# EXTRACTION OF FERROUS ION FROM AQUEOUS SOLUTION ON ACID TREATED ACTIVATED CARBON BY ABSORPTION METHOD

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The aim of the present research work is to evaluate the efficiency of locally available activated low cost adsorbents to absorb heavy metalion like Fe(II) from an aqueous solution as an alternative to existing commercial adsorbents. By introducing the concept of adsorptive capacity, one would be able to distinguish between the respective effectiveness of the different adsorbents. Environment factors such as temperature, PH and concentration of other ions would influence the adsorption process. The adsorption characteristics could be depicted by conventional adsorption isotherms(Langmuir and Freundlich).

The dried Zea mays dust were carbonized by treating with concentrated sulphuric acid in the weight ratio 1:1 (w/v). Thus obtained charred masses were heated for 8 hours in a muffle furnace at $400^0$C to complete carbonization and activation. The resulting carbons were washed with distilled water until a constant PH of the slurry was reached. Then the carbons were dried for four hours at $100^0$C in a hot air oven. The dried material was ground well to a fine powder and sieved well using the sieves of desired particle size range. The carbon obtained from Zea mays dust was hereafter designed as ZDC.

**ADSORPTION OF Fe(II) ONTO ZDC**

**EFFECT OF CONTACT TIME AND INITIAL FERROUS ION CONCENTRATION**

The experimental results of adsorptions of ferrous ion onto ZDC at various Concentrations (5, 10, 15, 20, and 25 mg/L) with contact time are shown in the figure (Fig. 4.1). The equilibrium data were collected in the table (Table 4.1),which reveals that the percent adsorption decreased with increase in initial ferrous ion concentration, whereas, the actual amount of ferrous ion adsorbed per unit mass of adsorbent increased with increase in ferrous ion concentration. It means that the adsorption is higlily dependent on initial concentration of ferrous ion. It is because of that, at lower concentration the ratio of the initial number of ferrous ion adsorbed onto the available surface area is low subsequently the fractional adsorption becomes independent of initial ferrous ion concentration. However, at high concentration the available sites of adsorption becomes fewer and hence the percentage removal of ferrous ion is dependent upon initial ferrous ion concentration. An equilibrium has been established at 40 minutes for all Fe(II) concentrations. The figure (Fig.4.1) reveals that the curve is single, smooth and continuous, leading to saturation, suggesting the possible monolayer coverage of the ferrous ion on the carbon surface.

## EFFECT OF CARBON DOSE

The adsorption of ferrous ion onto ZDC was studied by varying the dose of adsorbent. The amount of Fe(II) ion adsorption increased with the increase in carbon dose and reached a maximum value after a particular dose (Fig.4.2). For an initial Fe(II) ion concentration of 15 mg/L, optimum ferrous ion removal was obtained at a maximum carbon dose of 25 mg. The increase in the adsorption of Fe(lI) ion with carbon dose was due to the introduction of more binding sites for adsorption and the availability of more surface area. Hence, the entire studies are carried out with the adsorbent dose of 25 mg of adsorbent/50 ml of the adsorbate solution.

## ADSORPTION ISOTHERMS

The experimental data was analyzed according to the linear form of the Langmuir and Freundlich isotherms. The linear plots of Ce/Qe versus Ce suggest the applicability of the Langmuir isotherms (Fig 4.3). Values of Qm and b were determined from slope and intercepts of the plots and are presented in the table (Table 4.2). From the results, it is clear that the value of adsorption efficiency Qm and adsorption energy b of the carbon increases on increasing the temperature. From the values, it is found that the maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on adsorbent surface with constant energy and there is no transmission of adsorbate in the plane of the adsorbent surface. The trend shows that the adsorbent prefers to bind acidic ions and that specification predominates on sorbent characteristics, when ion exchange is the predominant mechanism. Furthermore, it confirms the endothermic nature of the processes involved in the system. To confirm the adorability of the adsorption process, the separation factor (RL) was calculated and presented in the table (Table 4.3). The values were found to be between 0 and I which confirm that the ongoing adsorption process is favourable.

The Freundlich equation was also employed for the adsorption of ferrous ion on the adsorbent. Linear plot of log Qe versus log Ce shows that the adsorption of ferrous ion follows the Freundlich isotherm (Fig. 4.4). The values of $K_F$ and n were found and provided in the table (Table 4.4). The furnished in the table (Table 4.4) shows that the increase of negative charge on the adsorbent surface that enhances the electrostatic force like, van der Walls between the carbon surface and ferrous ion, which increases the adsorption of ferrous ion. The Values clearly show the dominance in the adsorption capacity. The intensity of adsorption is an indicative of the bond energies between ferrous ion and adsorbent and the possibility of slight chemisorption rather than physisorption. The possibility of multilayer adsorption of ferrous ion through the percolation process cannot be ruled out. However, the values of $n>1$ indicates that the adsorption is much more favourable.

