

# Adsorptive Removal of Harmful Fe (II) Ions From Aquatic Environment Using Plant Materials

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**Abstract-** The various treatment processes have been developed for the removal of metal ions/dyes from wastewater. Among those processes, adsorption is Eco friendly, cheaper and easier to handle. Activated carbon materials have gained special attention in water pollution mitigation researches and this study presents the adsorption of metal ions by activated carbon obtained from Mullugo Cerviana Leaves. The operating variables like adsorbent dose, solution pH, contact time, initial concentration of metal ions; temperature and other ions have been studied. Equilibrium data has been analyzed with Langmuir and Freundlich isotherms models. The isotherms parameter such as adsorption capacity, intensity of adsorption and dimensionless separation factor has been calculated. The thermodynamic parameters like  $\Delta G^0$ ,  $\Delta H^0$ , and  $\Delta S^0$  have also been calculated. The nature of adsorption process has been identified and proved by FT-IR and XRD studies. These results have been showed that the activated Mullugo Cerviana Leaves could be used as a low cost adsorbent for the removal of metal ions from the aqueous solution.

**Keywords-** Iron, Activated Mullugo Cerviana Leaves Carbon (AMCL);

## I. INTRODUCTION

### 1. Environmental Pollution

#### Water has been termed as Elixir of life

It is well known that water is a universal solvent and is a major constituent of all living organisms. Our biological green sphere is a natural environment of living creature. It surrounds the earth and contains surficial parts of the lithosphere, lower part of atmosphere and hydrosphere. Water the very important resource covers about 70% of the earth's surface, In it 97% of the water is salty, while remaining one third is fresh water; while two thirds of this is frozen into glaciers and polar ice caps. The remaining unfrozen fresh water is found largely as groundwater, with only a small fraction found above the ground or in the air.

The quality of water is a key of vital concern for the survival of mankind since it is directly linked with human life. Several cities and civilizations have disappeared due to shortage of water because of climatic changes. Hence Availability of water attribute to the distribution of plants, animals as well as human.

There can be clearly noticed that there is a delicate balance between man and environment, which is badly disturbed by human habitation either or indirectly. While thousands of contaminants have found their way to the environment through water. There is sad fact that distribution of heavy metals in to the environment.

#### Pollution:

Water pollution is the contamination of water bodies (eg. lakes, rivers, oceans and ground water) when pollutants are discharged directly or indirectly into the water bodies without adequate treatment to remove harmful compounds. Water pollution affects plants and organisms living in these bodies of water. They also influence pH, BOD, COD and temperature of water bodies. Industrial effluents, domestic effluents and agricultural wastes are the important courses of water pollution.

#### Iron Toxicity:

Iron an essential mineral responsible for human health, playing a vital role in immune function, cardio vascular health and cognitive development, found in water as either soluble or relatively insoluble forms. Water forms such as Groundwater, oxygen free reservoirs, dead-ends in water distribution systems and hard mineral coatings within pipes contain soluble iron in domestic water supplies. The primary sources of iron in drinking water are from natural geologic sources and corroding distribution systems and household pipe fittings. Iron-based materials such as cast iron and galvanized steel have been widely used in our water distribution systems and house hold plumbing, also concluded for Iron supplement in water.

The detrimental effects of chronic iron toxicity are due in part to iron accumulation in various organs such as heart, liver, brain, pancreas and joints. Many of the symptoms of iron toxicity are due to displacement by iron instead of zinc, copper, manganese and other vital nutrients. Iron toxicity is commonly associated with personality characteristics of a strong ego, rigidity, tenaciousness, hostility, stubbornness and irritability. This is due to the hyper action of iron which increases the adrenal hormone, aldosterone. Iron in excess can damage the liver and other organs leading to premature aging and even death. Some of the notable defects includes anger, arthritis, birth defects, bleeding gums, cancer, cardiomyopathies, cirrhosis of the liver, constipation, diabetes, diarrhoea, dizziness, fatigue, grayish-hued skin, headaches, heart failure, hepatitis, hostility, hyperactivity, hypertension, infection, liver disease, mental problems, metallic taste in mouth, nausea, nervousness, rheumatoid arthritis, scurvy, sickle-cell anemia, strabismus (rapid eye movements) are the noticeable metabolic dysfunctions of iron deficiency and iron toxicity

## II. AIM & SCOPE OF THE RESEARCH

The aim of this research work is to study the removal of Fe(II) ion from aqueous solution by adsorption technique using locally available activated low cost adsorbent as an alternative to the already existing commercial adsorbents.

## III. MATERIALS AND METHODS

### 1. Chemicals

All the chemicals used for the present study were commercially available of high purity Analar grade (Merck India or SRL India), double distilled water was used throughout the work and the second distillation was made over alkaline permanganate.

### 2. Preparation of metal ion solutions

The metal ions chosen for the adsorption studies in the present research work are Iron (II) ion. Stock solutions (1000 mg/L). The required Iron stock was prepared by dissolving required amount of metal salt in one litre of distilled water was shown in below.

