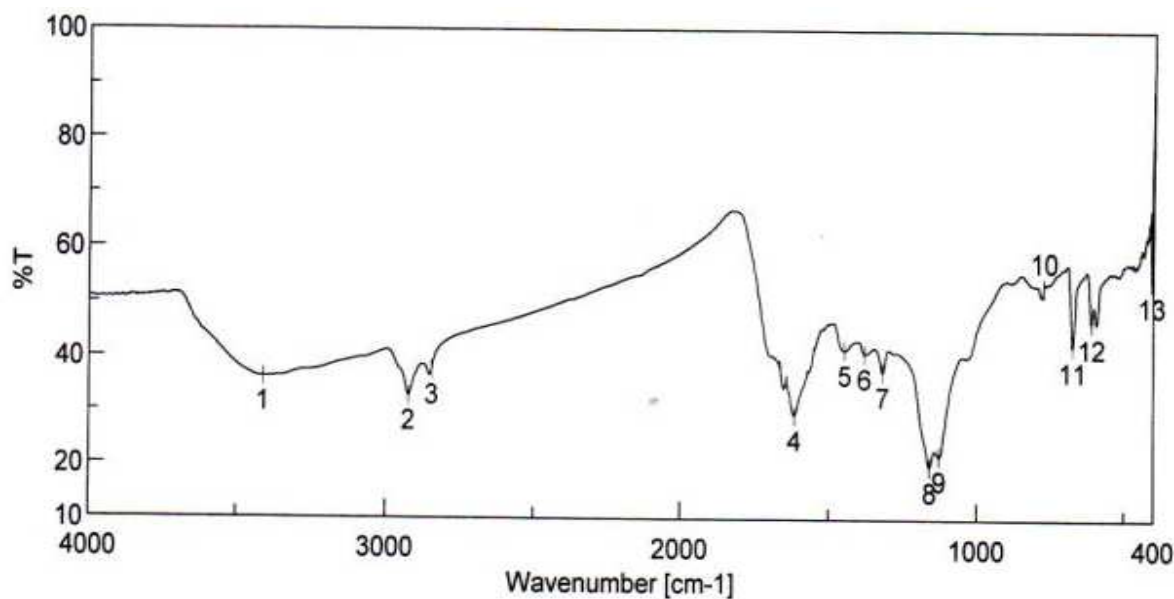
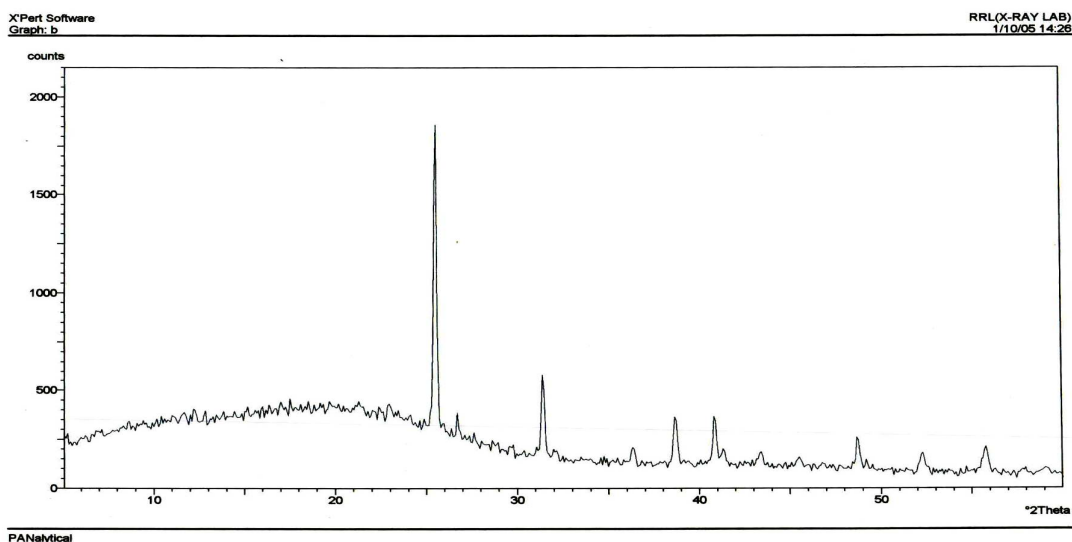


Fig.7.a- FT-IR Spectrum of TPC before adsorption

**Fig 7.b- FT-IR Spectrum of TPC after the adsorption of ferrous ion****Fig.7.1a- XRD pattern of TPC before adsorption**

Desorption studies

The effect of various reagents used for desorption studies indicate that hydrochloric acid is a better reagent for desorption, because we could get more than 90% 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. Desorption of metal ion by mineral acids and alkaline medium indicates that the metal ion was adsorbed onto the activated carbon through by physisorption mechanisms [23].