## KINETICS OF ADSORPTION

The 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 investigation, the kinetics of ferrous ion removal has been carried out by Natarajan-Khalaf plot to understand the behaviour of the selected adsorbent. The adsorption of ferrous ion from an aqueous solution follows reversible first order kinetics, when a single species was considered on a heterogeneous surface. The rate

constants were calculated from the slopes of the linear plots of log co/ct versust for different concentrations of ferrous ion at various temperatures. The data furnished in the tables (Table 4.5 and Table 4.6), is an 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 to the concentration of adsorbate in aqueous solution given by $K_0$. The calculated values presented in the table (Table 4.5), indicates that Ko values decrease with increase in the concentration of the ferrous ion and increase with increase in temperature.

A clear examination of the effect of ferrous ion concentrations on the rate constant Kad (Table 4.6) values, help to describe the mechanism of ferrous 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 ferrousion concentration and rate of reaction will not be linear. It shows that pore diffusion limits the overall rate of ferrous ion adsorption.

**INTRAPARTICLE DIEFUSION**

The contact-time experimental results can be used to study the rate limiting step in the adsorption process, as shown by Weber and Morris. 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 external surface, one might then postulate that the rate-limiting step may be either film formation or intraparticle diffusion. As they act in series, the slower of the two will be the rate-determining step. The rate constant for intraparticle diffusion is obtained using the equation,

$Qt = Kpt^{1/2} + C$

Here. Kp is the intraparticle diffusion coefficient. The nature of the plots suggests that the initial curved portion is attributed to the film formation or boundary layer diffusion effect and the subsequent linear portion is due to the intraparticle diffusion effect. The Kp values were obtained from the slope of the linear portions of the curves (Qt versus $t^{0.5}$) at each ferrous ion concentration (Table 4.7 & Fig 4.5). The Kp 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 ZDC increased with the increase in temperature of the system from 30°-60°C. The $\Delta H°$ and $\Delta S^0$ values obtained from the slope and intercept of van't Hoff plots were presented in table (Table 4.5). The values are within the range of 1 to 93 KJ/mol indicates the favourability of physisorption. From the order, it is found that physisorption is much more favourable for ferrous ion. The positive values of $\Delta H^0$ show 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 increases, this rules out the possibility of chemisorption. However, a very low $\Delta H^0$ value depicts that the ferrous ion isphysisorbedonte adsorbent.

The negative value of $\Delta G^0$ (Table 4:5) shows that the adsorpton is highly favourable for ferrous ion. However, it also indicates that the metal ion adsorption was spontaneous. The positive values of $\Delta S^0$ (Table 4.5) show the increased disorder and randomness at the solid solution interface of Fe(II) with the ZDC. During the adsorption, there are some structural changes in the ferrous ion and in the adsorbent. 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. From the results, it is found that more efficient is physisorption. The enhancement of adsorption capacity of the ZDC at higher temperatures was attributed to the enlargement of pore size and activation of the adsorbent surface.

**EFFECT OF PH**

The experiments carried out at different pH show that there was a change in the percent removal of ferrous ion over the entire pH range (Fig.4.6). This indicates the strong force of interaction between the ferrous ion and ZDC that either $H^+$ or $OH^-$ ions could influence the adsorption capacity. In other words, the adsorption of ferrous ion on ZDC does involve ion exchange mechanisms that have been an influence on the ferrous ion adsorption while varying the pH. This observation is in line with Langmuir and Freundlich isotherms and positive $\Delta H°$ value obtained, also indicates irreversible adsorption which is probably due to polar interactions.

**EFFECT OF OTHER IONS**

The effect of other ions like $Ca^{2+}$ and $Cl^-$ on the adsorption process was also studied at different concentrations. The ions were added in concentration of 15 mg/L of ferrous ion solutions and the contents were agitated for 60 min at 30°C. The results showed in figure (Fig. 4.7) reveals that low concentration of $Cl^-$ does not affect the percentage of adsorption of ferrous ion on ZDC, because the interaction of $Cl^-$ at available sites of adsorbent through competitive adsorption is not so effective. While the concentration of other ion $Ca^{2+}$ increases, the interference of these ions at available surface sites of the sorbent through competitive adsorption also increases which, decreases the percentage adsorption. The interference was more in the presence of $Ca^{2+}$ compared with that of $Cl^-$ ion. This is so because ions with smaller hydrated radii decrease the swelling pressure within the sorbent and increase the affinity of the sorbent for such ions.

**DESORPTION STUDIES**

Desorption studies help to elucidate the nature of adsorption and the recycling of the spent adsorbent and the ferrous ion. The effect of various reagents used for desorption studies indicate that hydrochloric acid is a better reagent for desorption, because more than 94% removal of adsorbed ferrous ion takes place. The reversibility of adsorbed ferrous ion in mineral acid or base is in agreement with the pH dependent results obtained. The desorption of ferrous ion by mineral acids and alkaline medium indicates that the ferrous ion was adsorbed onto the activated carbon by physisorption as well as by chemisorption mechanisms.

## EVIDENCES FOR ADSORPTION

The FT-IR spectra of ZDC before and after adsorption of ferrous ion are shown in the figures (Fig. 4.8a and Fig. 4.8b). It could be seen that the slight reduction of stretching vibration adsorption bands, clearly indicates the adsorption of ferrous ion on the ZDC by physical forces and not by chemical combination. The XRD diagrams of ZDC and ferrous ion-adsorbed ZDC are shown in the figures (Fig. 4.9a and Fig. 49b). The intense main peak shows the presence of highly organized crystalline structure of raw ZDC. But, after the adsorption of ferrous ion, the intensity of highly organized peaks is slightly diminished. This was attributed to the adsorption of ferrous ion on the upper layer of the crystalline structure of the ZDC surface by means of physisorption.