Table 1. Weight of the salt taken for the preparation of stock solutions

Metal ions	Metal salt	Weight to be dissolved for one litre (g)
Fe(II)	FeSO <sub>4</sub> .7H <sub>2</sub> O	4.9786

### 3. Preparation of Adsorbent

The natural plant material Mullugo Cerviana Leaves was collected from nearby Ariyalur district and were washed with distilled water several times to let it free from dirt. They were then Carbonized with concentrated Sulphuric acid (w/v) and washed with water. Later, the primary carbon was activated at 600 oC for 8 hrs in a muffle furnace. The activated carbon was then kept at room temperature in an inert atmosphere of nitrogen and washed with hot distilled water then to it 0.5 N Hydrochloric was added until the pH of the material reaches 7.0. Then it was dried in a hot air oven at 110 0C, ground well and sieved to obtain the desired particular size and stored in desiccators for further use.

### 4. Characterization of AMCL adsorbent

AMCL is widely useful due to its characteristic specific surface area, high chemical and mechanical stability. Usually chemical nature and pore structure of the material determines the sorption activity. AMCL fulfills the above criteria fully.

### 5. Determination of Particle size

The particle size of the adsorbent AMCL was measured using the Carl Zeiss Light microscope (AxioStar plus). Fitted with ocular micrometer with a dimension of 10x to determine the size of particle of the adsorbent. Each division on the scale of the ocular meter is measured at an interval of 0.01mm.

### 6. Density

The sieved adsorbent was closely packed in a dry graduated glass tube and weighed. Series of ten duplicate experiments were carried out, the difference in mass of the graduated glass tube before close packing was noted. The mean mass of the adsorbent/volume gives the density of the AMCL adsorbent.

### 7. Moisture content

The moisture content of the adsorbent was found out using moisture balance. One gram of the adsorbent is placed in a petriplate and it was heated in a ventilated drying oven at 120 0C for 2 hours. After heating, the plate was quickly covered, cooled in a desiccator and weighed. The loss in weight of the adsorbent represents the mechanical or hygroscopic moisture.

### 8. Ignition loss

One gram of adsorbent was placed in pre weighed silica crucible and it was ignited at 1000 OC for 4 hours in an electric muffle furnace. Then it was cooled in desiccators and weighed. The weight loss was calculated as loss on ignition.

### 9. Water soluble matter

Five gram of the adsorbent was weighed and transferred into a 500 ml beaker. About 100 ml of distilled water was added and heated to boiling with continuous stirring for 5 min until the flame was removed. The adsorbent material was allowed to settle and the supernatant liquid was filtered through a crucible fitted with an asbestos mat. Duplicate experiment was also carried out thrice. The combined filtrate was concentrated to less than 100 ml over a water bath, cooled and made up to the mark in a standard flask. Exactly 50 ml of the concentrate was transferred in to a china dish and evaporated to almost dryness and finally dried in an electric oven, maintained at 105 +/- 5 OC, cooled in a desiccator and weighed. The procedure of drying and weighing was repeated at 30 minutes intervals, until the difference between two consecutive weighing was less than 5 mg. The percentage of water soluble matter was then calculated as

$$\text{Water soluble matter (\%)} = \frac{M \times 100 \times 2}{(M1/100)(100 - X)}$$

Where, M = mass of the residue in grams

M1= mass of the adsorbent taken for test in grams (5g)

X = percent of moisture present in the material

### 10. pH of aqueous solutions

About 100 mg of adsorbent was mixed with 50 ml of distilled water and equilibrated for 1 hour by agitating in a thermostated shaker at 120 rpm. The pH of the supernatant was measured using pH meter.

### 11. Zero point charge (pHzpc)

The pH at zero potential charge (pHzpc) of the carbon was measured using the drift method. The pH of 0.01M NaCl was adjusted between 2 to 12 by adding diluted solutions of hydrochloric acid or sodium hydroxide. Nitrogen was bubbled through the solution at 25 OC to remove dissolved carbon dioxide until the initial pH is stabilized. Then 50 mg of adsorbent was added to 50 ml of the solution, and after pH had stabilized (typically after 24 hours), the final pH was recorded. The graphs of final pH versus initial pH were used to determine zero point charges at which initial pH and final pH values were equal. The results obtained from the above characterization studies are given in Table 3.2.

Table 2. Characterization of the adsorbent

Analysis	Value
pH <sub>zpc</sub>	6.67
Specific gravity	0.205
Moisture content, %	0.095
Bulk density, g cm <sup>-3</sup>	0.100
Particle density, g cm <sup>-3</sup>	0.230
Conductivity, μS/cm	40.26
Surface area, m <sup>2</sup> /g	22.21
Na <sup>+</sup> , mg L <sup>-1</sup>	95
K <sup>+</sup> , mg L <sup>-1</sup>	420

### 12. Concentration of the Fe(II)

Concentration of the Fe(II) ions before and after adsorption was measured using an UV-Visible double beam spectrophotometer (Systronics 2203). Standards for establishment of calibration was prepared by diluting the stock solutions so as to be in the gradual concentration of 10 to 250 mg/L of the Fe(II) ions and the absorbance of the solution at the respective wave length was recorded. The wave length of maximum absorbance for Fe(II) ions are at 530 nm.

### 13. Batch equilibration method

All experiments were carried out at the temp range of 30, 40, 50 and 60 °C respectively in batch mode. Batch mode was selected because of its simplicity and reliability. The batch experiments were carried out in different Erlenmeyer glass flasks of 250 ml capacity. Prior to each experiment, a predetermined amount of adsorbent was added to each flask. With constant stirring (120 rpm) for each run throughout the experiment to ensure equal mixing. Then each flask was filled with a known volume of sample, then the samples were withdrawn from the shaker at the predetermined time interval, filtered and the residual concentration of the Fe(II) ions were measured by UV-Visible Spectrometer.

