WORLD JOURNAL OF PHARMACEUTICAL RESEARCH
SJIF Impact Factor 6.805
Volume 5, Issue 12, 481-496. Research Article ISSN 2277– 7105

REMOVAL OF FE(III) IONS IN AQUEOUS MEDIUM USING PLANTAIN TREE CARBON – AN ECOFRIENDLY APPROACH

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Article Received on
10 Oct. 2016,
Revised on 30 Oct. 2016,
Accepted on 19 Nov. 2016
DOI: 10.20959/wjpr201612-7190

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ABSTRACT

The present adsorption study explored the ability of Plantain Tree Carbon (PTC) for the removal of Fe(III) ions from aqueous solution. Batch experiments were conducted. The sorbent, which was prepared by a simple and concise method, was able to bind heavy metal *viz.*, Fe(III) ions with very high efficiency. The adsorption study was confirmed through characterization tests *viz.*, Fourier transform infrared spectroscopy, X-ray diffraction, scanning electron microscopy and elemental analysis for the adsorbent before and after the adsorption process. The Freundlich isotherm model fitted well to the experimental metal sorption.

KEYWORDS: Plantain Tree Carbon, Batch experiments, isotherm modeling, kinetic modeling.

1. INTRODUCTION

The indiscriminate release of heavy metals into soils and waters is a major health concern worldwide, as the metals cannot be broken down to non-toxic forms and therefore have long-lasting effects on the ecosystem. Many heavy metals are toxic even at very low concentrations; Iron, Manganese, Arsenic, Cadmium, Chromium, Copper, Lead, Mercury, Nickel, Selenium, Silver, Zinc etc. are not only cytotoxic but also carcinogenic and mutagenic in nature.[1] Removal of heavy metals from wastewater is a very important factor with respect to human health and the environment.[2] The use of potentially low-cost sorbents to remove heavy metals from aqueous solutions has been intensely studied.[3] Iron overload may lead to debilitating andlife-threateningproblems such as diabetes, heart failure, and poor growth. According to the EPA, the acceptable value of iron in drinking water is 0.3 mg/l[4].

2. MATERIALS AND METHODS

All the chemicals employed in the present study were purchased from Alfa Aesar Company and were used as received. Double distilled water was used throughout the work and the second distillation was made over alkaline permanganate. The glassware used in the present study were of Borosil grade. The amount of Fe^{3+}ionsin the samples was estimatedcolorimetricallyfollowing the standard procedure using Spectrophotometer.

In the present study, the effects of various parameters, viz. pH, adsorbent dose, initial metalion concentration and contact time on the biosorptioncapacitywere investigated. Different isotherm models were applied to the experimental data. Kinetic and thermodynamic parameters for the adsorption process were also determined.

2.1 PREPARATION OF PLANTAIN TREECARBON (PTC)

The rinds of plantain trees (*Musa paradisiaca*) were collected from vegetable waste in the Gandhi Market, Tiruchirappalli during June, 2013 and shadow dried. The dried rinds of plantain trees were carbonized by treating with concentrated sulphuric acid in the weight to volume ratio of 1:1 (w/v). The charred mass thus obtained was cooled to room temperature, washed with excess water to remove free acid completely, filtered and dried at 110°C in an air oven for about an hour. Then, the material was heated for 2 hoursin a muffle furnace at 150°C for complete carbonization and activation. The resulting carbon was filtered and washed with distilled water until a constant pH of the slurry was reached. Then, it was dried for about an hour at 110°C in a hot air oven. The dried material was ground well and sieved to the desired particle size range. The plantain tree carbon thus obtained was designated as PTC.

2.3 **ADSORPTION EXPERIMENTS**

A stock solution (1000 mg/l) of Fe(III) ions was prepared by dissolving therequired amount offerric ammonium sulphatein one litre of distilled water. Using this stock solution, experimental solutions with desired concentrations of Fe^{3+} ions were prepared.

Batch adsorption experiments were carried out at room temperature (30±1°C) and were conducted under a variety of conditions, *viz.*,adsorbent size(75-425 µm), contact time (5–50 min), pH (3–7),initial Fe(III) ion concentration (25–200 mg/l), temperature (27°– 47°C), agitation speed(50-200rpm)and PTC dose (0.25–2 g/50 ml). The mixtures weretakenin125 mlstoppered bottlesandagitatedonamechanicalshaker. The samples were filtered after analysis through Whatman 40 filter paper. The concentrations of metal ions were estimated colorimetrically. Experimental analysis was repeated. The amount of metalion adsorbed by the biosorbent at equilibrium (q_e, mg/g) was calculated as follows:

$$q_e = \frac{(C_o - C_e)V}{m}$$

WhereVis the volume of solution taken(ml),$C_0$is the initialconcentration of metal ion in mg/l,$C_e$is the equilibrium metal ionconcentration in mg/l, andmis the mass of the adsorbent(PTC) in grams. The percent removal (%) of Fe^{3+} ions was calculated using thefollowing equation:

$$Removal(\%) = \frac{(C_0 - C_e)}{Co} X100$$

3. RESULTS AND DISCUSSION

3.1 EFFECT OF PARTICLE SIZE

Particles with small sizes have large surface areas and large adsorption capacities. For example, a sample of activated carbon has a larger surface area (smaller particle size) than a comparable mass of solid carbon does (larger particle size). Smaller particle sizes reduce the internal diffusion and mass transfer limitation of theadsorbate'spenetrationinto the adsorbent (i.e., equilibrium is more easily achieved and nearly full adsorption capability can be attained) compared to larger size particles. It can be observed that the maximum adsorption efficiency ofFe(III) is achieved with PTC particle sizesof 75- 150 µm. There is a decrease in adsorption efficiency when the particle size is greater. This may be due to the lack of availability of adsorption sites. Smaller particle size showed maximum adsorption, which may be due to the availability of a larger surface area.[5]

