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AN ECOFRIENDLY APPROACH FOR THE REMOVAL OF NI(II) IONS IN AQUEOUS MEDIUM USING PLANTAIN TREE CARBON

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ABSTRACT

The present adsorption study explored the ability of Plantain Tree Carbon (PTC) for the removal of Ni(II) ion 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.*, Ni(II) 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 experimental metal sorption.

KEYWORDS: Plantain Tree Carbon, Batch experiments, FT-IR, XRD, SEM-EDX.

1. INTRODUCTION

The indiscriminate release of heavy metals into the soil and waters is a major health concern worldwide, as they cannot be broken down to non-toxic forms and therefore have long-lasting effects on the ecosystem. Many of them are toxic even at very low concentrations; Nickel, Iron, Manganese, Arsenic, Cadmium, Chromium, Copper, Lead, Mercury, 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 environmental considerations.[2] The use of potentially low-cost sorbents to remove heavy metals from aqueous solutions has been intensely studied[3]. Nickel is well known toxic heavy metal pollutant which is present effluents of electroplating industries to the tune of 20-

200ppm. Nickel is found in the environment as a result of various natural and industrial activities. The higher concentration causes harmful effects like headache, dizziness, nausea, dry cough, tightness of the chest, vomiting, shortness of breath, cyanosis, chest pain and rapid respiration.[4-7]

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 glasswares used in the present study were of Borosil grade. The amount of Ni^{2+} ions from the samples were estimated colorimetrically following the standard procedure using Spectrophotometer.

In the present study, the effects of various parameters, viz. pH, adsorbent dose, initial metal ion concentration and contact time on the biosorption capacity, were 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 TREE CARBON (PTC)

The rinds of plantain tree (*Musa paradisiaca*) were collected from the vegetable waste in Gandhi Market, Tiruchirappalli during June, 2013 and shadow dried. The dried rinds of plantain tree were carbonized by treating with concentrated sulphuric acid in the weight ratio of 1:1 (w/v). The charred mass thus obtained was cooled to room temperature, washed with excess of 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 hours in 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 desired particle size range. The plantain tree carbon thus obtained was designated as PTC.

2.3 ADSORPTION EXPERIMENTS

Stock solution (1000 mg/l) of Ni(II) ions was prepared by dissolving required amount of Nickel ammonium sulphate in one litre of distilled water. Using this stock solution, with desired concentrations of Ni^{2+} ions were prepared.

Batch adsorption experiments were carried out at room temperature (30±1°C). Adsorption experiments were conducted at different conditions, *viz.*, adsorbent size(75-425 µm), contact time (5–50min), pH (3–7), initial Ni(II) ion concentration (25–200mg/l), temperature (27° – 47° C), agitation speed (50-200 rpm)and PTC dose (0.25–2g/50ml). The mixtures were taken in a 125 ml stoppered bottles and agitated on a mechanical shaker. The samples were filtered after analysis through Whatman 40 filter paper. The concentrations of Ni(II) ions were estimated colorimetrically. Experimental analysis was repeated. The amount of metal ion adsorbed by the biosorbent at equilibrium (q_e, mg/g) was calculated as follows.

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

Where V is the volume of solution taken(ml), C_0 is the initial concentration of metal ion in mg/l, C_e is the equilibrium metal ion concentration in mg/l and m is the mass of the adsorbent(PTC) in grams. The percent removal (%) of Ni^{2+} ions were calculated using the following equation

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

3. RESULTS AND DISCUSSION

3.1 EFFECT OF PARTICLE SIZE

Particles with small size have large surface area and a large adsorption capacity. For example, activated carbon has larger surface area (smaller particle size) than carbon (larger particle size). Smaller particle sizes reduce internal diffusion and mass transfer limitation to penetrate of the adsorbate inside the adsorbent (i.e., equilibrium is more easily achieved and nearly full adsorption capability can be attained) as compared to larger size particles. It can be observed that the maximum adsorption efficiency is achieved with particle size 150 – 250 µm for Ni(II) by PTC. There is a decrease in adsorption efficiency when the particle size increases. This may due to the lack of availability of the adsorption sites. Lower particle size showed maximum adsorption which may due to the availability of larger surface area.[8]