## IV. RESULTS AND DISCUSSION

### 1. Effect of contact time and initial Fe(II) ions concentration

The experimental results for the adsorption at various concentrations (25 to 125 mg L<sup>-1</sup>) with contact time are shown in Fig. 4.1. The respective data are presented in Table 4.1, revealing that, percentage adsorption decreased with increase in initial Fe(II) ions concentration, but the actual amount of Fe(II) ions adsorbed per unit mass of AMCL increased with increase in Fe(II) ions concentration. It means that the adsorption is highly dependent on initial concentration of Fe(II) ions. It is because of the reason that at lower concentration, the ratio of the initial number of Fe(II) ions to

the available surface area is low. Subsequently the fractional adsorption becomes independent of initial concentration. However, at higher concentrations, the available sites of adsorption becomes fewer and hence the percentage removal of Fe(II) ions is dependent upon initial concentration. Equilibrium has been established at 50 minutes for all concentrations. Fig. 4.1 reveals that the curve is single, smooth and continuous leading to saturation, suggesting the possibility of monolayer coverage of the Fe(II) ions on the AMCL adsorbent surface.

**2. Effect of Dosage**

The adsorption of Fe(II) ions on AMCL was studied by varying the dosage of adsorbent (25-125 mg/50 ml) for 50 mg L<sup>-1</sup> of Fe(II) ions concentration. The percentage of adsorption increased with increase in the AMCL dose (Fig.4.2). This may be due to the increased AMCL surface area and availability of more adsorption sites. Hence, the remaining parts of the experiments were carried out with an optimum dose of the adsorbent (25 mg/50 ml).

**3. Effect of pH**

One of the most important parameters controlling the adsorption process is pH. The effect of pH of the solution on the adsorption of Fe(II) ions on AMCL was determined. The result was shown in Figure 4.3. The pH of the solution was controlled by the addition of HCl or NaOH. The uptake of Fe(II) ions at pH 7.5 to 8.0 was the minimum and a maximum uptake was obtained at pH 3.0-6.7. However, when the pH of the solution was increased (more than 8.5), the uptake was slightly increased. Since, AMCL bears the change in pH of the solution results in the formation of different ionic species and change in the AMCL surface. At pH values lower than 6.7, the Fe(II) ions can enter into the pore structure. At a pH value higher than 6.7, the zwitter-ionic form in water may increase the aggregation of Fe(II) ions to form a bigger molecular form (dimer) and becomes unable to enter the pore structure of the AMCL surface.

**4. Effect of the Ionic strength on the Adsorption of Fe(II) ions**

The effect of sodium chloride on the adsorption of Fe(II) ions onto AMCL were studied. In the low solution concentration of NaCl had little influence on the adsorption capacity. At higher ionic strength the adsorption of Fe(II) ions will be increased due to the partial neutralization of the positive charge on the AMCL surface and a consequent compression of the electrical double layer by the chloride ion. The chloride ion can also enhance adsorption of Fe(II) ions

onto AMCL by the pairing of their charges and hence reducing the repulsion between the Fe(II) ions. This initiates AMCL to adsorb more amount of positive Fe(II) ions.

**5. Theory of Adsorption isotherms**

To quantify the sorption capacity of the absorbent for the removal of Fe(II) ions, the most commonly used isotherm are namely Freundlich and Langmuir isotherms.

The sorption isotherm is highly significant in the removal of metal ions and dyes by the adsorption technique, as it provides an approximate estimation of the sorption capacity of the adsorbent. The equilibrium data for the removal of metal ions and dyes by the sorption on the adsorbent at different temperature have been used in Langmuir and Freundlich isotherms.

Langmuir isotherm:  $C_e/Q_e = 1/Q_m b + C_e/Q_m \dots \dots \dots (4.1)$

Freundlich isotherm:  $\log Q_e = \log K + 1/n \log C_e \dots \dots (4.2)$

Where, C<sub>e</sub> is the equilibrium concentration of the adsorbate adsorbed per unit mass of adsorbent at equilibrium (mg/g); Q<sub>m</sub> and ‘b’ are Langmuir constants related to the adsorption capacity and energy of adsorption, respectively. The values of Q<sub>m</sub> and ‘b’ have been obtained from the linear correlation of C<sub>e</sub>/Q<sub>e</sub> against C<sub>e</sub>. The Freundlich constants K<sub>f</sub> and ‘n’ are the measures of adsorption capacity and intensity of adsorption respectively and these values have been calculated from the linear correlations of log Q<sub>e</sub> Vs log C<sub>e</sub>. The essential characteristics of the Langmuir isotherm can be described by a separation factor R<sub>L</sub>, which is defined as R<sub>L</sub> = 1/(1+bC<sub>0</sub>) where, ‘b’ is the Langmuir constant and C<sub>0</sub> is the initial concentration of the metal ions or dyes. The values of R<sub>L</sub> indicate the shape of the isotherm as follows.

Table 3.

