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Iron and Malachite Green Removal By Adsorption Mangifera Indica (Mango Tree Leaf) Shell As Low Cost Adsorbent

S. Chitradevi ,Associate Professor,
Rajalakshmi Institute of Technology Department of Chemistry Chennai – 602 124
Corresponding Author:S. Chitradevi

Abstract: *Eco-friendly adsorbent has been reported as an alternative to the current expensive methods of removing of iron and malachite green (MG) dye from aqueous solution. Iron is also an essential constituent of human body which helps for better regulation of the body. Certain amount of Iron is required for both the male and female body to avoid Iron deficiency in the body, despites this Iron can be harmful for the human body if intake in larger amounts.The effects of different variables, adsorbent dosage, initial dye concentration, pH, contact time, temperature etc.Iron metal used for different purpose*

Keywords: *Iron, Malachite green, P^H, Earth, Environment*

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I. Introduction

1. WATER POLLUTION

Our earth's surface is covered by nearly 71% of water. Water is one the most essential resource available on the earth.Water is vital for all known forms of life. On earth, nearly 97% of the planet's water is found in seas and oceans and is unfit for human consumption because of the high salt content. Nearly 2% is locked in glaciers and the ice caps of Antarctica and Greenland, and only the remaining 1% is available as fresh water in rivers, lakes, streams, reservoirs and ground water which is suitable for human consumption[1]. Water pollution is a contamination of water bodies (eg., lakes, rivers, oceans and ground water) when pollutants are discharged directly or indirectly into water bodies without adequate treatment to remove harmful compounds. Water pollution affects plants and organisms living in these bodies of water. They also change the values of pH, BOD, COD and temperature of water bodies[2]. Industrial effluents, domestic effluents and agricultural wastes are the important sources of water pollution.

The effluents of industries of dairy products, sugar, fruits, vegetables and yeast, beer, distilleries, soft drinks, pickles, slaughter house, synthetic mills, cotton industries, tanneries, paper and pulp mills, anti- biotics, synthetic drugs, organic chemical industries, explosives, pesticides, fertilizers, rubber industries, steel mills and iron foundries, metal plating, photographic industries contain alkalis, acids, greezes, fats, lactose, colloidal solids, dissolved organic compounds, high suspended matters, high dissolved solids, containing nitrogen and fermented starches, protein and blood, sulphide ions, heavy metals , dyes, detergents, fibres, toxic organics, vitamins , phenols, alcohols, trinitrotoluene, chlorides, cyanides and cyanides of heavy metals, lime stone, oil, suspended solids of coal and clay are some of the sources of water pollution.

Specifications for some of the important parameters for drinking water insisted by Bureau of Indian Standards[3], Ministry of drinking water and sanitation, Government of India, New Delhi are listed in table - 1.1:

Table - 1.1

Sl. No.	Characteristic properties	Unit	Requirement (acceptable limit)	Permissible limit in the absence of alternate sources
1	Total Dissolved Solids (TDS)	Milligram/litre	500	2000
2	Colour	Hazen unit	5	15
3	Turbidity	NTU	1	5
4	Total hardness	Milligram/litre	200	600
5	Ammonia	Milligram/litre	0.5	0.5
6	Free residual chlorine	Milligram/litre	0.2	1
7	pH	---	6.5 – 8.5	6.5 – 8.5
8	Chloride	Milligram/litre	250	1000
9	Fluoride	Milligram/litre	1.0	1.5
10	Arsenic	Milligram/litre	.01	0.05
11	Iron	Milligram/litre	0.3	0.3
12	Nitrate	Milligram/litre	45	45

13	Sulphate	Milligram/litre	200	400
14	Selenium	Milligram/litre	0.01	0.01
15	Zinc	Milligram/litre	5.0	15
16	Mercury	Milligram/litre	0.001	0.001
17	Lead	Milligram/litre	0.01	0.01
18	Cyanide	Milligram/litre	0.05	0.05
19	Copper	Milligram/litre	0.05	1.5
20	Chromium	Milligram/litre	0.05	0.05
21	Nickel	Milligram/litre	0.02	0.02
22	Cadmium	Milligram/litre	0.003	0.003
23	E–Coli or Thermo tolerance Coli forms	Number/100ml	NIL	NIL

1.2 Effects Of Water Pollution

Polluted water, when consumed by human beings, causes various health problems which are either short-term or long-term in nature. Inorganic and organic toxins in water can produce indigestion, diarrhoea, fever, etc., Continued ingestion of heavy metals may cause several problems including mental retardation, nervous disorder, failure of vital organs, cancer and even death[2].

The pollutants in water can get incorporated in edible aquatic creatures such as fish, crab, prawn, etc., and when consumed by human beings lead to various illnesses. The pollutants may decrease the dissolved oxygen (DO) in the water, and therefore decrease the population of aquatic lives.

Certain pollutants may accelerate the growth of algae, weeds, etc., causing deterioration in water quality. Polluted water is a carrier of pathological microorganisms which can cause immense harm to public health. Microorganisms are the catalysts for many aquatic chemical reactions that can change the chemistry of water and its composition.