The SEM diagrams of raw ZDC and ferrous ion-adsorbed ZDC are shown in the figures (Fig. 4.10a and Fig 4.10b). The bright spots show the presence of tiny holes on the crystalline structure of raw ZDC. However, after treatment with ferrous ion, the bright spot become black which shows the adsorption of the ferrous ion on the surface of ZDC.

**Table 4.1-Equilibrium parameters for the adsorption of ferrous ion onto ZDC.**

| $[Fe(II)]_{ini.}$ mg/L | Temp., °C | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 30 | 40 | 50 | 60 | 30 | 40 | 50 | 60 | 30 | 40 | 50 | 60 |
| | C mg /L | | | | Q mg/g | | | | Ferrous ion removed % | | | |
| 5 | 0.1715 | 0.1228 | 0.0812 | 0.0554 | 9.6570 | 9.7544 | 9.8376 | 9.8892 | 96.57 | 97.54 | 98.37 | 98.89 |
| 10 | 1.2587 | 1.0525 | 0.7747 | 0.5756 | 17.4826 | 17.8950 | 18.4506 | 18.8488 | 87.41 | 89.47 | 92.25 | 94.24 |
| 15 | 2.8849 | 2.4254 | 1.9841 | 1.5944 | 24.2302 | 25.1492 | 26.0318 | 26.8112 | 80.76 | 83.83 | 86.77 | 89.37 |
| 20 | 5.5546 | 4.9721 | 4.3599 | 3.7529 | 28.8908 | 30.0558 | 31.2802 | 32.4942 | 72.22 | 75.13 | 78.20 | 81.23 |
| 25 | 7.7945 | 7.0572 | 6.3160 | 5.6435 | 34.4110 | 35.8856 | 37.3680 | 38.7130 | 68.82 | 71.77 | 74.73 | 77.42 |

**Table 4.2- Lanmuir constants and statistical parameters for the adsorption of ferrous ion onto ZDC.**

| S.No | Temp., $^0$C | Statistical Parameter, $r^2$ | Langmuir constants | |
|---|---|---|---|---|
| | | | Qm | b |
| 1 | 30 | 0.9972 | 37.174 | 0.8848 |
| 2 | 40 | 0.9934 | 38.314 | 1.0653 |
| 3 | 50 | 0.9905 | 39.370 | 1.3956 |
| 4 | 60 | 0.9979 | 40.485 | 1.7770 |

**Table 4.3- Dimensionless separation factor ($R_L$)**

| [Fe(II)] ini., mg/L | Temp., $^0$C | | | |
|---|---|---|---|---|
| | 30 | 40 | 50 | 60 |
| 5 | 0.184 | 0.158 | 0.125 | 0.101 |

| | | | | |
|---|---|---|---|---|
| 10 | 0.102 | 0.085 | 0.066 | 0.053 |
| 15 | 0.070 | 0.058 | 0.045 | 0.036 |
| 20 | 0.053 | 0.045 | 0.034 | 0.027 |
| 25 | 0.043 | 0.036 | 0.027 | 0.022 |

**Table 4.4- Freundlich constants and statistical parameter for the adsorption of ferrous ion onto ZDC**

| S.No | Temp., $^0$C | Statistical Parameter, $r^2$ | Freundlich constants | |
|---|---|---|---|---|
| | | | Kf | n |
| 1 | 30 | 0.9923 | 3.4140 | 3.0459 |
| 2 | 40 | 0.9916 | 3.5561 | 3.1496 |
| 3 | 50 | 0.9935 | 3.7284 | 3.3068 |
| 4 | 60 | 0.9938 | 3.8876 | 3.4246 |

**Table 4.5- Equilibrium constant and thermodynamic parameters for the adsorption of ferrous ion onto ZDC**

| [Fe(II)]ini., mg/L | Temp., °C | | | | | | | | □H° kJ/mol | □S° J/K/mol |
|---|---|---|---|---|---|---|---|---|---|---|
| | 30 | 40 | 50 | 60 | 30 | 40 | 50 | 60 | | |
| | K0 | | | | -□□G° J/mol | | | | | |
| 5 | 28.15 | 39.71 | 60.57 | 89.25 | 8408 | 9581 | 11020 | 12434 | 32.53 | 134.89 |
| 10 | 6.94 | 8.50 | 11.90 | 16.37 | 4882 | 5569 | 6652 | 7739 | 24.33 | 96.05 |
| 15 | 4.19 | 5.18 | 6.56 | 8.40 | 3614 | 4282 | 5051 | 5894 | 19.41 | 75.86 |
| 20 | 2.60 | 3.02 | 3.58 | 4.32 | 2407 | 2878 | 3430 | 4057 | 14.23 | 54.80 |
| 25 | 2.20 | 2.54 | 2.95 | 3.42 | 1994 | 2428 | 2912 | 3412 | 12.35 | 47.28 |