3.2 EFFECT OF pH

The amount of metal ion adsorbed onto a sorbent is significantly influenced by the pH of the solution; also, the pH determines the behavior of the metal ions in aqueous solution. For PTC, the adsorption capacity increases from pH 3.00 to 5.00 (due to the weak inhibitory effect of H_3O^+ ions). Above pH 7.00, ferrichydroxideis precipitated. The maximum removal of Fe^{3+} ions onto PTC took place at pH 5.00.[6]

3.3 EFFECT OF CONTACT TIME

The variation in percentage of metal ions removed by PTC with contact time was determined. The percentage of metal ions removed approached equilibrium within 30 min. for the adsorption of Fe^{3+}ions by PTC. The fast adsorption is likelydue to the initial concentration gradient between the adsorbate in solution and the number of vacant sites available on the surface of the adsorbent at the beginning. The progressive increase in adsorption and consequent attainment of equilibrium may be due to the limited mass transfer of adsorbate molecules from the bulk liquid to the external surface of the adsorbent.[7]

3.4 EFFECT OF METAL ION CONCENTRATION

In general, the adsorption capacity decreases as the metal ion concentration increases from 25 to 200 mg/l, which must be due to the progressive increase in the electrostatic interaction between the metal ions and the absorbent active sites. Moreover, this can be explained by the fact that more adsorption sites were being covered as the metal ion concentration increased, and the higher initial concentrations led toan increase in the affinity of the metal ions towards the active sites.[8]

3.5 EFFECT OF ADSORBENT DOSAGE

An initial increment in adsorption capacity with an increase in adsorbent dosage is expected because, as the number of adsorbent particles increases, the surface area available for metal ion attachment increases. The present study reveals that as the adsorbent dose was increased from 0.25 g to 2.25 g there was an increase in the adsorption of metal ions onto the surface of the adsorbents. It is plausible that with a higher dosage of adsorbent, there would be a greater availability of activesites for theFe^{3+}ions.[9]

3.6 EFFECT OF AGITATION SPEED

An agitation speed of fewer than 150 rpm favors the optimal removal of metal ions by PTC. The maximum removal of Fe^{3+}ions by PTC occurred at 50 rpm. A high agitation speed may shift the equilibrium process of adsorption and desorption towards desorption.

3.7 EFFECT OF TEMPERATURE

In the present work, the sorption of Fe^{3+}ions in themetal ion solution by PTC was carried out in the temperature range of 27 to 47ºC. Low temperatures favor the adsorption process by PTC. The decrease in adsorption with increasing temperature suggests weak adsorption interaction between the biomass surface (PTC) and the metal ion, which supports physisorption.