The production of synthetic organic chemicals has multiplied about 10 times per year after 1950. These include plastics, fuels, fibres, solvents, detergents, food additives, paints, insecticides and pharmaceutical. Their presence in water imparts objectionable and offensive tastes, colors and smell and causes various diseases.

1.3. Other health effect

Alzheimer
Neurodegenerative diseases
Cancer
Diabetes mellitus
Arteriosclerosis

II. Materials And Methods

2.1 Materials

2.1.1 Chemicals

2.1.3 Preparation of metal ion solutions

The metal ions chosen for the adsorption studies in the present work are Iron (III), ions. Stock solutions (1000 mg/L) of Fe (III), ions were prepared by dissolving required amount of metal salt in one litre of distilled water. The weights of the respective salts taken are listed in table.3.1

Table 2.1 Weight of the salts taken for the preparation

Metal ion	Metal salt	Weight to be dissolved for one litre (g)
Fe (III)	$FeSO_4$.7H2O	5.9785

2.1.4 Preparations of dye solutions

The dyes employed for the adsorption studies in the present work are malachite green. All the dyes for the study were commercially available high purity Analar grade (Merck, India) and used without further purification. Stock solution (1000 mg/L) of the dyes was prepared by dissolving required amount of the respective dye in one litre of distilled water. The weights of the respective dyes taken are listed in table.3.2

Table 2.2 Weight of the dyes taken for the preparation of stock solutions

Dyes	Weight to be dissolved for one litre (g)
Malachite Green	1

2.2 Preparation of Adsorbent

The natural plant material Mangifera indicaleaf was collected from nearby Thiruvalluvar district the leaves were washed with distilled water several times to remove the dirt and dust and was Carbonized with concentrated Sulphuric Acid (w/v) and washed with water. Afterward, the primary carbon was activated at 400^oC for 8 hrs in muffle furnace to obtain activated carbon. The activated carbon was there after kept at room temperature in an insert atmosphere of nitrogen and washed with hot distilled water and 0.5 N Hydrochloric and until the pH of the material reached 7.0 the activated carbon was also dried in a hot air oven at 110 ^0C, ground and sieved to obtain the desired particular size and stored in desiccators for further use.

2.3 Characterization of *ACTNC* adsorbent

The wide usefulness of *ACTNC* is a result of its specific surface area, high chemical and mechanical stability. The chemical nature and pore structure usually determine the sorption activity[4,5]. The *ACTNC* carbon utilized in the present research work was characterized[6-8] as follows:

2.3.1 Determination of Particle size

The particle size of the adsorbent *ACTNC* was measured using the Carl Zeiss Light microscope (Axiostar plus). The ocular micrometer with a dimension of 10x was attache in order to determine the particle sizes of adsorbent. Each division in the scale of the ocular meter is 0.01mm. The length and breadth of each particle were measured. By application of multiplication factors, the size of the particle was calculated.

2.3.3 Moisture content

The moisture content of the adsorbent was analysed using the moisture balance. One gram of the adsorbent placed in a petriplate 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 represented the mechanical or hydroscopic moisture.

2.3.4 Loss on ignition

One gram of adsorbent was placed in pre weighed silica crucible and it was ignited at 1000^0C for 4 hours in an electric muffle furnace. Then it was cooled in a desiccator and weighed. The weight loss was calculated as loss on ignition.

2.3.5 Water soluble matter

Five gram of the adsorbent was weighed and transferred into a 500ml beaker. About 100ml of distilled water was added and heated to boiling with continuous stirring. Stirring was continued for 5 minutes after the flame was removed. The adsorbent material was allowed to settle and the supernatant liquid was filtered through a gooch crucible fitted with an asbestos mat. The procedure was repeated thrice with the residue in the beaker using 100ml of water each time. The combined filtrate was concentrated to less than 100ml over a water bath, cooled and made up to 100ml mark in a standard flask. Exactly 50ml of the concentrate was transferred to a china dish and evaporated to almost dryness as a boiling water bath and finally dried in an electric oven, maintained at 105 +/- 5^0C, 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 5mg. The percent of water soluble matter was then calculated by the following formula

Water soluble matter (%) = $M \times 100 \times 2 / (M_1/100)(100 - X)$

Where, M = mass of the residue in grams
M_1 = mass of the adsorbent taken for test in grams (5g)
X = percent of moisture present in the material

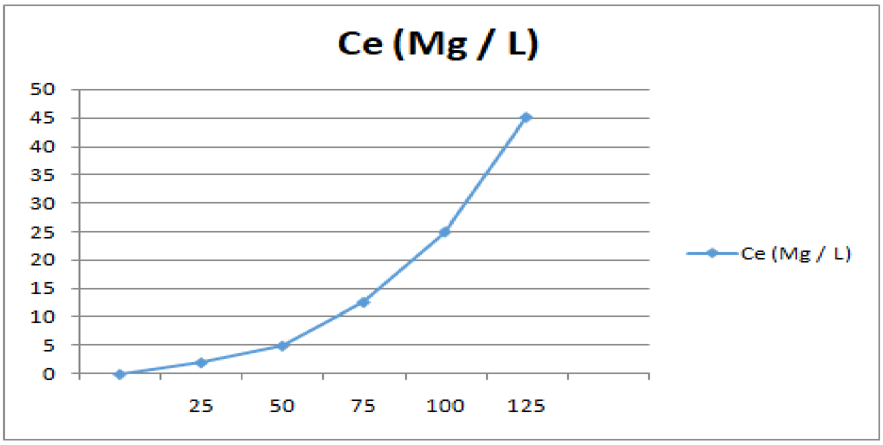
2.3.6 pH of aqueous solutions

About 100 mg of adsorbent was mixed with 50ml 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.