3.2 EFFECT OF pH

The amount of metal ion adsorbed on to 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, ferric hydroxide get precipitated. The maximum removal of Ni^{2+} ions onto PTC took place at pH 6.00.[9]

3.3 EFFECT OF CONTACT TIME

The variation of percentage metal ions removal by PTC with contact time was determined. The percentage of metal ions removal approached equilibrium within 40 min. for the adsorption of Ni^{2+} ions by PTC. The fast adsorption may probably due 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 consequently the attainment of equilibrium may be due to limited mass transfer of the adsorbate molecules from the bulk liquid to the external surface of adsorbent.[10]

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 by the fact that more adsorption sites were being covered as the metal ion concentration increases and higher initial concentrations lead to an increase in the affinity of the metal ions towards the active sites.[11]

3.5 EFFECT OF ADSORBENT DOSAGE

The initial increment in adsorption capacity with increase in adsorbent dosage is expected, because, as the number of adsorbent particles increases, the surface area available for metal ions 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 on to the surface of the adsorbents. It is plausible that with higher dosage of adsorbent, there would be greater availability of active sites for the Ni^{2+} ions.[12]

3.6 EFFECT OF AGITATION SPEED

The agitation speed less than 150 rpm favors the maximum removal of metal ions by PTC. Maximum removal of Ni^{2+}ions by PTC occurred at 100 rpm. The high agitation speed may shift the equilibrium process of adsorption and desorption towards the desorption.

3.7 EFFECT OF TEMPERATURE

In the present work, the sorption of Ni^{2+} ions in the metal ion solution by PTC was carried out in the temperature range of 27- 47ºC. Low temperatures favor the adsorption process for PTC. The decrease in adsorption with increasing temperature, suggest weak adsorption interaction between biomass surface (PTC) and the metal ion, which supports physisorption.