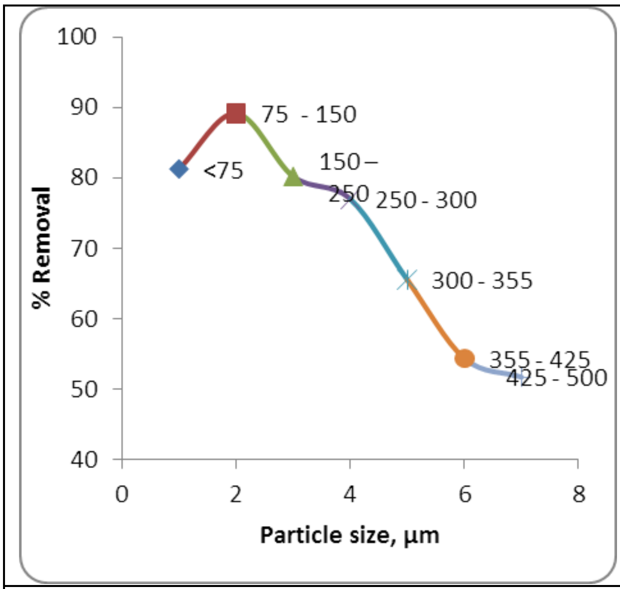

Fig. 1 Effect of variation of PTC size on the removal of Fe(III) ions

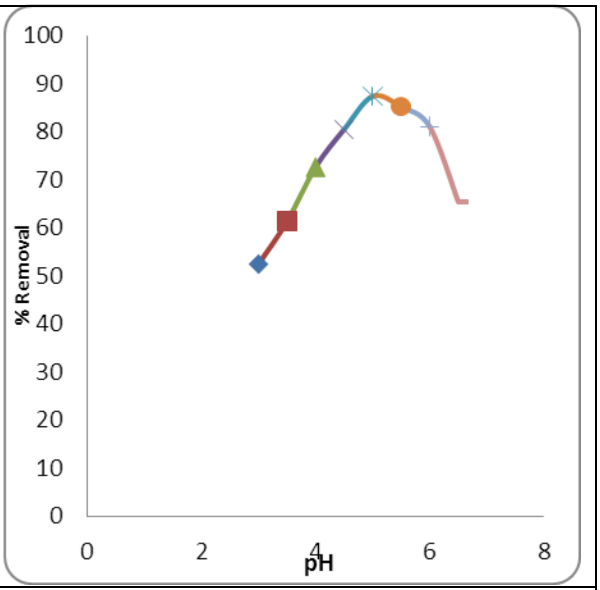

Fig. 2Effect of pH on the removal of Fe(III) ions

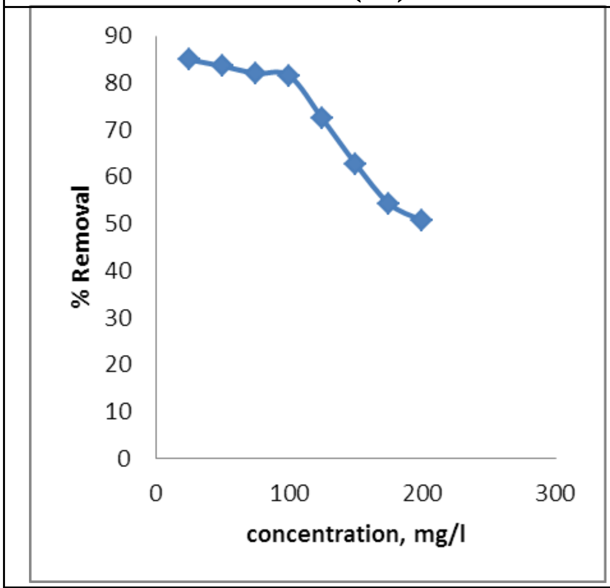

Fig. 3 Effect of Variation of Concentration on the removal of Fe(III) ions

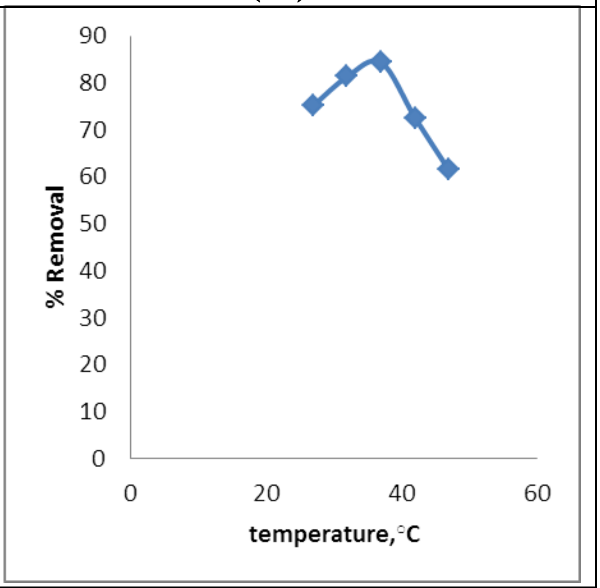

Fig. 4 Effect of Temperature on the removal of Fe(III) ions

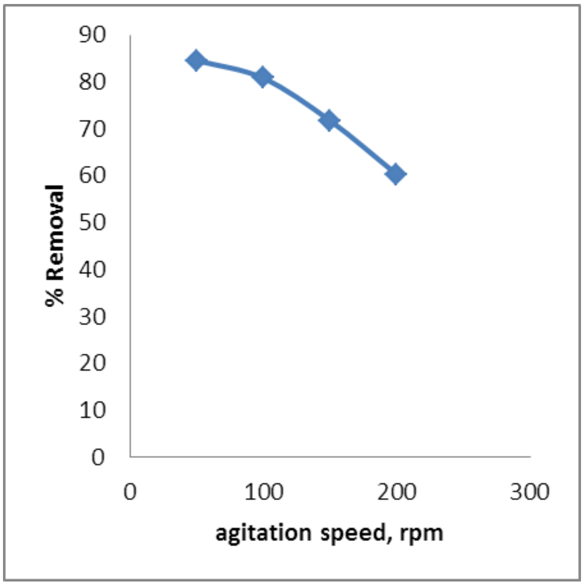

Fig. 5 Effect of Agitation speed on the removal of Fe(III) ions

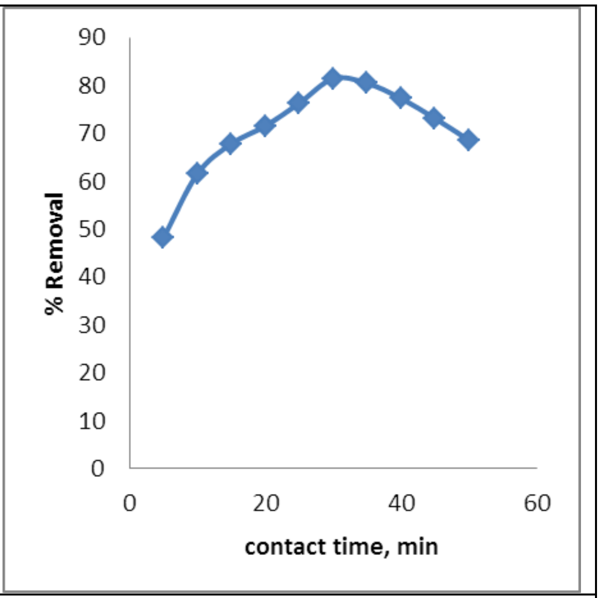

Fig. 6Effect of Contact Time on the removal of Fe(III) ions

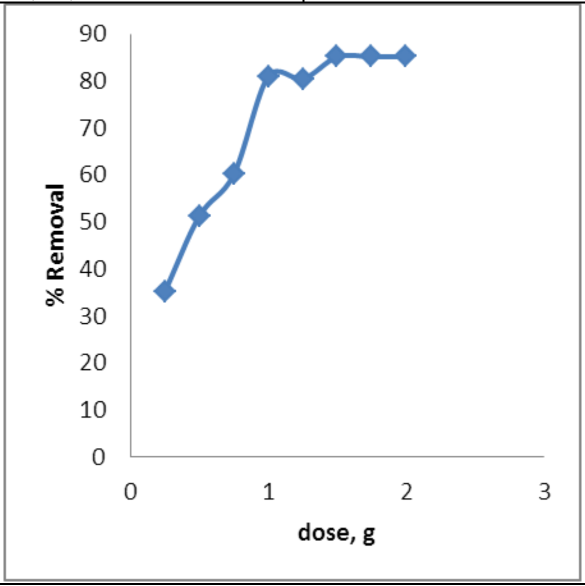

Fig. 7 Effect of Adsorbent on the removal of Fe(III) ions

4. INSTRUMENTAL ANALYSIS

The characterization of PTC before and after adsorption using FT-IR[10], XRD[11] and SEM[12] with EDX confirmed the adsorption of Fe^{3+} ions onto the adsorbent.

4.1 FT- IR Spectra

The FT - IR spectrum(Fig. 8) obtained for PTC showed a broad band at 3431.54 cm^{-1}, characteristic of the OH stretching vibrations, including hydrogen bonding, of chemisorbed water. The band at 2831.63 cm^{-1}could be attributed to C-H stretching of aliphatic carbon or due to CH_2 or CH_3 deformation. The peak at 1596.41 cm^{-1} is related to C=C stretching for unsaturated aliphatic structures. The presence of transmittance peaks at 872.07 cm^{-1} and