Table 2.3: Characterization of the adsorbent

Properties	***ACTNC***
Particle size (mm)	0.090
Density (g/cc)	0.193
Moisture content (%)	0.178

Loss on ignition (%)	0.010
Water soluble matter (%)	0.080
pH of aqueous solution	5.200
pH_{zpc}	6.500



2.4 Methodology

Concentration of the metal ions/dyes before and after adsorption was measured using a double UV-Visible spectrophotometer (Systronics 2203). Standards for the establishment of calibration cure for UV-Visible spectrophotometer analysis was prepared by diluting the stock solutions so as to have 10 to 250 mg/L of the metal ions/dyes and the absorbance of the solution at the respective wave length was recorded. The wave length of maximum absorbance for Iron Malachite Green are given in table 3.4.

Table:2.4: Wave Length For The Estimation Of Metal Ions/Dyes

Metal ions and Dyes	**Wave length (nm)**
Iron (III)	530
Malachite Green	614

III. Adsorption Studies

3.1 Batch equilibration method

All experiments were carried out at 30, 40, 50 and 60°C temperature in batch mode. Batch mode was selected because of its simplicity and reliability. The batch experiments were done in different Erlenmeyer glass flasks of 250 ml capacity. Prior to each experiment, a predetermined amount of absorbent was added to each flask. The stirring was kept constant (150 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 ion/dye solution with an initial concentration of 10 mg/L to 250 mg/L. the flask containing the sample was withdraw from the shaker at the predetermined time interval, filtered and the residual concentration of the metal ion/dye was measured.

3.2 Dosage of adsorbents

Different doses consisting of 10 to 125 mg/50 ml of the adsorbent mixed with the metal ion/dye solutions and the mixture was agitated in a mechanical shaker. The percentage of adsorption for different doses was determined by keeping all other factors constant.

3.3 Initial concentration

In order to determine the rate of adsorption, experiments were conducted with different initial concentrations of dyes ranging from 50 to 250 mg/L and metal ions ranging from 25 to 125 mg/L. All other factors were kept constant.

3.4 Contact time

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

3.5 Initial pH

Adsorption experiments were carried out at a wide range of pH of the solution i.e. 3-9. The acidic and alkaline pH of the medium was maintained by adding the required amounts of hydrochloric acid and sodium hydroxide solution. The parameters like particle size of the adsorbents, metal ion or dye concentration, dosage of the adsorbents, and temperature were kept constant while carrying out the experiments.

3.6 Temperature

The adsorption experiments were performed at four different temperature viz. 30, 40, 50, and 60^oC in a thermo stated shaker machine (Remi, India). The constancy of the temperature was maintained with an accuracy of ±0.5^oC.

3.7 Adsorption 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 adsorbents. The equilibrium data for the removal of metal ions and dyes by sorption on the three adsorbents at different temperature have been used in Langmuir and Freundlich isotherms.

Langmuir isotherm: $Ce/Qe=1/Q_mb + Ce/Q_m$……. (3.1)
Freundlich isotherm: $\log Qe = \log K + 1/n \log Ce$…. (3.2)

Where, Ce is the equilibrium concentration of the adsorbate adsorbed per unit mass of adsorbent at equilibrium (mg/g); Q_m and b are Langmuir constants related to the adsorption capacity and energy of adsorption, respectively. The values of Q_m and b have been obtained from the liner correlation of Ce/Qe against Ce. The Freundlich constants K 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 Qe versus log Ce. The essential characteristics of the Langmuir isotherm can be described by a separation factor R_L, which is defined as $R_L = 1/(1+bCo)$ where b is the Langmuir constant and Co is the initial concentration of the metal iron or dye. The values of R_L indicate the shape of the isotherm as follows[9]

R_L value	**Types of isotherm**
$R_L>1$	Unfavorable
$R_L=1$	Linear
$0<R_L<1$	Favorable
$R_L=0$	Irreversible

3.7.2 The pseudo-second- order equation

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

$dq_t / d_t = k_2(q_e-q_t)^2$ ……………..…. (3.3)

Where, k_2 is the rate constant of pseudo- second- order adsorption (g $mg^{-1}min^{-1}$). 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

$1/(q_e – q_t) = 1/q_e + k_2t$ ………… (3.4)

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:*

$t/q_t = (1/k_2q_e^2)+ ((1/q_e)t$ ……………….(3.5)

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

$h = k_2q_e^2$ ……………………(3.6)

Equation (3.5) and (3.6) becomes,

$t / q_t = 1 / h + 1 / q_e\ t$ …………….. ..(3.7)

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 (γ) are summarized

3.7.2 The Elovich equation

The Elovich model equation is generally expressed as

$dq_t / d_t = \alpha \exp(-\beta q_t)$ ………. (3.8)

Where, α is the initial adsorption rate (mg g^{-1} min^{-1}) and β is desorption constant (g mg^{-1}) during any one experiment. Which simplify the Elovich quation. Chien and Clayton (1980) assumed αβt>>t and by applying boundary conditions $q_t = 0$ at t= 0 and $q_t = q_t$ at t = t Eq.(3.8) becomes:

$q_t = 1/\beta \ln(\alpha\beta) + 1/\beta \ln(t)$ …………… (3.9)

If adsorption fits the Elovich model, a plot of q_t vs. ln(t) should yield a linear relationship with a slope of (1/β) and an intercept of (1/β) ln (αβ). The Elovich model parameters α, β, and correlation coefficient (γ) are summarized.