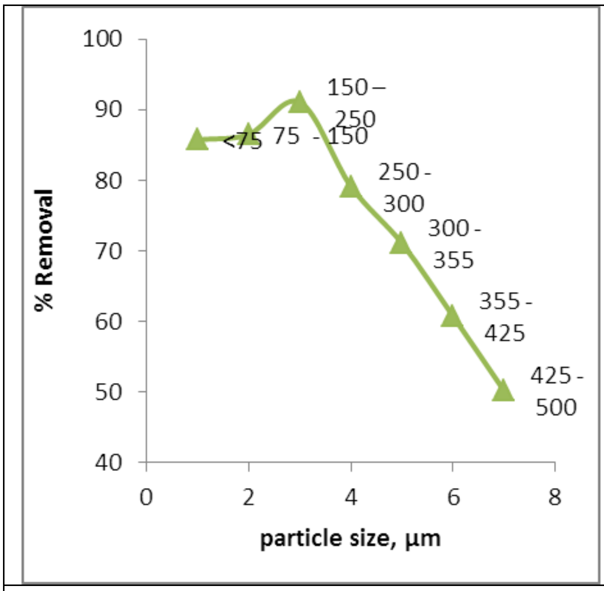

Fig. 1 Effect of variation of PTC size for the removal of Ni(II) ions

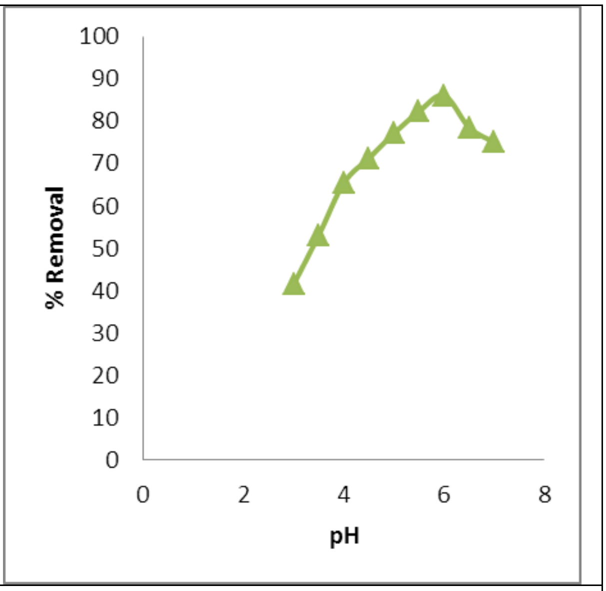

Fig. 2 Effect of pH for the removal of Ni(II) ions

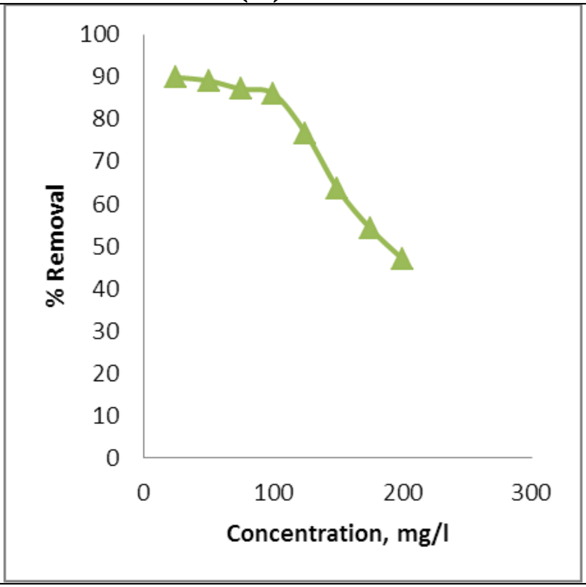

Fig. 3 Effect of Variation of Concentration for the removal of Ni(II) ions

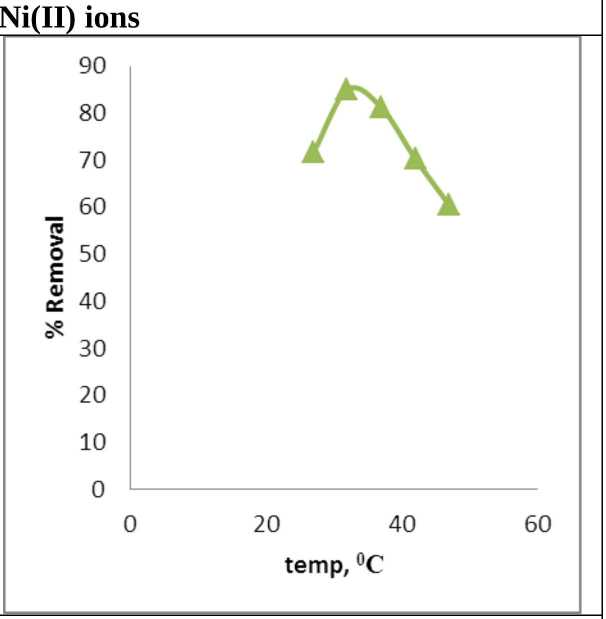

Fig. 4 Effect of Temperature for the removal of Ni(II) ions

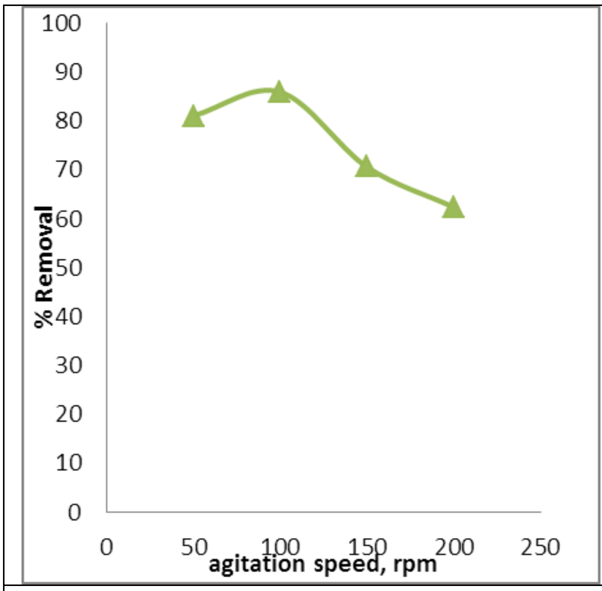

Fig. 5 Effect of Agitation speed for the removal of Ni(II) ions

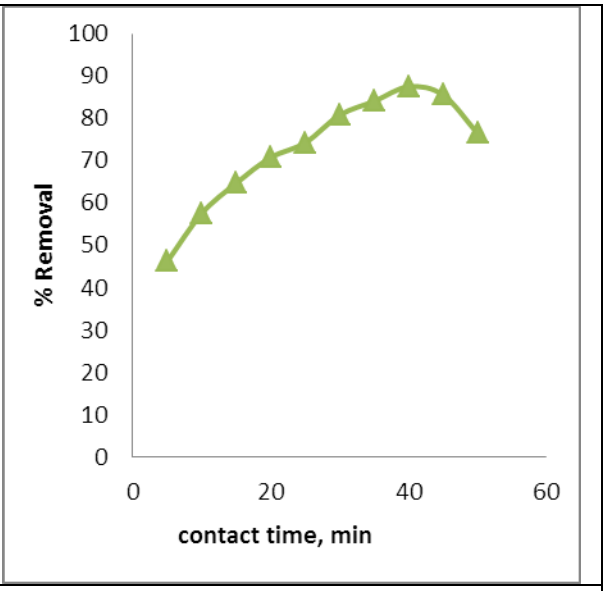