775.34 cm^{-1} in PTC are due to the out-of-plane aromatic C-H deformation vibration containing isolated hydrogen atoms. The bands between 1538-1650 cm^{-1} and 1360-1470 cm^{-1} are assigned to asymmetric and symmetric stretching vibrations of carboxylate ions.

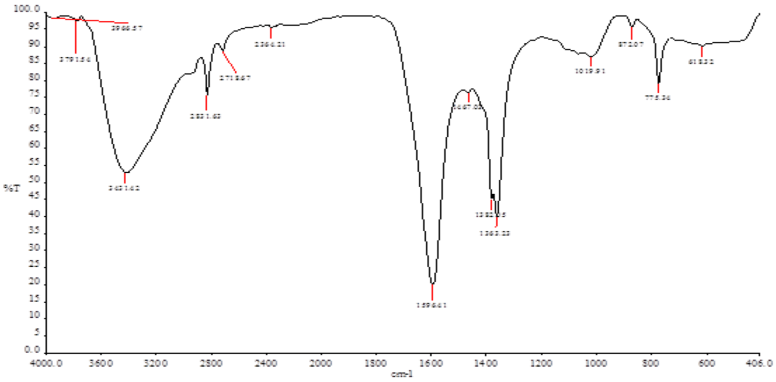

Fig. 8FTIR spectrum of PTC before adsorption

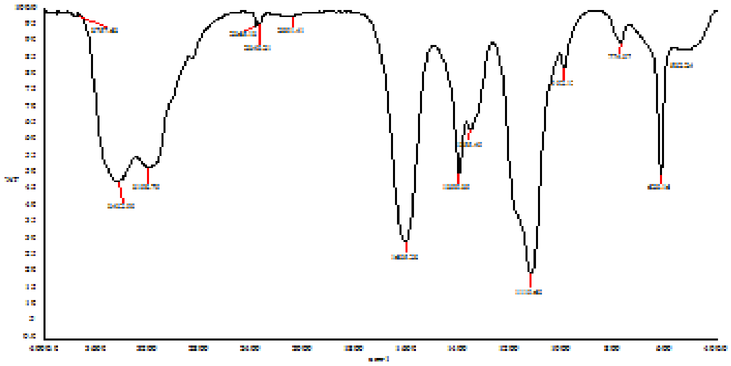

Fig. 9FTIR spectrum of PTC after adsorption of Fe(III) ions

4.2 X-RAY DIFFRACTION ANALYSIS BEFORE AND AFTER ADSORPTION OF IRON PTC

X-ray Diffraction (XRD) analysis was used to identify the crystallographic structure of the samples. XRD analysis was carried out witha Goniometer=PW3050/60XRD system with Cu-Kα radiation. XRD analysis commonly measures crystalline and amorphous phasesby sharp narrow diffraction peaks and broad (halo) peaks, respectively. The XRD patterns for PTC before and after adsorption of iron are shown in Fig.10 & Fig. 11, respectively. The pattern for pure PTC showed °2Th. peaks at 29.40 and 47.56. The Sharp peaks present in the figures indicated the crystalline nature of the material. In addition, several other low intensity peaks corresponding to other crystalline phases of carbon have also been observed. The porous structures of the adsorbents have decreased after adsorption.

After the adsorption of Fe^{3+} ions, the intensity of the highly organized peaks is slightly diminished. This is attributed to the adsorption of metal ionsonto the upper layer of the crystalline structure of the carbon surface by means of physisorption.