3.8 Desorption studies

Desorption studies help to elucidate the nature of adsorption and recycling of the spent adsorbent and the metal ions and dyes. If the adsorbed metal ions or dyes can be desorbed using water, then the attachment of the metal ion or dye on the adsorbent by weak bonds. If sulphuric acid or alkaline water desorp the metal ion or dye, then the adsorption is by ion exchange. If organic acids, like acetic acid can desorp the metal ion or dye, then the metal ion or dye is held by the adsorbent through chemisorption[10]. The effect of various regents used for desorption studies are carried out by using 0.2 M hydrochloric acid, sulphuric acid, nitric acid, sodium chloride and water.

3.9 Data Analysis

The experimental data were analyzed using mirocal origin (version 8) Computer Software. The goodness of fit was discussed using correlation coefficient r, and standard deviation, sd.

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

IV. Result And Discussion

4.1. Adsorption Of Ferrous (Iii) Ion

4.1.1. Effect of contact time and initial Fe (III) ions concentration

The experimental results for the adsorption at various concentrations (25 to 125 mg L^{-1}) with contact time are shown in Figure .1. The respective data are presented in Table-.1, revealing that, percent adsorption decreased with increase in initial Fe (III) ions concentration, but the actual amount of Fe (III) ions adsorbed per unit mass of *ACTNC* increased with increase in Fe (III) ions concentration. It means that the adsorption is highly dependent on initial concentration of Fe (III) ions. It is because of the reason that at lower concentration, the ratio of the initial number of Fe (III) ions molecules to the available surface area is low. Subsequently the fractional adsorption becomes independent of initial concentration. However, at higher concentrations, the available site of adsorption becomes fewer and hence the percentage removal of Fe (III) ions is dependent upon initial concentration[189]. Equilibrium has been established at 50 minutes for all concentrations. Figure-4.1 reveals that the curve is single, smooth and continuous leading to saturation, suggesting the possibility of monolayer coverage of the Fe (III) ions on the *ACTNC* adsorbent surface.

4.2 Effect of Dosage

The adsorption of Fe (III) ions on *ACTNC* was studied by varying the dosage of adsorbent (25 - 125 mg / 50ml) for 25 mg L^{-1} of Fe (III) ions concentration. The percent of adsorption increased with increase in the *ACTNC* dose (Figure 4.2). This may be due to the increased *ACTNC* surface area and availability of more adsorption sites[7]. Hence the remaining parts of the experiments were carried out with an optimum dose of the adsorbent (25 mg/50 ml).

4.3 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 (III) Ions on *ACTNC* was determined. The result is shown in Figure. 4.3. The pH of the solution was controlled by the addition of HCl or NaOH. The uptake of Fe (III) ions at pH 6.5 was the minimum and a maximum uptake was obtained at pH 3.0 - 6.5. However, when the pH of the solution was increased (more than 6.5), the uptake was increased. If *ACTNC* bears that a change in pH of the solution results in the formation of different ionic species, different *ACTNC* surface changes. At pH values lower than 6, the Fe (III) ions can enter the pore structure. At a pH value higher than 6, the zwitterions form in water may increase the aggregation of Fe (III) ions to form a bigger molecular form (dimer) and become unable to enter the pore structure of the *ACTNC* surface[6].

4.4 Effect of the Ionic strength

The effect of sodium chloride on the adsorption of Fe (III) ions on *ACTNC* in a low solution concentration of NaCl had little influence on the adsorption capacity. At higher ionic strength the adsorption of Fe (III) ions will be increased due to the partial neutralization of the positive charge on the *ACTNC* surface and a consequent compression of the electrical double layer by the chloride ion[7]. The chloride ion can also enhance adsorption of Fe (III) ions onto *ACTNC* by the pairing of their charges and hence reducing the repulsion between the Fe (III) ions molecules adsorbed on the surface. This initiates *ACTNC* to adsorb more of positive Fe (III) ions. The result is shown in Figure. 4.5.

4.5 Theory of Adsorption isotherm

To quantify the sorption capacity of the absorbent for the removal of Fe (III) ions, the most commonly used isotherm, namely Freundlich and Langmuir has been adopted.

4.5.1 Freundlich isotherm

The value of K_f and n are calculated from the intercept and slope of the plot of log q_e vs log C_e respectively. The constant K_f and n values are given in table 4.2. In general K_f value increases the adsorption capacity for a given adsorbate increases. The magnitude of the exponent 1/n gives an indication of the favorableness of adsorption. The value of $n > 1$ represents favorable adsorption condition[11] (or) the value of 1/n lying in the range of 1 to 10 confirms the favorable condition for adsorption. This is further supported by Langmuir isotherm.