Fig. 6 Effect of Contact Time for the removal of Ni(II) ions

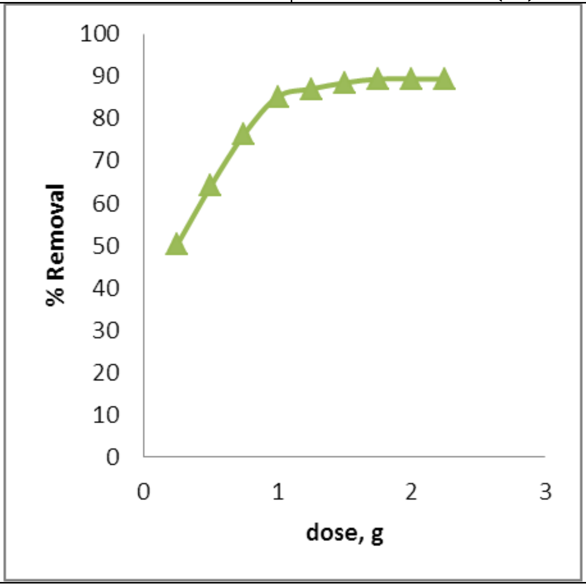

Fig. 7 Effect of Adsorbent for the removal of Ni(II) ions

1. INSTRUMENTAL ANALYSIS

The characterization of PTC before and after adsorption using FT-IR[13], XRD[14] and SEM[15] with EDX confirmed the adsorption of Ni^{2+} 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 out-of-plane aromatic C-H deformation vibration containing isolated hydrogen atoms. Bands between 1538-1650 cm^{-1} and 1360-1470 cm^{-1} are assigned to asymmetric and symmetric stretching vibrations of carboxylate ion.