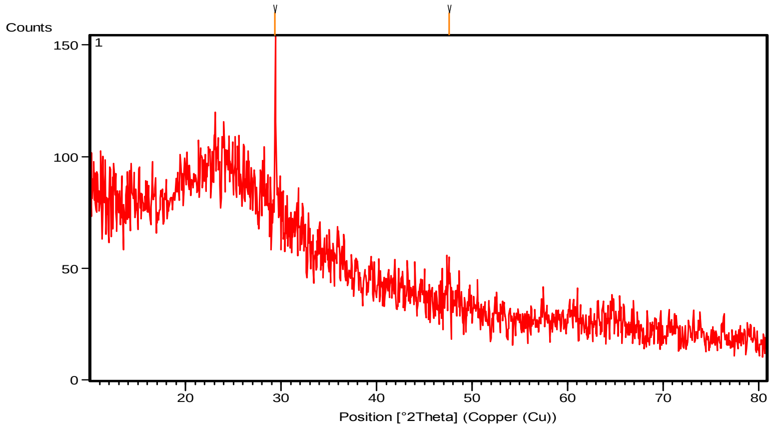

Fig. 10XRD of PTC before adsorption

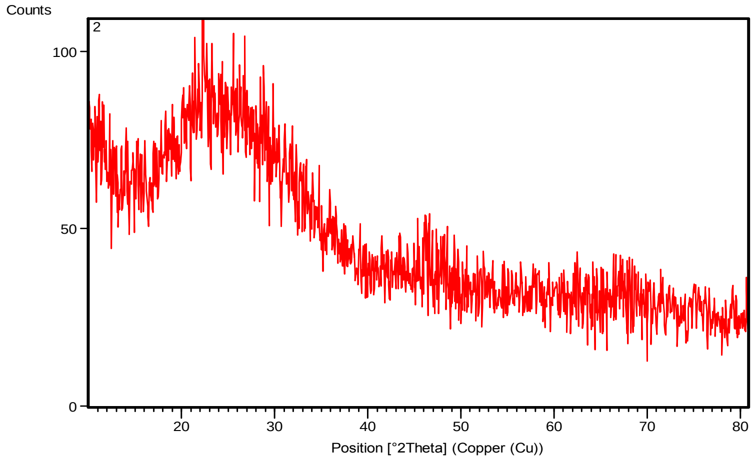

Fig. 11XRD of PTC after adsorption of Fe(III)

4.3 SEM EDX STUDY FOR PTC BEFORE AND AFTER ADSORPTION

The change in surface morphology in SEM image after the sorption process indicates the presence of heavy metal ions; the same was confirmed by the EDX analysis.

The cell wall thickness and cell diameters for PTC were measured using Digital Micrograph software, after calibrating the SEM images with their respective scale bars. The cell wall thickness was measured using the standardized testing method of full width half maximum, after integrating for at least 100 px. The cell diameters were also calculated after integrating the length for at least 100 px. Each data point of cell wall thickness and cell diameters mentioned in this work is an average of 5 independent measurements at different places in the sample.

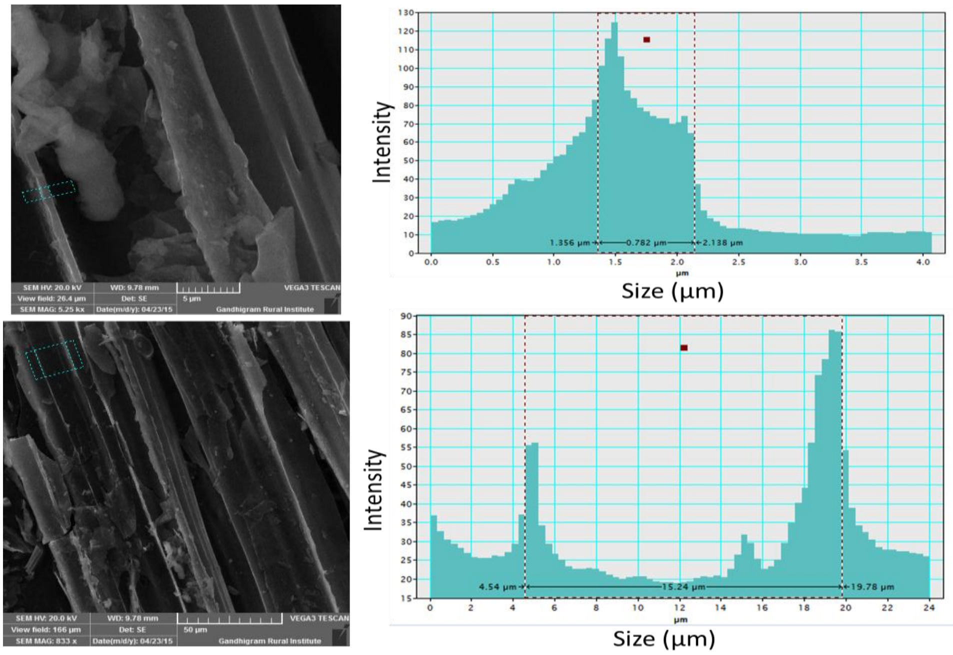

Fig. 12 Cell wall thickness and cell diameters measured for PTC using Gatan Micrograph

Significant differences were seen in the surface morphologies after the adsorption of $Fe^{3+}$by PTC. The surface morphological changes in the PTC cells after the adsorption of Fe^{3+}ions are shown in Figure 12.