4.5.2 Langmuir isotherm

The Langmuir isotherm model[12] 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) 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[8] by the equation. The parameter R_L indicates the nature of shape of the isotherm accordingly. The R_L values between 0 and 1 indicate favorable adsorption for all initial concentrations (C_o) and temperatures studied. The calculated R_L values are given in Table. 4.3.

4.6 Thermodynamic treatment of the adsorption process

The thermodynamic treatment of the sorption data indicates that $\Delta G°$ 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 (III) ions. The positive values of $\Delta H°$ 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 Fe (III) ions adsorption increases, this rules out the possibility of chemisorptions. The low $\Delta H°$ value that depicts Fe (III) ions is physisorbed onto adsorbent *ACTNC*. The negative values of $\Delta G°$ (Table-4.4) show the adsorption is highly favorable and spontaneous. The positive values of $\Delta S°$ (Table-4.4) show the increased disorder and randomness at the solid solution interface of Fe (III) ions with *ACTNC* adsorbent. While in the adsorption there are some structural changes in the Fe (III) ions and the adsorbent occur. 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 *ACTNC* at higher temperatures was attributed to the enlargement of pore size and activation of the adsorbent surface.

4.7 Adsorption kinetics

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 (III) ions adsorption on the *ACTNC* were analyzed using pseudo second-order[13] Elovich [14] and intra-particle diffusion[15] kinetic models.

The conformity between experimental data and the model predicted values was expressed by the correlation coefficient (γ), (γ, values close or equal to 1). A relatively high correlation coefficient (γ) value indicates that the model successfully describes the kinetics of Fe (III) ions adsorption on *ACTNC* adsorbent.

The pseudo-second-order rate constants k_2, the calculated h values, and the correlation coefficients (γ) and the Elovich model parameters α, β, and correlation coefficient (γ) are summarized in table 4.5. The slope of the plot of qt Vs $t^{1/2}$ will give the value of the intra -particle diffusion coefficient (k_{id}) and correlation coefficient (γ) 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 intra-particle parameters are summarized in table 4.5.

4.8 Desorption studies

Desorption studies help to elucidate the nature of adsorption and recycling of the spent adsorbent and the Fe (III) ions. The effect of various reagents used for desorption studies indicate that hydrochloric acid is a better reagent for desorption, because of more than 70% removal of adsorbed Fe (III) ions. The reversibility of adsorbed Fe (III) ions in mineral acid or base is in agreement with the pH dependent results obtained. Desorption of Fe (III) ions by mineral acids and alkaline medium indicates that the Fe (III) ions were adsorbed *ACTNC* through physisorption[16].

4.9 Evidence of Adsorption

The IR spectra of the raw *ACTNC* carbon and after adsorption of metal ion have shown in Figure 4.5a and 4.5b. It could be seen that the slight reduction of stretching vibration adsorption bands. This clearly indicates the adsorption of metal ion on the adsorbent by physical forces not by chemical combination. The XRD diagrams of *ACTNC* carbon and metal ion-adsorbed carbon have shown in Figure 4.6a and 4.6b. The intense main peak shows the presence of highly organized crystalline structure of raw *ACTNC* carbon, after the adsorption of metal ion, the intensity of the highly organized peaks is slightly diminished. This has attributed to the adsorption of metal ion on the upper layer of the crystalline structure of the carbon surface by means of physisorption.

Table: 4.1. Equilibrium Parameters For The Adsorption Of Iron (Iii) Ion Onto *Actnc*

M_0	Ce (Mg / L)				Qe (Mg / L)				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	2.042	2.156	2.606	2.524	44.70	44.68	44.90	44.95	89.41	89.37	89.81	89.91
50	5.014	4.845	5.248	4.897	89.10	88.31	89.06	90.25	80.10	81.31	85.06	91.25
75	12.63	11.09	11.95	10.65	122.3	124.20	126.3	128.6	79.55	83.80	83.10	85.79
100	25.04	24.54	12.84	28.44	146.5	148.7	176.3	143.1	73.05	75.35	87.10	70.65
125	45.12	41.30	24.84	32.98	158.3	169.3	202.3	184.0	65.31	68.72	80.22	73.23

Table4.2.:Langmuir And Freundlich Isotherm Parameter For The Adsorption Of Iron (Iii) Ion Onto *Actnc*

Temp. (°C)	Langmuir Parameters		Freundlich Parameters	
	Q_m	b	K_f	n
35°C	165.24	0.1464	45.452	2.2773
45°C	217.13	0.1054	45.814	2.0330
55°C	371.76	0.0637	41.189	1.5603
60°C	212.67	0.1416	47.524	2.2604

Table: 4.3.: Dimensionless Seperation Factor (R_l) For The Adsorption Of Iron (Iii) Ion Onto *Actnc*

(C_i)	Temperature °C			
	30°C	40°C	50°C	60°C
30	0.2068	0.2402	0.3596	0.2030
50	0.1116	0.1370	0.2610	0.1518
75	0.0745	0.1137	0.1454	0.0819
100	0.0547	0.0690	0.1356	0.0606
125	0.0424	0.0543	0.1232	0.0422