**Table 4.6- Rate constants for the adsorption of ferrous ion ( $10^3$Kad, $min^{-1}$) and the rate constant for forward ($10^3$ k1,$min^{-1}$) and reverse ($10^3$ k2, $min^{-1}$) process**

| [Fe(II)]ini., mg/L | Temp., °C | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 30 | 40 | 50 | 60 | 30 | | 40 | | 50 | | 60 | |
| | kad | | | | k1 | k2 | k1 | k2 | k1 | k2 | k1 | k2 |
| 5 | 69.57 | 77.72 | 88.16 | 99.79 | 67.36 | 2.39 | 75.81 | 1.90 | 86.73 | 1.43 | 98.69 | 1.10 |
| 10 | 35.31 | 39.16 | 45.77 | 53.94 | 30.86 | 4.44 | 35.04 | 4.12 | 42.23 | 3.54 | 50.84 | 3.10 |
| 15 | 26.93 | 29.80 | 34.02 | 38.05 | 21.75 | 5.18 | 24.98 | 4.82 | 29.52 | 4.50 | 34.01 | 4.04 |
| 20 | 20.82 | 22.40 | 24.57 | 26.84 | 15.04 | 5.78 | 16.83 | 5.56 | 19.21 | 5.35 | 21.80 | 5.03 |
| 25 | 18.77 | 10.48 | 22.96 | 24.31 | 12.92 | 5.85 | 14.69 | 5.78 | 17.16 | 5.80 | 18.82 | 5.49 |

**Table 4.7- Intraparticle diffusion parameter ($K_P$) for adsorption of ferrous ion onto ZDC**

| [Fe(II)]ini., mg/L | Kp (mg/g/$min^{0.5}$) |
|---|---|
| 5 | 0.253 |
| 10 | 0.278 |
| 15 | 0.295 |
| 20 | 0.319 |
| 25 | 0.346 |

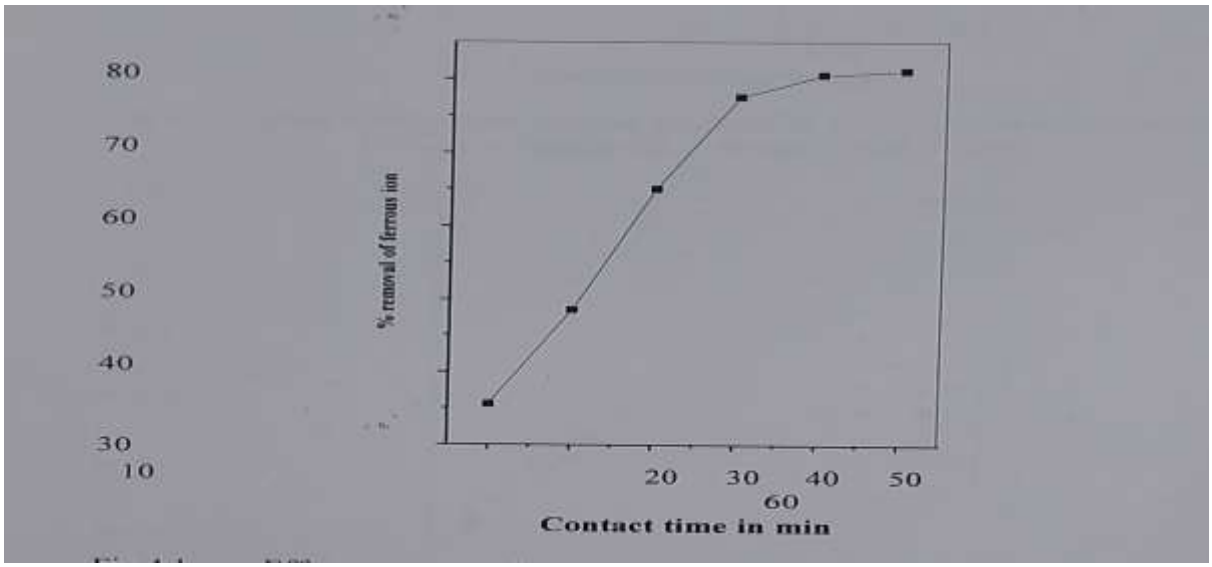


**Fig 4.1- Effect contact time on the removal of ferrous ion onto ZDC [Fe]=15mg/L; Adsorbent dose = 25mg/59 mL; Temp=30$^0$C**