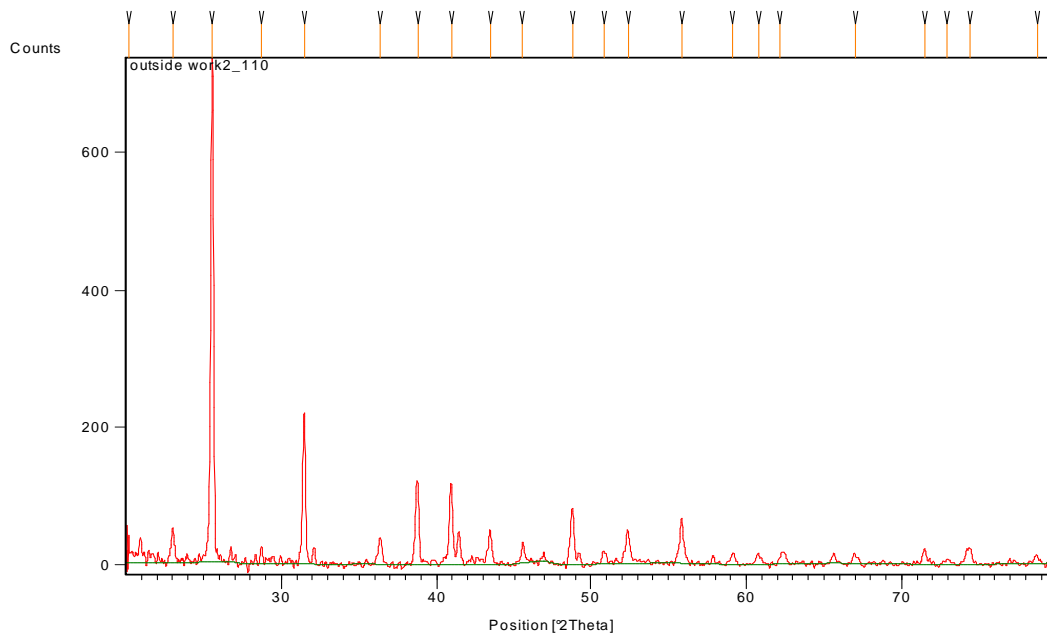


Fig.7.1b- XRD pattern of TPC after the adsorption of ferrous ion

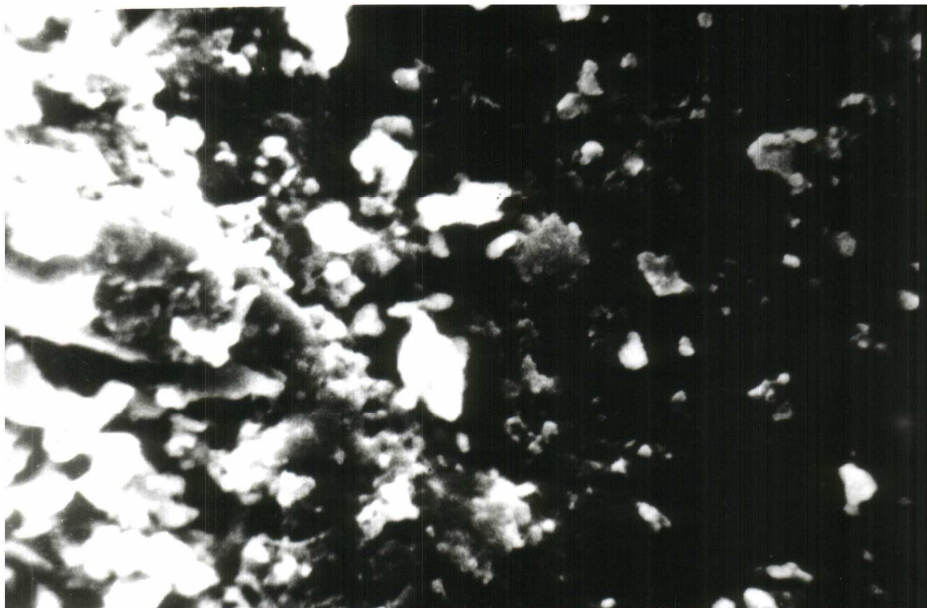


Fig.7.2a- SEM image of TPC before adsorption



Fig. 5.38b- SEM image of TPC after the adsorption of ferrous ion

CONCLUSION

The present research work indicates the applicability of Thespesia Populnea bark as an effective low cost adsorbent for the removal of ferrous ion from aqueous solution. The adsorption process was highly dependent on solution pH and temperature. The kinetic of Fe (II) ion sorption on TPC was based on the assumption of the Pseudo- second –order mechanism with chemisorption being important. In this work, TPC has been found to be a good adsorbent for the removal of ferrous ions from aqueous solutions. The adsorption of ferrous ion on TPC was proved by using FT-IR spectrum, XRD diagrams and SEM diagrams. The equilibrium data were correlated and fitted with the Langmuir isotherm satisfactorily.

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