Table: 4.4. : Thermodynamic Parameter For The Adsorption Of Iron (Iii) Ion Onto *Actnc*

(C_0)	ΔG°				ΔH°	ΔS°
	30°C	40°C	50°C	60°C		
25	-5472.67	-5641.3	-5832.4	-5957.41	1.5360	22.40
50	-5792.81	-5242.43	-5131.9	-6541.48	3.4496	28.046
75	-3733.83	-4180.38	-4384.8	-4569.05	8.3780	41.896
100	-2438.41	-2520.39	-5560.4	-2254.5	6.2538	32.422
125	-1255.76	-1829.25	-3440.9	-2750.56	17.286	64.307

Table: The Kinetic Parameters For The Adsorption Of Iron (Iii) Ion Onto *Actnc*

C_0	Temp °C	Pseudo second order				Elovich model			Intraparticle diffusion		
		q_e	k_2	γ	H	α	β	γ	K_{id}	γ	C
25	**30**	48.57	0.0021	0.9952	8.6257	94.65	0.1503	0.9959	1.6554	0.994	0.1684
	40	47.20	0.0018	0.9983	12.089	138.5	0.2206	0.9968	1.7542	0.995	0.1099
	50	47.00	0.0017	0.9960	12.149	297.7	0.2401	0.9982	1.7713	0.997	0.0998

	60	48.04	0.0022	0.9940	8.172	113.8	0.1555	0.9948	1.6686	0.999	0.1602
50	**30**	97.08	0.0024	0.9946	13.464	140.4	0.0734	0.9961	1.6339	0.998	0.1737
	40	93.22	0.0020	0.9988	19.166	151.2	0.1054	0.9987	1.7311	0.997	0.1170
	50	92.06	0.0018	0.9954	23.169	334.8	0.1137	0.9967	1.7559	0.998	0.1068
	60	91.87	0.0018	0.9990	22.278	152.4	0.1017	0.9989	1.7426	0.992	0.1187
75	**30**	121.37	0.0022	0.9987	25.091	113.7	0.0701	0.9984	1.6789	0.994	0.1277
	40	123.18	0.0022	0.9967	26.075	130.5	0.0702	0.9967	1.6897	0.991	0.1255
	50	124.93	0.0021	0.9961	27.618	198.3	0.0727	0.9983	1.7088	0.992	0.1186
	60	127.89	0.0021	0.9981	27.756	144.8	0.0682	0.9943	1.7079	0.991	0.1245
100	**30**	149.42	0.0025	0.9975	24.508	479.3	0.0507	0.9982	1.5890	0.992	0.1502
	40	150.43	0.0023	0.9969	28.794	939.6	0.0547	0.9972	1.6250	0.991	0.1354
	50	144.56	0.0011	0.9973	31.172	106.6	0.0537	0.9969	1.6418	0.993	0.1337
	60	139.49	0.0013	0.9989	76.512	163.9	0.0938	0.9981	1.7270	0.991	0.0773
125	**30**	164.67	0.0025	0.9928	23.317	406.0	0.0451	0.9948	1.5155	0.992	0.1555
	40	182.03	0.0024	0.9941	30.027	526.6	0.0431	0.9994	1.5540	0.994	0.1530
	50	189.94	0.0015	0.9948	31.296	625.9	0.0423	0.9972	1.5785	0.991	0.1490
	60	198.22	0.0024	0.9959	33.344	892.2	0.0427	0.9963	1.6093	0.992	0.1408

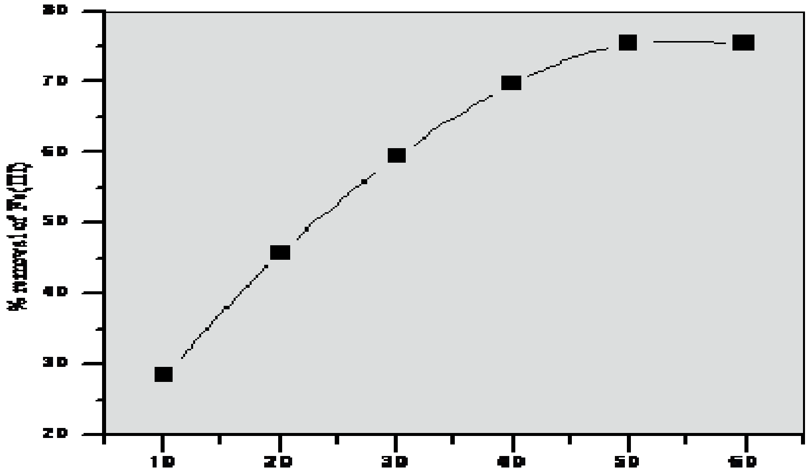


Fig. 4.1-Effect of contact time on the removal of Fe(III) ion
[Fe(III)]= 25 mg/L: adsorbent dose=25mg/50ml: pH=6.5: Temp=30°C