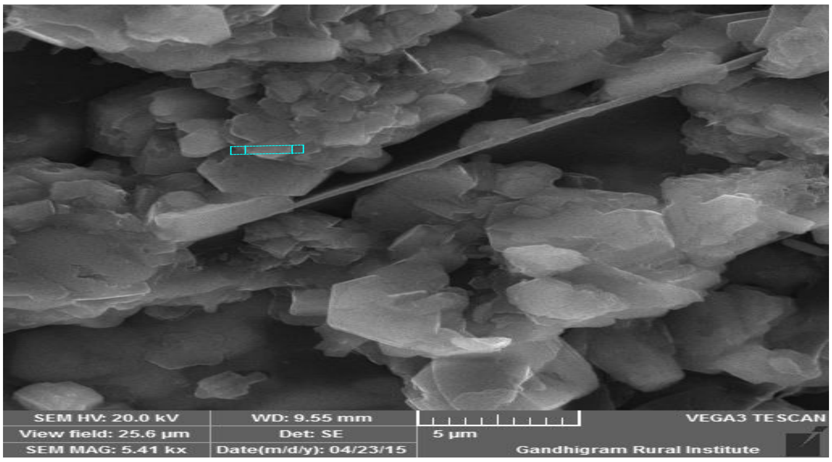

Fig. 13 Morphological changes in PTC after the removal of Fe^{3+}ions

In addition to the visual measurements of cell wall thickness and cell diameters, Energy dispersive spectroscopy (EDX) was conducted inside the SEM on different samples of PTC before and after the removal of Fe^{3+} ions. So the difference in cell wall thickness by EDX spectraanalysis (Fig. 14) and the morphological changes on the surface, in synergy, provide the evidence for the adsorption process. Adsorption is further confirmed by the presence of iron in the EDX spectrum of PTC after the adsorption study.

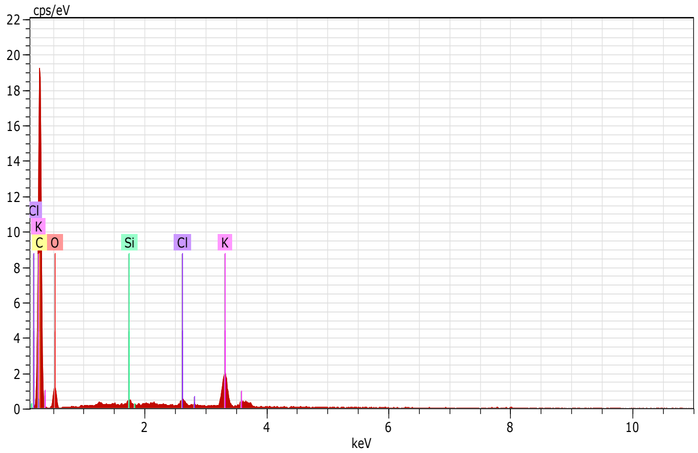

Fig. 14 EDX spectrum for PTC

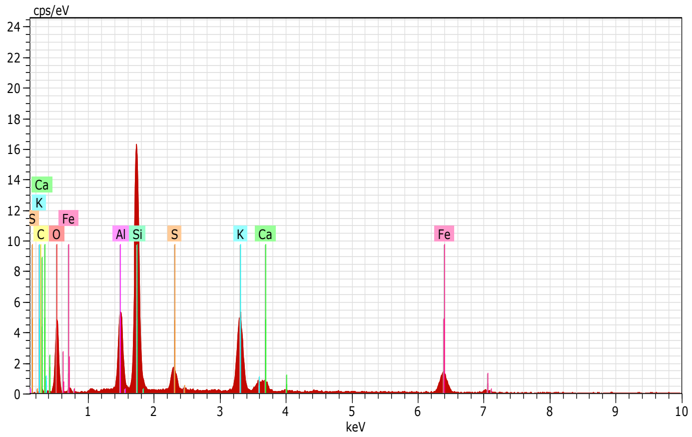

Fig. 15 EDX spectrum for PTC after the adsorption of Fe^{3+}ions

5. ADSORPTION ISOTHERM

Analysis of adsorption equilibrium data isimportant for optimizing the design of an adsorption system. Adsorption isothermexpresses the relationship between metal ions adsorbed onto theadsorbents and metal ions in solution. It also provides important design parameters for an adsorption system. Several isothermmodels have been widely used to model the equilibrium of adsorption systems. Langmuir and Freundlich models were used in the case of the adsorption of Fe(III) ions onto PTC.

The formation of a monolayer adsorbate on the adsorbent was representedby the Langmuir isotherm model.[13]

Thereby, the Langmuir isotherm represents the equilibrium distribution of metal ions between the solid and liquid phases. The Langmuir isotherm is applicable for monolayer sorption onto a surface containing a finite range of indistinguishable sites. The model assumes uniform energies of sorption onto the surface and no transmigration of adsorbate within the plane of the surface. Based on these assumptions, Langmuir has drawn the subsequent equation:

$$q_e = \frac{Q_0 K_L C_e}{1 + K_L C_e}$$

Langmuir sorption parameters were determined by remodeling the equationinto a linear type:

$$\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{Q_0 K_L C_e}$$

Where,

C_e = equilibrium concentration of adsorbate (mg/l)

q_e= amount of Fe^{3+} (PTC) at equilibrium (mg/g)

Q_o = maximum monolayer coverage capacity (mg/g)

K_L = Langmuir isotherm constant (l/g)