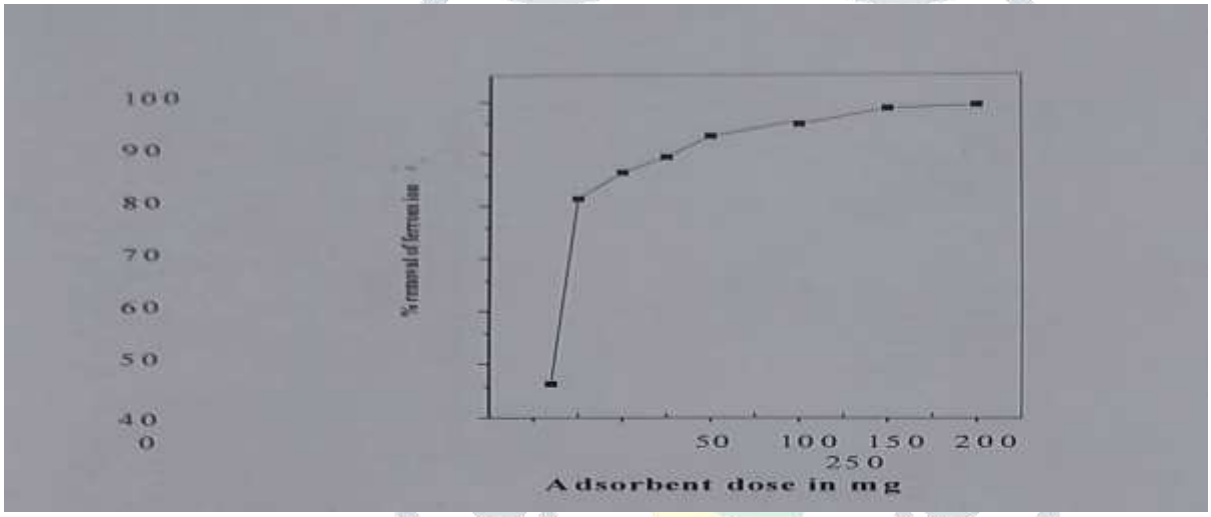


**Fig 4.2- Effect of adsorbent dose on the removal of ferrous ion onto ZDC [Fe}= 15 mg/L; Contact time = 60min; Temp = 30$^0$C**