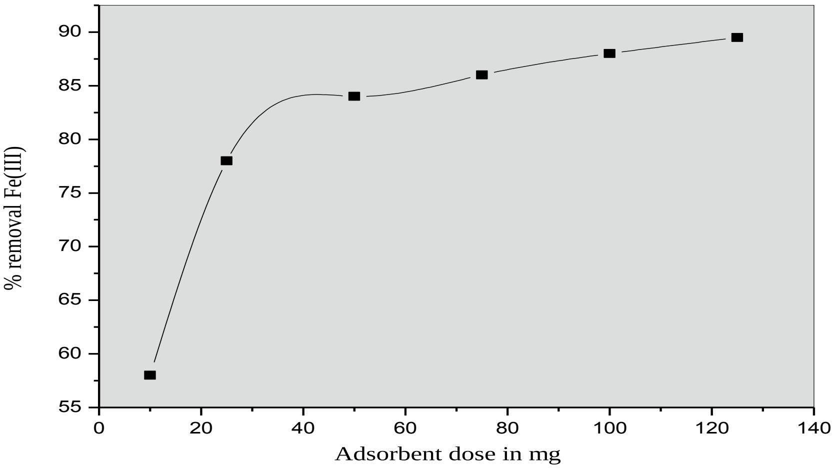


Fig. 4.2-Effect of adsorbent dose on the removal of Fe(III) ion
[Fe(III)]=25 mg/L: Contact time=50 min:pH=6.5:Temp=30^{0}C

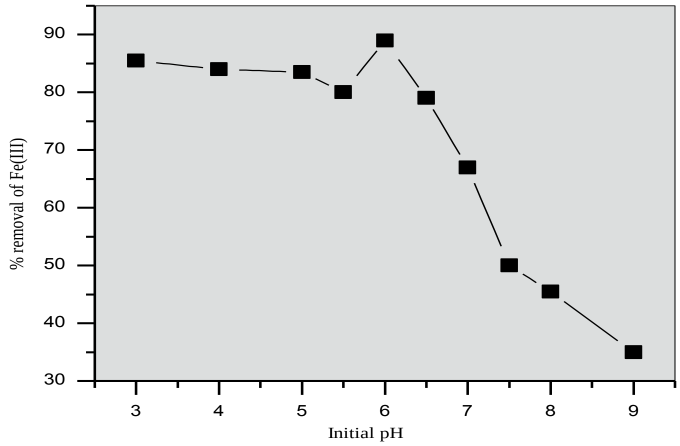


Fig. 4.3-Effect initial pH on the removal of Fe(III) ion
[Fe(III)]= 25 mg/L:Contact time=50 min:Adsorbent dose=25 mg/50 ml

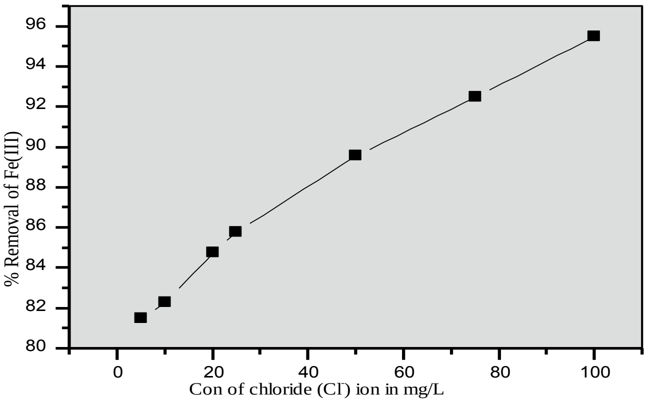


Fig: 4.4-Effect of ionic strength on the adsorption of Fe(III) ion
[Fe(III)]= 25mg/L;Contact Time 50 min; Adsobent Dose=25mg/50 ml