R <sub>L</sub> VALUE	TYPES OF ISOTHERM
R <sub>L</sub> >1	Unfavorable
R <sub>L</sub> =1	Linear
0<R <sub>L</sub> <1	Favorable
R <sub>L</sub> =0	Irreversible

The value of K<sub>f</sub> and n are calculated from the intercept and slope of the plot of log q<sub>e</sub> Vs log C<sub>e</sub> respectively. The obtained constant K<sub>f</sub> and n values are given in Table 4.2. In general K<sub>f</sub> value, adsorption capacity increases with the given adsorbate concentration increases. The magnitude of the exponent 1/n gives an indication of the favorability of adsorption. The value of n>1 represents favorable adsorption condition (or) the value of 1/n lying in the range of 1 to 10

confirms the favorable condition for adsorption. Here, the adsorption of Fe(II) ions onto AMCL matches above condition.

The Langmuir isotherm model is based on the assumption that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface.  $Q_m$  is the amount of adsorbate at complete monolayer coverage (mg/g) which gives the maximum adsorption capacity of the adsorbent and  $b$  (L/mg) is the Langmuir isotherm constant that relates to the energy of adsorption (or rate of adsorption). The linear plot of specific adsorption capacity  $C_e/q_e$  against the equilibrium concentration ( $C_e$ ) shows that the adsorption obeys the Langmuir model. The Langmuir constants  $Q_m$  and  $b$  were determined from the slope and intercept of the plot respectively and are presented in table (4.2). The values suggest the suitability of adsorption of Fe(II) ions onto AMCL. In order to find out the feasibility of the isotherm, the essential characteristics of the Langmuir isotherm can be expressed in terms of dimensionless constant separation factor  $R_L$  [9] by the equation. The parameter  $R_L$  indicates the nature of shape of the isotherm accordingly. The obtained  $R_L$  values were in between 0 and 1 indicates the favorable adsorption for all initial concentrations Fe(II) ions onto AMCL. The calculated  $R_L$  values are given in Table. 4.3.

## 6. Thermodynamic treatment of the adsorption process

The standard free energy change ( $\Delta G^0$ ) enthalpy change ( $\Delta H^0$ ) and entropy change ( $\Delta S^0$ ) were calculated from the variation of the thermodynamic equilibrium constant  $K_0$ . The values of  $K_0$  for the adsorption process were determined by the reported method. The thermodynamic parameters were calculated using the following equations.

$$K_0 = C_{\text{solid}}/C_{\text{liquid}} \dots \dots \dots (4.3)$$

$$\Delta G^0 = -RT \ln K_0 \dots \dots \dots (4.4)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \dots \dots \dots (4.5)$$

$$\ln K_0 = \Delta G^0/(RT) = \Delta S^0/(R) - \Delta H^0/(RT) \dots \dots \dots (4.6)$$

$$\log K_0 = \Delta S^0/(2.303R) - \Delta H^0/(2.303RT) \dots \dots \dots (4.7)$$

$\Delta H^0$  and  $\Delta S^0$  were determined from the slope and intercept of the plot of  $\ln K_0$  versus  $1/T$  and these were tabulated.

The thermodynamic treatment of the sorption data indicates that  $\Delta G^0$  values were negative at all temperatures. From the results it could be made out that physisorption is much more favorable for the adsorption of Fe(II) ions. The positive values of  $\Delta H^0$  show the endothermic nature of adsorption and it governs the possibility of physical adsorption. In the case of physical adsorption, while

increasing the temperature of the system, the extent of Fe(II) ions adsorption increases, this rules out the possibility of chemisorptions. The low  $\Delta H^0$  value that depicts Fe(II) ions are physisorbed onto adsorbent AMCL. The negative values of  $\Delta G^0$  (Table 4.4) show the adsorption is highly favorable and spontaneous. The positive values of  $\Delta S^0$  (Table 4.4) show the increased disorder and randomness at the solid solution interface of Fe(II) ions with AMCL adsorbent. While the adsorption there are some structural changes in the Fe(II) ions and the adsorbent were made. The adsorbed water molecules, which have been 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 AMCL at higher temperatures was attributed to the enlargement of pore size and activation of the adsorbent surface.

## 7. Adsorption kinetics

The study of the adsorption dynamics describes the solute uptake rate and evidently this rate controls the residence time of adsorbate uptake at the solid-solution interface [9]. The kinetics of adsorption on the adsorbent was analyzed using pseudo second-order, Elovich and Intra-particle diffusion kinetic models.

The conformity between experimental data and the model predicted values was expressed by the correlation coefficient ( $\gamma$ ), ( $\gamma$ , values close or equal to 1). The relatively high correlation coefficient ( $\gamma$ ) value indicates that the model which successfully describes the kinetics of adsorption on the adsorbent.

### The pseudo-second-order equation

The pseudo-second-order adsorption kinetic rate equation is expressed as

$$dq_t / dt = k_2(q_e - q_t)^2 \dots \dots \dots (4.8)$$

Where,  $k_2$  is the rate constant of pseudo-second order adsorption ( $g \text{ mg}^{-1} \text{ min}^{-1}$ ). For the boundary conditions  $t = 0$  to  $t = t$  and  $q_t = 0$  to  $q_t = q_t$  the integrated form of Eq. (3.3) becomes

$$1/(q_e - q_t) = 1/q_e + k_2 t \dots \dots \dots (4.9)$$

This is the integrated rate law for a pseudo-second-order reaction. Eq. (3.4) can be rearranged to obtain Eq. (3.5), which has a linear form:

$$t/q_t = (1/k_2 q_e^2) + ((1/q_e)t) \dots \dots \dots (4.10)$$

If the initial adsorption rate (h) ( $\text{mg g}^{-1}\text{min}^{-1}$ ) is:

$$h = k_2 q_e^2 \dots\dots\dots (4.11)$$

Equation (3.5) and (3.6) becomes

$$t / q_t = 1 / h + 1 / q_e t \dots\dots\dots (4.12)$$

The plot of  $(t/q_t)$  and  $t$  of Eq. (3.7) should give a linear relationship from which  $q_e$  and  $k_2$  can be determined from the slope and intercept of the plot, respectively. The pseudo-second-order rate constants  $k_2$ , the calculated ‘h’ values, and the correlation coefficients ( $\gamma$ ) are summarized