The values of Q_0 and K_L were computed from the slope and intercept of theLangmuirplot of $1/q_e$ versus $1/C_e$as given in Fig. 16. The essentialfeaturesof the Langmuir isotherm may be expressed in terms of equilibrium parameter R_L, which is a dimensionless constant mentioned as the separation factor or equilibriumparameter:

$$R_L = \frac{1}{1 + \left(1 + K_L C_0\right)}$$

This isotherm is used to describe the adsorption characteristics for the heterogeneous surface. These data often fit the empirical equation proposed by Freundlich.[14]

$$Q_e = K_f C_e^{\frac{1}{n}}$$

Where K_f = Freundlich isotherm constant n = adsorption intensity

C_e = equilibrium concentration of adsorbate

Q_e = amount of Fe^{3+} ions adsorbed per gram of adsorbent at equilibrium

By linearizing the above equation,

$$\log Q_e = \log K_f + \frac{1}{n}\log C_e$$

The constant K_f is an approximate indicator of adsorption capacity, while 1/n is a function of the strength of adsorption in the adsorption process. If n = 1 then the partition between the two phases is independent of the concentration. If the value of 1/n is below one it indicates a normal adsorption. On the other hand, a value of 1/n above one indicates cooperative adsorption.

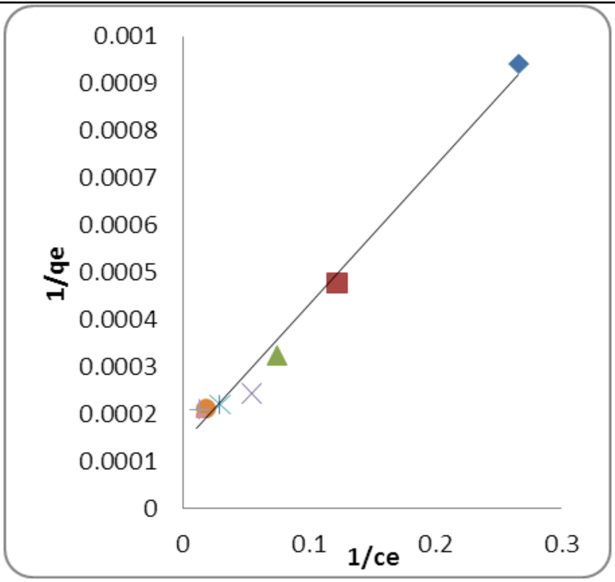

Fig. 16 Langmuir isotherm for Fe(III) ionremoval by PTC

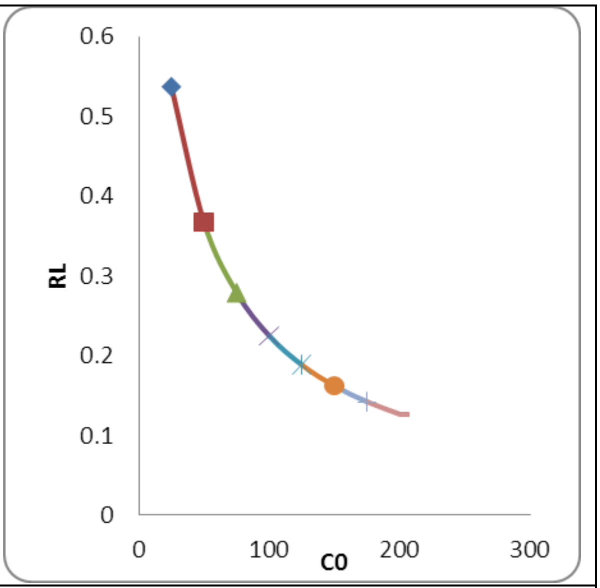

Fig. 17 R_L for Fe(III) ionremoval by PTC

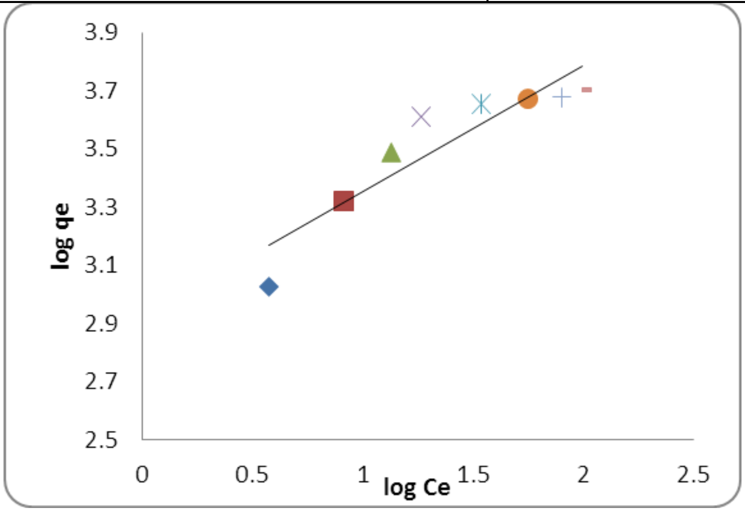

Fig. 18 Freundlich isotherm for Fe(III) ionremoval by PTC

From the Langmuir study, the separation parameter for PTC was calculated to confirm the favorable ion exchange/adsorption. The R^2 value proved the fitness of the Langmiur isotherm model for the adsorption process. The Freundlich isotherm results for the various initial metal ion concentrations revealed that the conditions were favourable for the sorption process.

5.1 KINETIC STUDIES

The Lagergren pseudo-first order[15] rate expression is given as:

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right)t$$

Whereq_e and q_t are the amounts of Fe^{3+} ions adsorbed (mg/g) ontoPTC at equilibrium and at time t, respectively and k_1 is the rate constant of pseudo first order adsorption (min^{-1}). The slope and intercept values of the straight line obtained by plotting log (q_e - q_t) against t is used to determine the pseudo first order rate constant (k_1) and the theoretical amount of adsorbed ion per unit mass of adsorbent $q_{e,\ \text{respectively}}$.