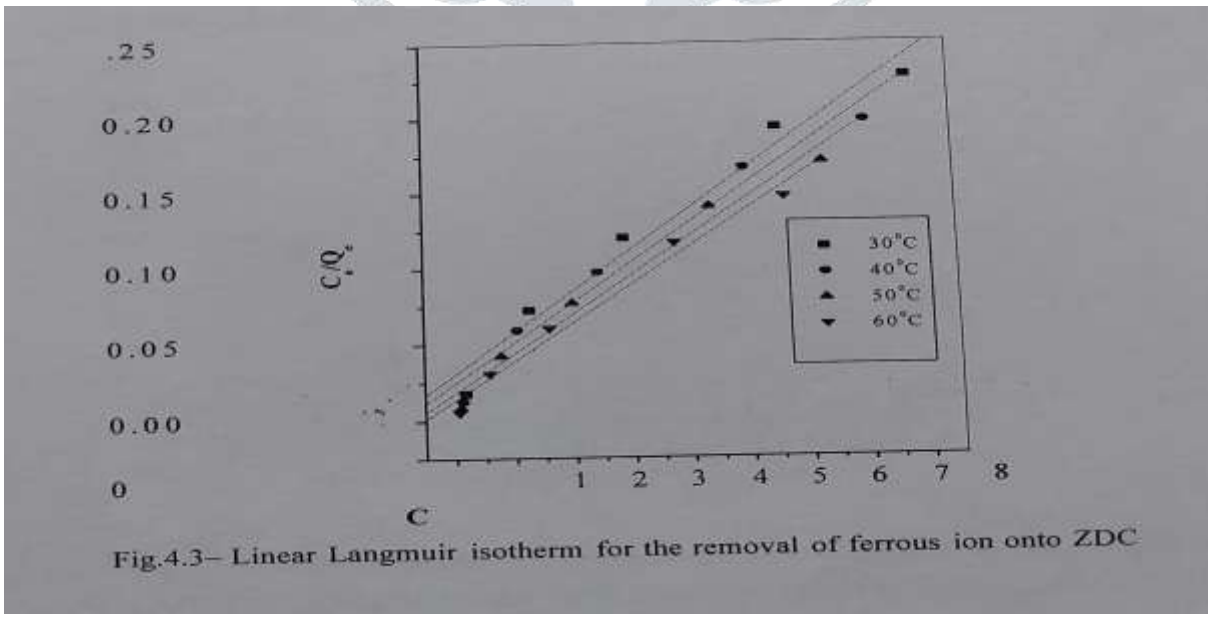


Fig.4.3– Linear Langmuir isotherm for the removal of ferrous ion onto ZDC

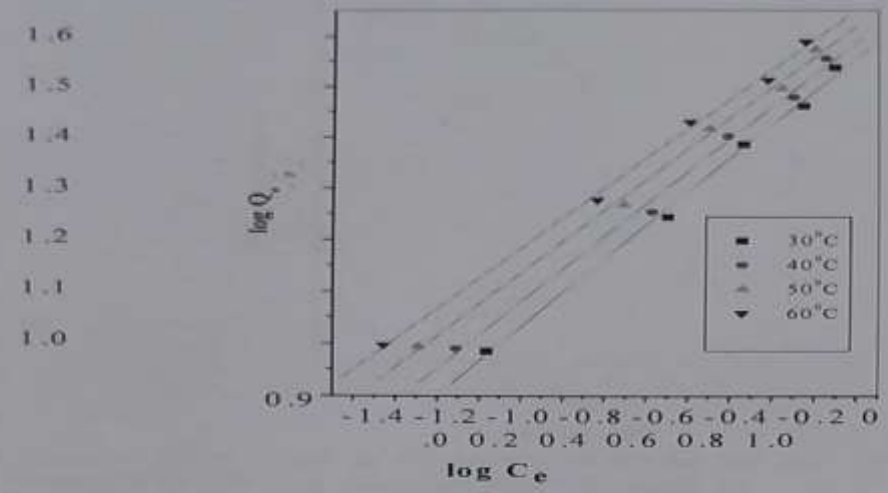


Fig.4.4 – Linear Freundlich isotherm for the removal of ferrous ion onto ZDC

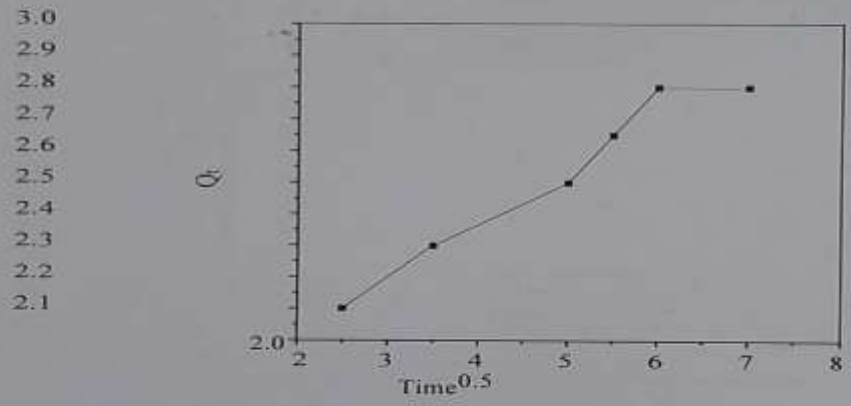


Fig.4.5 – Effect of intraparticle diffusion on the adsorption of ferrous ion [Fe] = 15mg/L; Temp = 30°C Adsorbent dose = 25mg/50mL

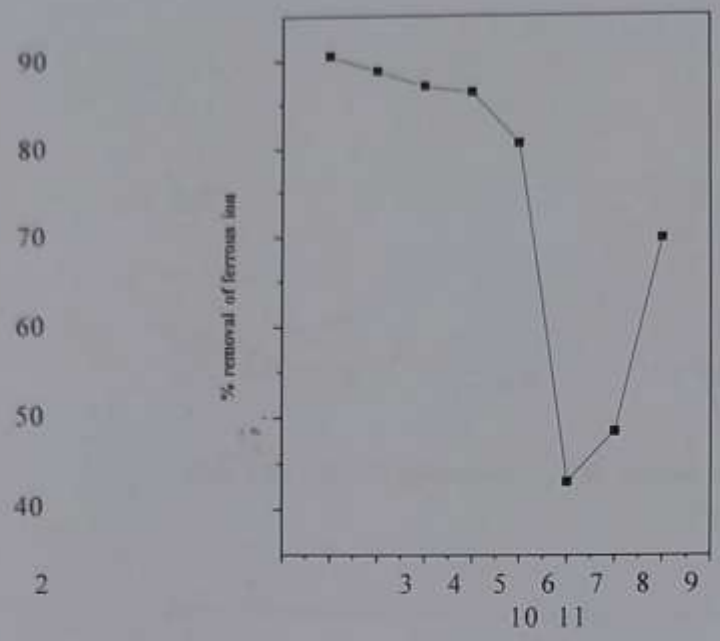


Fig.4.6 – Effect of pH on the removal of ferrous ion onto ZDC [Fe]=15 mg/L; Contact time = 60 min; Adsorbent dose = 25 mg/50 mL

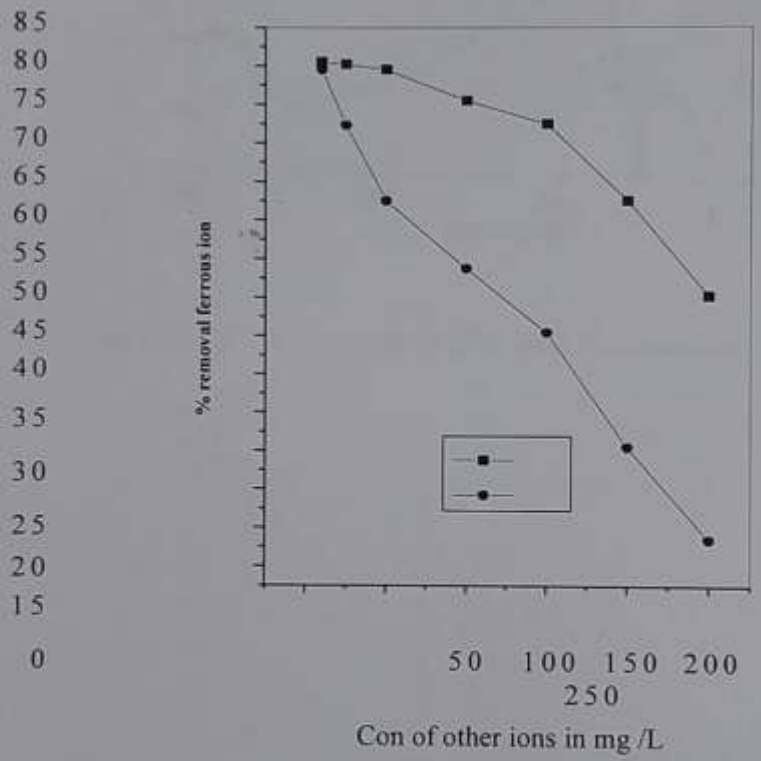


Fig.4.7 – Effect of other ions on the removal of ferrous ion onto ZDC [Fe]=15 mg/L; Contact time = 60 min; Adsorbent dose = 25 mg/50 mL