**The Elovich equation**

The Elovich model equation is generally expressed as

$$dq_t / dt = \alpha \exp (-\beta q_t) \dots\dots\dots (4.13)$$

Where,  $\alpha$  is the initial adsorption rate ( $\text{mg g}^{-1} \text{min}^{-1}$ ) and  $\beta$  is the desorption constant ( $\text{g mg}^{-1}$ ) during any one experiment. In order to simplify the Elovich equation. Chien and Clayton assumed  $\alpha\beta t \gg 1$  and by applying boundary conditions  $q_t = 0$  at  $t = 0$  and  $q_t = q_t$  at  $t = t$  Eq.(3.8) becomes:

$$q_t = 1/\beta \ln (\alpha\beta) + 1/\beta \ln (t) \dots\dots\dots (4.14)$$

If the adsorption fits the Elovich model, a plot of  $q_t$  Vs  $\ln(t)$  should yield a linear relationship with a slope of  $(1/\beta)$  and an intercept of  $(1/\beta) \ln (\alpha\beta)$ . The obtained Elovich model parameters  $\alpha$ ,  $\beta$ , and correlation coefficient ( $\gamma$ ) are summarized.

**Intra-particle diffusion model**

The intra-particle diffusion model used here refers to the theory proposed by Weber and Morris [10] based on the following equation for the rate constant:

$$q_t = k_{id} t^{(1/2)} + C \dots\dots\dots (4.15)$$

Where,  $k_{id}$  is the intra-particle diffusion rate constant ( $\text{mg g}^{-1}\text{min}^{-1/2}$ ) and  $C$  is the constant. If the rate limiting step is the intra-particle diffusion, the graphical representation of ( $q_t$ ) adsorbent ions ( $\text{mg g}^{-1}$ ) depending on the square root of the contact time ( $t^{1/2}$ ) should yield a straight line passing through the origin. The slope of the plot of  $q_t$  Vs  $t^{1/2}$  will give the value of the intra-particle diffusion coefficient ( $k_{id}$ ) and correlation coefficient ( $\gamma$ ) indicates the fitness of this model. The intercept value indicates that the curve is not passing through the origin.

So, the intra-particle diffusion is not only a rate controlling step. The values of intra-particle parameters were summarized. The study of adsorption dynamics describes the solute uptake rate and evidently this rate controls the residence time of adsorbate uptake at the solid-solution interface. The kinetics of Fe(II) ions adsorption on the AMCL were analyzed using pseudo second-order Elovich and intra-particle diffusion kinetic models.

The conformity between experimental data and the model predicted values was expressed by the correlation coefficient ( $\gamma$ ), ( $\gamma$ , values close or equal to 1). The experimentally obtained high correlation coefficient ( $\gamma$ ) value indicates that the models which were used successfully describes the kinetics of Fe(II) ions adsorption on AMCL adsorbent. The pseudo-second-order rate constants,  $k_2$ , the calculated corresponding ‘h’ values and the correlation coefficients ( $\gamma$ ) and the Elovich model parameters  $\alpha$ ,  $\beta$  and correlation coefficient ( $\gamma$ ) were summarized in table 4.5.

The slope of the plot of  $q_t$  Vs  $t^{1/2}$  gives the value of the intra-particle diffusion coefficient ( $k_{id}$ ) and correlation coefficient ( $\gamma$ ). The obtained values indicate the fitness of this model and the thickness of the formed layer on the boundary. The intercept value indicates that the curve is not passing through the origin. So, the intra-particle diffusion is not only a rate controlling step but some others were also involved during the percolation of Fe(II) ions onto AMCL. The calculated intra-particle parameters are summarized in table 4.5.

**8. Desorption studies**

Desorption studies help to elucidate the nature of adsorption and recycling of the spent adsorbent and the Fe(II) ions. The effect of various reagents used for desorption studies indicate that hydrochloric acid is a better reagent for desorption because more than 70% removal of adsorbed Fe(II) ions. The reversibility of adsorbed Fe(II) ions by mineral acid is in agreement with the pH dependent results obtained. The desorption of Fe(II) ions by mineral acids medium indicates that the Fe(II) ions were adsorbed by AMCL through physisorption mechanism.

**9. Evidence of Adsorption**

The IR spectra of the raw AMCL and after the adsorption of Fe(II) ions were shown in Fig.4.4a and 4.4b. From the peaks, one could see the slight reduction of stretching vibration in the adsorption bands. This one clearly indicates that the adsorption of Fe(II) ions on the adsorbent by physical forces and not by chemical combination.

The XRD diagrams of AMCL and Fe(II) ion-adsorbed carbon was shown in Fig.4.5a and 4.5b. The intense main peak shows the presence of highly organized crystalline structure of raw AMCL, after the adsorption of Fe(II) ions, the intensity of the highly organized peaks was slightly diminished. This was attributed to the adsorption of Fe(II) ion on the upper layer of the crystalline structure of the carbon surface by means of physisorption.