The pseudo first order plot showed reasonably good linearity till equilibrium time. This indicates that the adsorption follows first order kinetics and weak vander Waals'forces (physisorption).

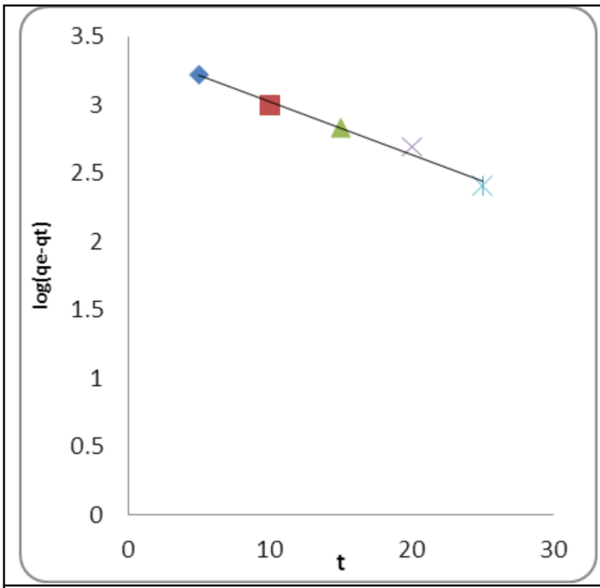

Fig. 19 Lagergren pseudo-first order model for Fe(III) ionremoval by PTC

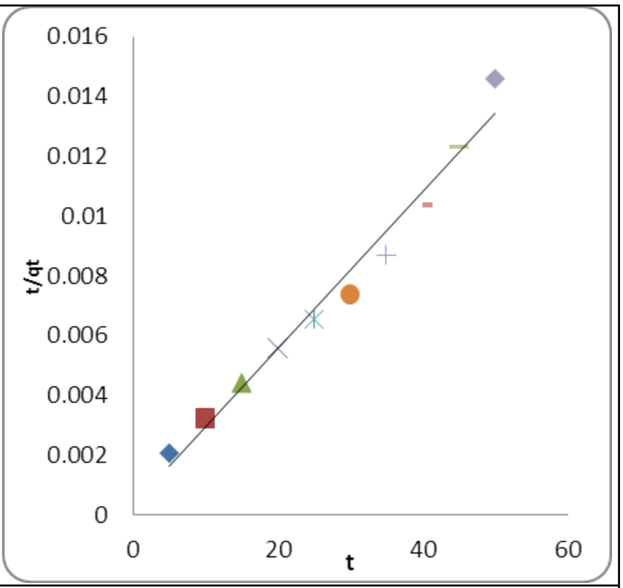

Fig. 20 Lagergren pseudo-second order model for Fe(III) ion removal by PTC

6. THERMODYNAMIC PARAMETER

The effect of temperature on the adsorption of Fe^{3+}ions on PTC at 27, 32, 37 42 and 47°C was studied. The results showed that the adsorption capacity of Fe^{3+}ions onto PTCdecreased with increasing temperature, indicating that the adsorption process was exothermic in nature. The pseudo-second order rate equation of Fe^{3+}ion adsorption onto PTC is expressed as a function of temperature by the Arrhenius equation as shown below:

$$\ln K = \ln A - \frac{Ea}{RT}$$

whereEa is the Arrhenius activation energy (kJ/mol); A, the Arrhenius factor; R, the gas constant; and T, the solution temperature. A positive activation energy is the energy required for adsorption to occur. However, a negative activation energy indicates the absence of an energy barrier requiredfor adsorption to occur. The lnK vs 1/T gives a straight line with slope –Ea/R and interceptln A. The negative value of the activation energy indicates that energy barriers are absent in the reaction process and that the reaction is exothermic. With increasing temperature, there is a reduction in the probability of colliding molecules capturing one another and this results in a negative activation energy.

Table 1 Thermodynamic parameters of adsorption of Fe(III) on PTC

S. No.	Thermodynamic Parameter	Temperature (K)	Thermodynamic Value
1	ΔG^o (kJ/mol)	300	12.06
		305	14.08
		310	13.40
		315	11.91
		320	10.82
2	ΔH^o (kJ/mol)		27.83
3	ΔS^o (J/(mol K))		47.79
4	Ea		27.83

7. CONCLUSION

An attempt was made to removeFe^{3+} ions from aqueous solution using PTC. PTC is an adsorbent obtained as a vegetable waste, which is found to have >90% efficiency for the removal of Fe^{3+}ions. Hence, the present adsorption study can be considered a green technique for the removal of Fe^{+} ions. The testing of PTC as an adsorbentfor removingFe(III) from aqueous solution wasperformed. Thebatch study parameters, pH of the solution, adsorbent dose, adsorbent concentration and contact time were found to be effectiveon the adsorption efficiency of Fe(III) ions. The experimental dataobtained from kinetic and isotherm studies well fitted the kinetic model and Freundlich isotherm model. Thethermodynamic study indicated that the adsorption of Fe(III) ions onto PTC is exothermic in nature. The results revealed that the preparations and use of PTC as an adsorbent is a simple and economicmethod. In addition, due to its biodegradability, PTC is consideredan eco-friendly adsorbent.

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