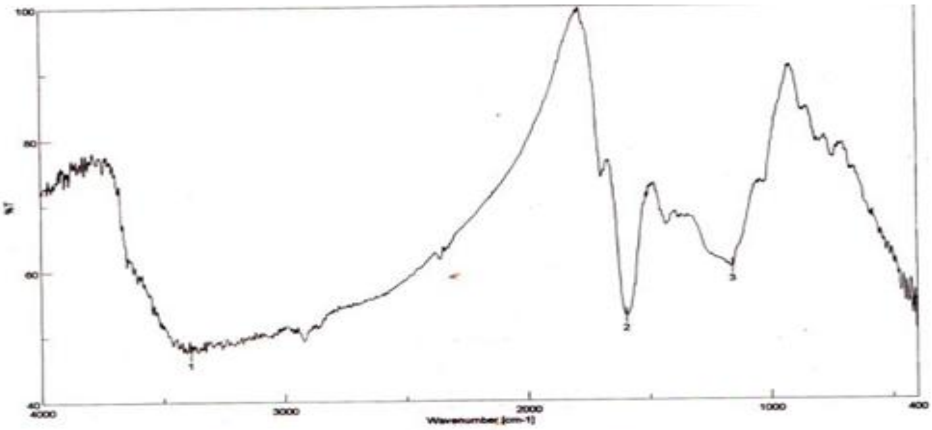


Fig.4.5a. FT-IR Spectrum before adsorption

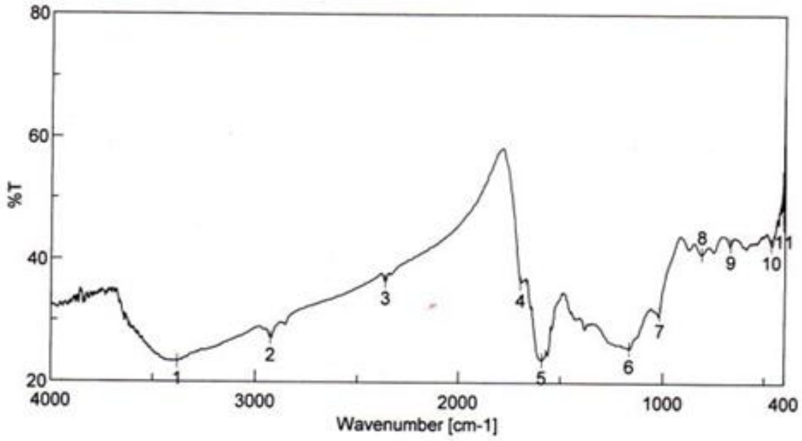


Fig. 4.5b. FT-IR Spectrum after adsorption of Fe (III) ion

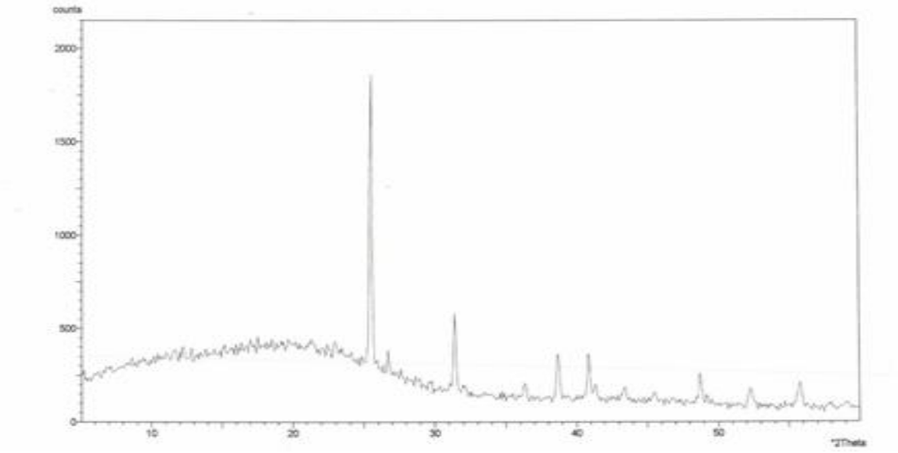


Fig.4.6a XRD pattern of*ACTNC* before adsorption

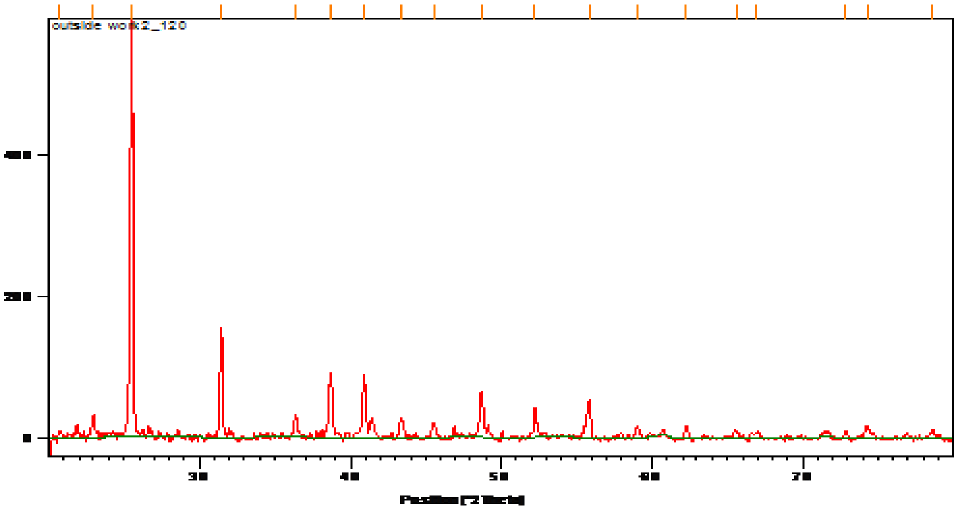


Fig. 4.6b. XRD pattern of *ACTNC* after adsorption of Fe (III) ion

V. Conclusion

Experiments were carried out to determine the effective adsorbent dose and adsorbent concentration in the removal of metal ions by *ACTNC*. The adsorption of metal ions increased up to 40 min for the adsorbent, beyond which the equilibrium was reached. The percentage adsorption, for a given adsorbent dose, decreased with increase in initial metal ion concentration and increased with increase in temperature. It was seen that the increase in dose of adsorbent increased the percentage of metal ion removal.

The adsorption of metal ions onto *ACTNC* is highly influenced by the pH of the medium. At low pH (below pH) the sorbent surface is protonated and it becomes difficult to adsorb the cations. the results of the present investigation are quite useful for the removal of heavy metal ions and dyes from aqueous solutions using batched or stirred tank flow reactors. Yet, additional research is needed to determine the useful capabilities and specific applications of these adsorbents with respect to other heavy metals and dyes and various real industrial wastewaters.

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