Table 4. Equilibrium Parameters For Adsorption Of Fe(Ii) Ion By Amcl

C <sub>0</sub>	Ce (mg / L)				Q <sub>e</sub> (mg / g)				Removal (%)			
	30°C	40°C	50°C	60°C	30°C	40°C	50°C	60°C	30°C	40°C	50°C	60°C
25	2.600	2.3640	2.1560	2.027	44.785	45.272	45.688	45.946	89.57	90.54	91.37	91.89
50	9.790	8.7625	7.3735	6.378	80.413	82.475	85.253	87.244	80.41	82.47	85.25	87.24
75	21.42	19.127	16.920	14.97	107.15	111.74	116.15	120.05	71.43	74.49	77.43	80.03
100	41.77	38.860	35.799	32.76	116.45	122.27	128.15	134.47	58.22	61.13	63.07	67.23
125	66.97	63.286	59.799	56.21	116.05	123.42	130.40	137.56	46.42	49.37	51.36	55.02

Table 5. Langmuir And Freundlich Isotherm's For The Adsorption Of Fe(Ii) Ion By Amcl

Temp. (C°)	Langmuir parameter		Freundlich parameter	
	Q <sub>m</sub>	b	K <sub>f</sub>	n
30°	125.404	0.2229	4.7951	3.2911
40°	133.516	0.2222	4.8733	3.1851
50°	227.610	0.0938	4.4842	1.9857
60°	148.891	0.2405	5.0665	3.0235

Table 6. Dimensionless Separation Factor (Rl) For The Adsorption Of Fe(Ii) Ion By Amcl

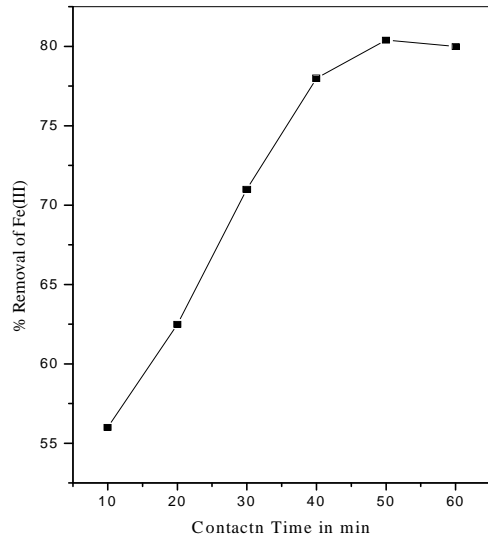
(C <sub>i</sub> )	Temperature °C			
	30°C	40°C	50°C	60°C
25	0.1521	0.1525	0.2987	0.1425
50	0.0823	0.0825	0.1756	0.0767
75	0.0564	0.0566	0.1243	0.0525
100	0.0429	0.0430	0.0962	0.0399
125	0.0346	0.0347	0.0785	0.0321

Table 7. Thermodynamic Parameters For The Adsorption Of Fe(Ii) Ion By Amcl

C <sub>0</sub>	ΔG°				ΔH°	ΔS°
	30° C	40° C	50° C	60° C		
25	-5416.99	-5879.04	-6338.76	-6721.41	7.8482	43.828
50	-3557.80	-4030.58	-4711.79	-5323.13	14.544	59.592
75	-2308.93	-2789.59	-3311.89	-3844.50	13.225	51.224
100	-836.604	-1179.30	-4273.23	-1990.51	19.780	68.714
125	-361.156	-65.4560	-2451.66	-558.477	16.969	55.395

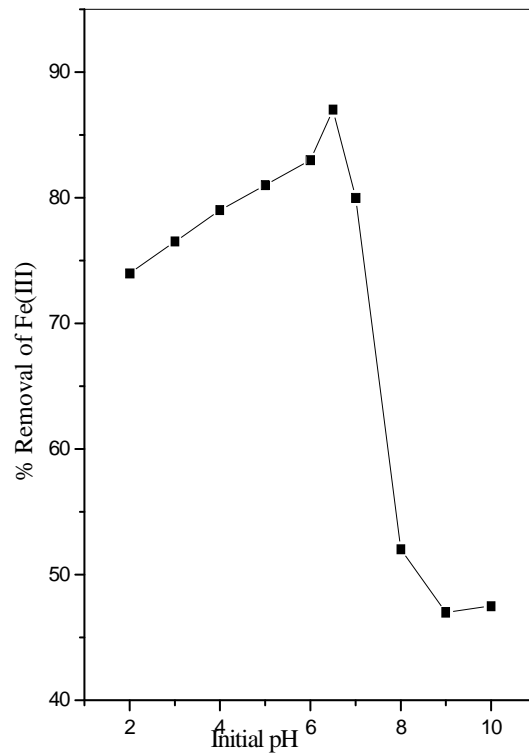
Table 8. The Kinetic Parameters For The Adsorption Of Fe(Ii) Ion By Amcl