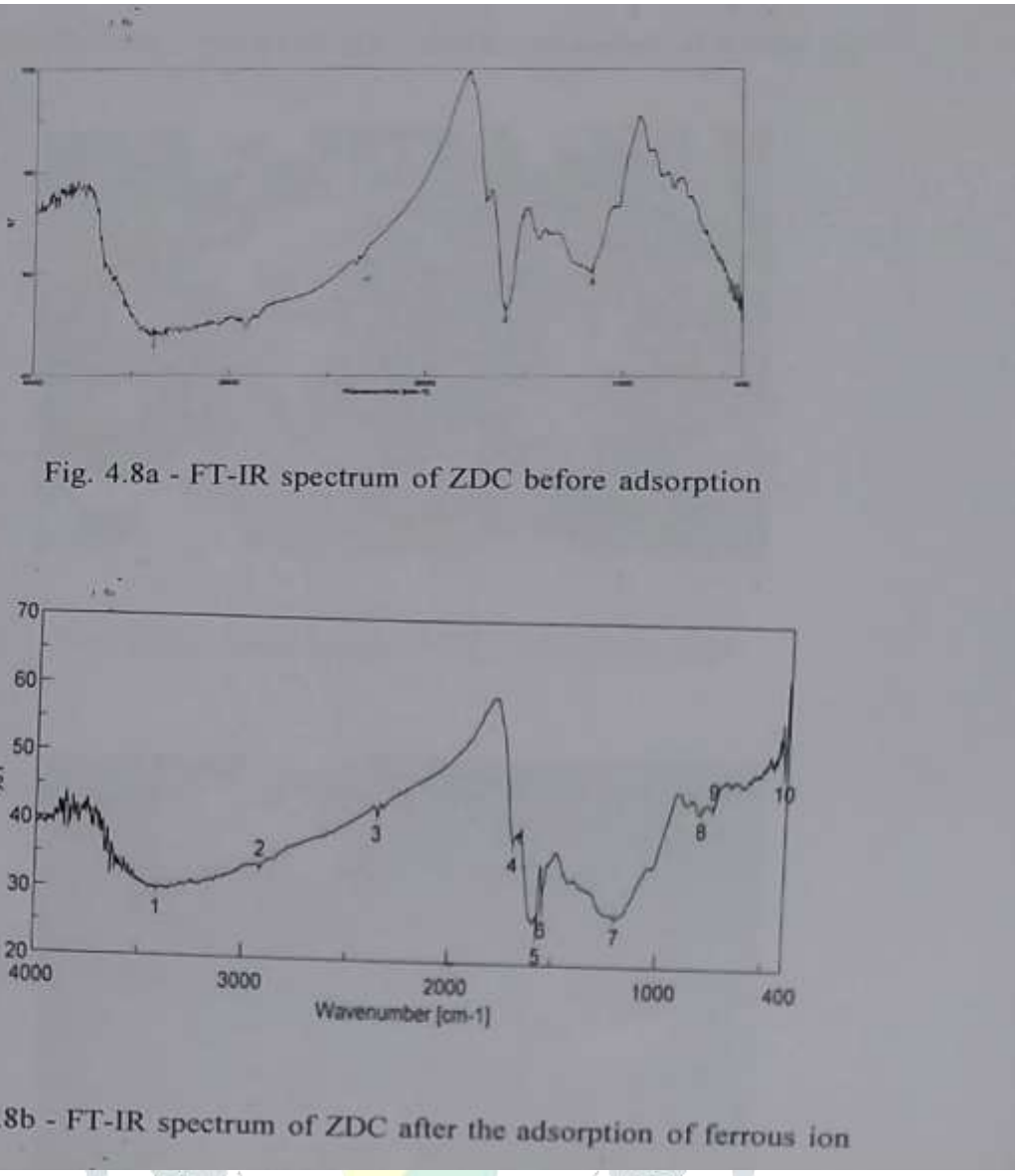


Fig. 4.8a - FT-IR spectrum of ZDC before adsorption

Fig. 4.8b - FT-IR spectrum of ZDC after the adsorption of ferrous ion

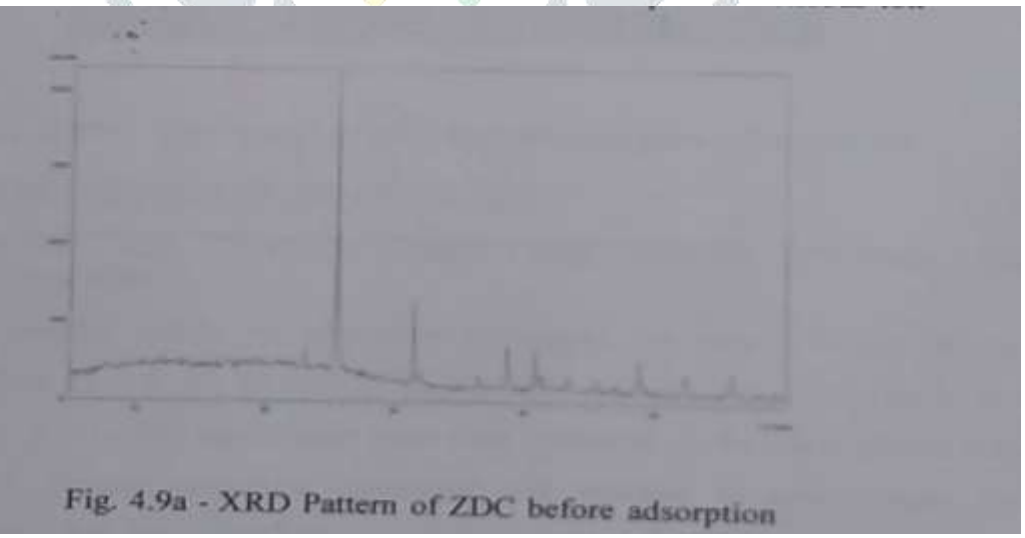

Fig. 4.9a - XRD Pattern of ZDC before adsorption

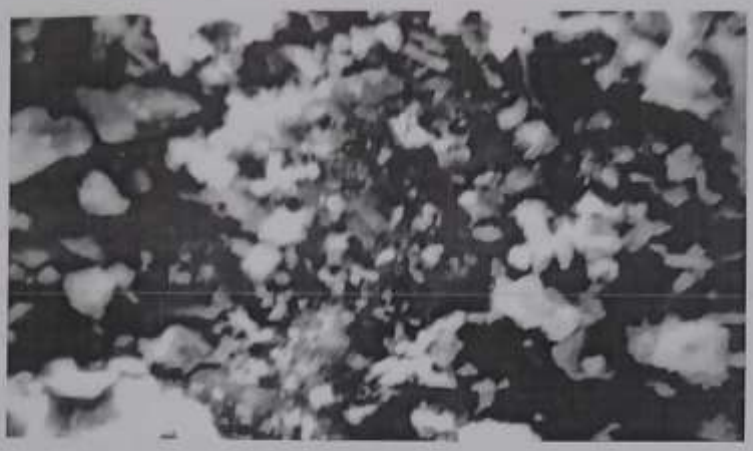

Fig. 4.10 a - SEM image of ZDC before adsorption

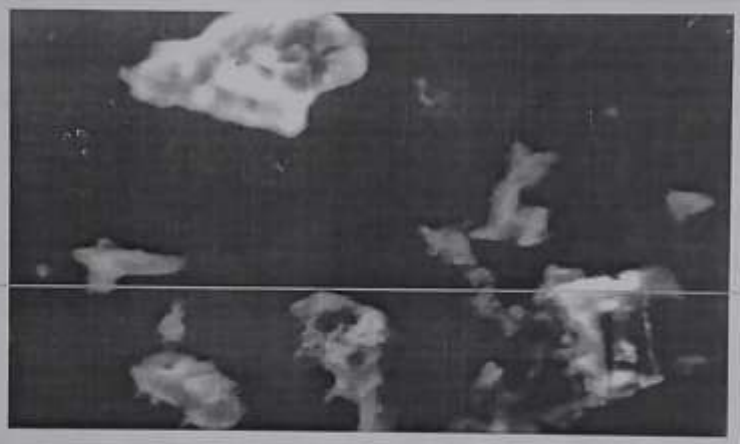

Fig. 4.10b - SEM image of ZDC after the adsorption of ferrous ion

**CONCLUSION:**

The experimental data will be analyse using Microcal Origin Software {Version 5.0}. The goodness of fit will also discuss using correlation coefficient r, and standard deviation, sd. The research work deals with the investigation on the equilibrium, kinetic and thermodynamic aspects of the adsorption of metal ion Fe(II) onto the chosen adsorbent Zea mays dust [ZDC}. The different parameters pertaining to the adsorption at equilibrium will determined in order to establish the behaviour of the adsorption process. In Order to determine the adsorption capacity of ZDC, isotherms studies will be performed and the data obtained from the equilibrium studies will fit in the rearranged Langmuir equation.

The activated carbon samples were characterized using FT-IR-8400 Shimadzu Spectrophotometer. The surface morphologies of activated ZDC was observed with XRD and SEM Patterns.

The adsorption of ferrous ion onto ZDC at various concentrations with contact time reveals that the percent adsorption decreased with increase in initial ferrous ion concentration, whereas, the actual amount of ferrous ion adsorbed per unit mass of adsorbent increased with increase in ferrous ion concentration. It means that the adsorption is highly dependent on initial concentration of ferrous ion. It is because of that, at lower

concentration the ratio of the initial number of ferrous ion adsorbed onto the available surface area is low subsequently the fractional adsorption become independent of initial ferrous ion concentration. However, at high concentration the available sites of adsorption becomes fewer and hence the percentage removal of ferrous ion is dependent upon initial ferrous ion concentration.

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