C <sub>0</sub>	Temp °C	Pseudo second order				Elovich model			Intra-particle Diffusion		
		q <sub>e</sub>	k <sub>2</sub>	γ	h	α	β	γ	K <sub>id</sub>	γ	C
25	30	51.858	0.0017	0.991	4.7564	19.341	0.1106	0.990	1.5190	0.991	0.2394
	40	51.822	0.0018	0.992	5.0771	24.201	0.1158	0.990	1.5492	0.991	0.2242
	50	51.754	0.0020	0.992	5.4632	30.829	0.1212	0.992	1.5775	0.991	0.2104
	60	52.142	0.0020	0.992	5.4599	29.719	0.1192	0.993	1.5759	0.991	0.2130
50	30	93.938	0.0009	0.993	7.9726	28.678	0.0588	0.994	1.4447	0.991	0.2541
	40	95.730	0.0009	0.993	8.4229	33.377	0.0594	0.996	1.4740	0.991	0.2432
	50	97.725	0.0009	0.993	9.4950	43.413	0.0607	0.997	1.5173	0.992	0.2278
	60	100.06	0.0009	0.994	9.8711	44.791	0.0592	0.998	1.5288	0.992	0.2279
75	30	129.47	0.0005	0.990	8.9990	25.875	0.0394	0.997	1.3267	0.993	0.2909
	40	132.49	0.0005	0.994	10.264	32.843	0.0401	0.996	1.3809	0.995	0.2712
	50	136.56	0.0006	0.995	11.543	40.600	0.0401	0.991	1.4268	0.996	0.2565
	60	139.37	0.0005	0.992	9.8926	45.751	0.0428	0.991	1.4513	0.990	0.2344
100	30	153.50	0.0003	0.990	7.1577	15.568	0.0294	0.995	1.0754	0.990	0.3820
	40	156.45	0.0003	0.990	8.1887	18.949	0.0297	0.996	1.1481	0.990	0.3526
	50	160.75	0.0003	0.990	9.3012	22.840	0.0298	0.997	1.2091	0.990	0.3305
	60	164.75	0.0004	0.990	11.073	29.878	0.0304	0.999	1.2824	0.990	0.3026
125	30	179.18	0.0001	0.990	5.0234	10.119	0.0241	0.992	0.7540	0.990	0.5072
	40	182.26	0.0001	0.996	5.7450	11.601	0.0236	0.993	0.8334	0.906	0.4768
	50	191.15	0.0001	0.997	6.1784	12.557	0.0227	0.994	0.8745	0.990	0.4670
	60	188.62	0.0002	0.999	7.5459	15.596	0.0232	0.998	0.9805	0.991	0.4213



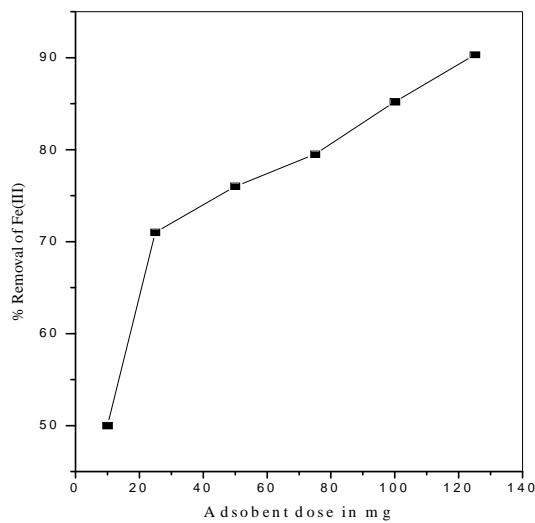
Fig;4.1- Effect of Contact time on the removal of Fe(III)ion  
[Fe(III)]=50mg/L; Adsorbent dose=25mg/50ml; Temp=30°C

Figure 1.



Fig; 4.3- Effect of Initial pH on the removal of Fe(III)ion  
[Fe(III)]=50mg/L; Conact time=50min; Adsorbent dose=25mg/50ml;Temp=30°C

Figure 3.



Fig; 4.2- Effect of Adsorbent dose on the removal of Fe(III)ion  
[Fe]=50 mg/L; Conact time=50m in; Adsorbent dose=25m g/50ml;Temp=30°C

Figure 2.

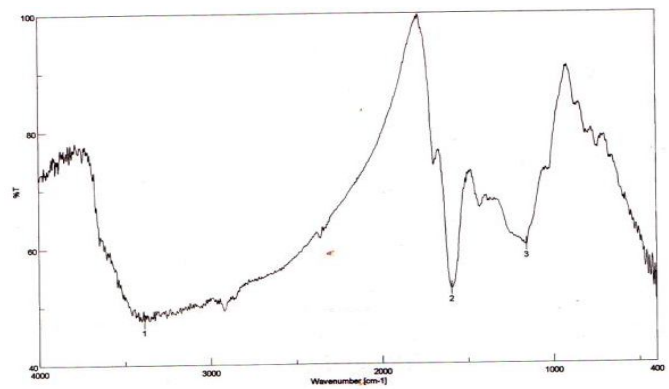


Figure 4. FT-IR Spectrum of AMCL before the adsorption of Fe(II)



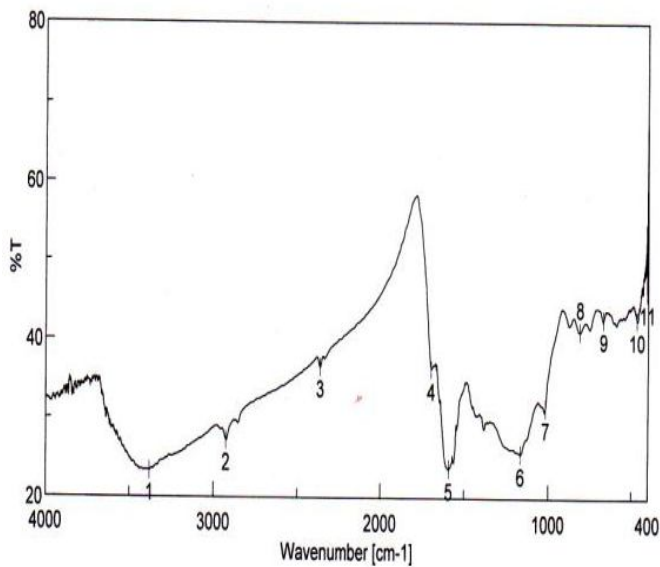


Figure 5. FT-IR Spectrum of AMCL after the adsorption of Fe(II) ion

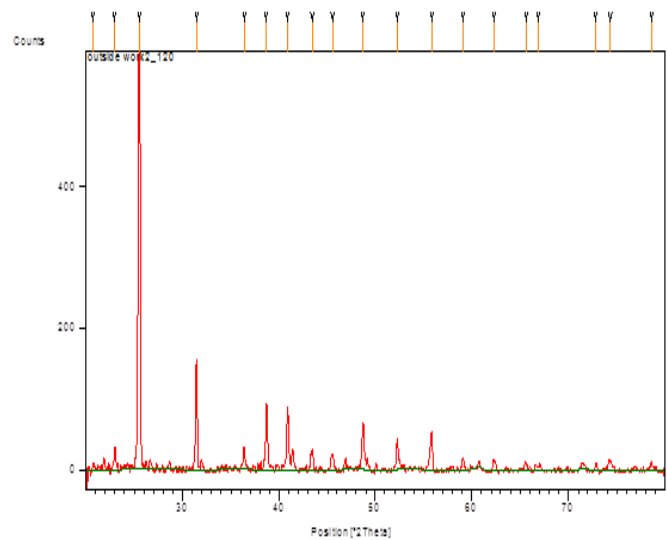


Figure 7. XRD pattern of AMCL after the adsorption of Fe(II) ion

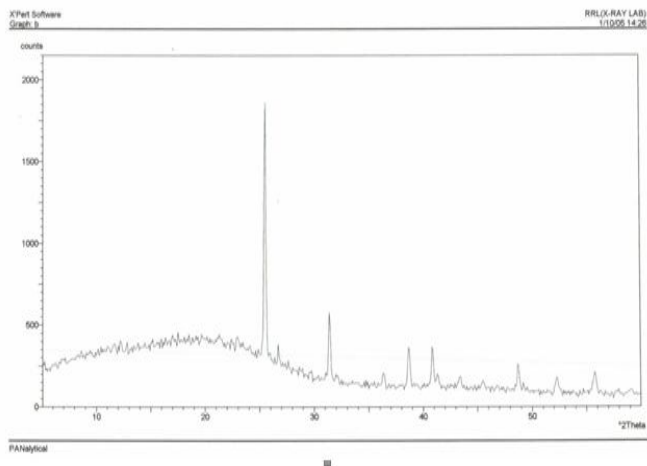


Figure 6. XRD pattern of AMCL before the adsorption of Fe(II)

## V. CONCLUSION

The work reported in this study deals with the investigation on the kinetic and thermodynamic aspects of the adsorption of Fe(II) onto the AMCL adsorbent. The different parameters pertaining to the adsorption at equilibrium were determined in order to establish the behavior of the adsorption process.

Batch experiments were carried out to determine the effective adsorbent dose and adsorbent concentration in the removal of Fe(II) ions by AMCL. The adsorption of Fe(II) ions on the surface of the AMCL, being a solid solution reaction; the extent of adsorption was directly proportional to the time of contact and adsorbent concentration. The adsorption of Fe(II) ions increased up to 50 min for the adsorbent beyond where the equilibrium was reached. The percentage adsorption, for a given adsorbent dose decreased with increase in initial Fe(II) ions concentration and increased with increase in temperature. It was seen that the increase in dose of adsorbent increased the percentage of Fe(II) ions removal.

Thermodynamic parameters are evaluated using the values of equilibrium constant at different temperatures viz. 303, 313, 323 and 333K with the help of Eyring equation, the values of  $\Delta G^0$  for the adsorption of Fe(II) onto AMCL were found to be negative while the values of  $\Delta H^0$  and  $\Delta S^0$  are positive. The values of enthalpy, entropy and free energy changes are shown in the above table.

The negative values of  $\Delta G^0$  indicated that the process was spontaneous with high affinity for Fe(II) ions. Further, the values of  $\Delta G^0$  increased with increase in temperature, which suggests that the spontaneity of adsorption is proportional to temperature. The positive values of  $\Delta S^0$  show that increased disorder at the solid/solution interface during the process. The positive values of  $\Delta H^0$  indicate that the adsorption process is endothermic in nature. The magnitude of the enthalpy change suggests that the adsorption take place via physisorption mechanism.

The Langmuir and Freundlich constants for the chosen adsorbent AMCL indicate that the capacity of the adsorbent to abate Fe(II) ions on reported in literature. The results of the present investigation are quite useful for the removal of Fe(II) ions from aqueous solutions using batched or stirred tank flow reactors. Yet, additional research is needed to determine the useful capabilities and specific applications of the AMCL adsorbent with respect to other heavy metals and various real industrial wastewaters.

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