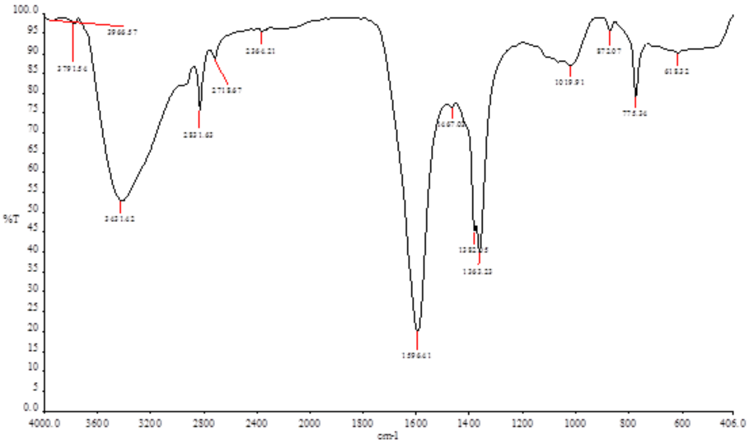

Fig. 8 FTIR spectrum of PTC before adsorption

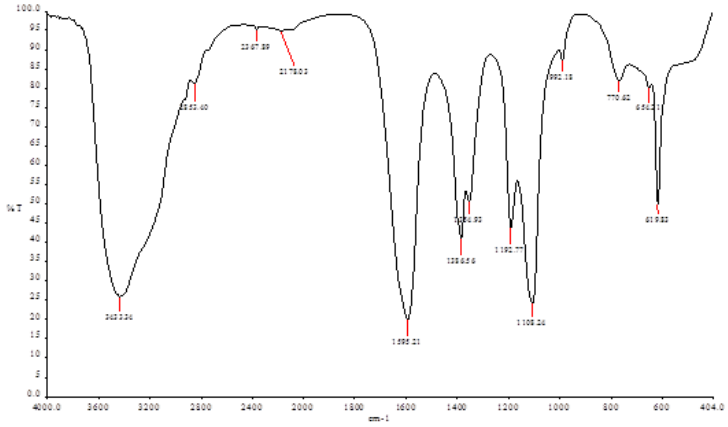

Fig. 9 FTIR spectrum of PTC after adsorption of Ni(II) ions

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

XRD analysis is made to identify the crystallographic structure of the samples X-ray Diffraction (XRD) analysis was carried out by using Goniometer=PW3050/60XRD system with Cu-Kα radiation. XRD analysis commonly measure crystalline and amorphous phases by sharp narrow diffraction peaks and broad (halo) peak respectively. The XRD patterns for PTC before and after adsorption of Nickel are shown in Fig.10 & Fig. 11 respectively. The pattern pure PTC showed °2Th. peak 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 carbons have also been observed. The porous structures of the adsorbents have been decreased after adsorption.

After the adsorption of Ni^{2+} ions, the intensity of the highly organized peaks are 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.

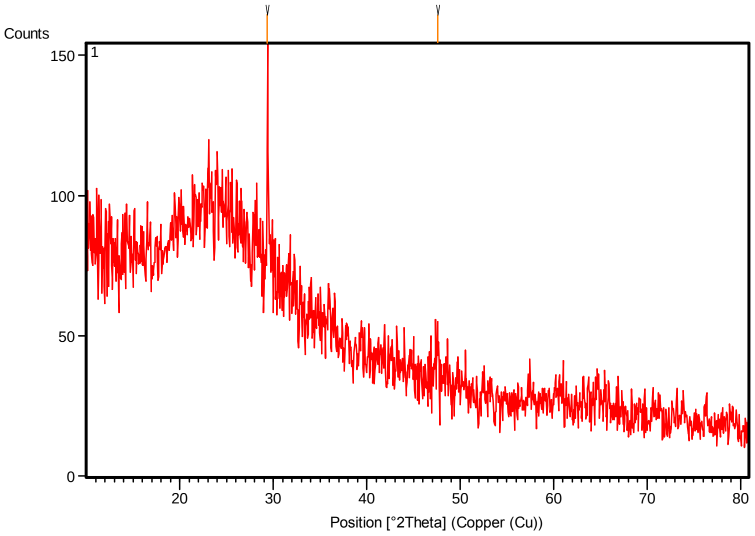

Fig. 10 XRD of PTC before adsorption

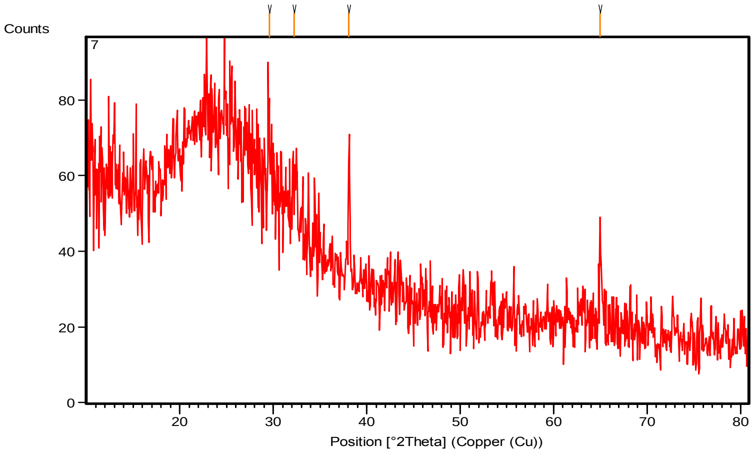

Fig. 11 XRD of PTC after adsorption of Ni(II)

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 measured at different places in the sample.

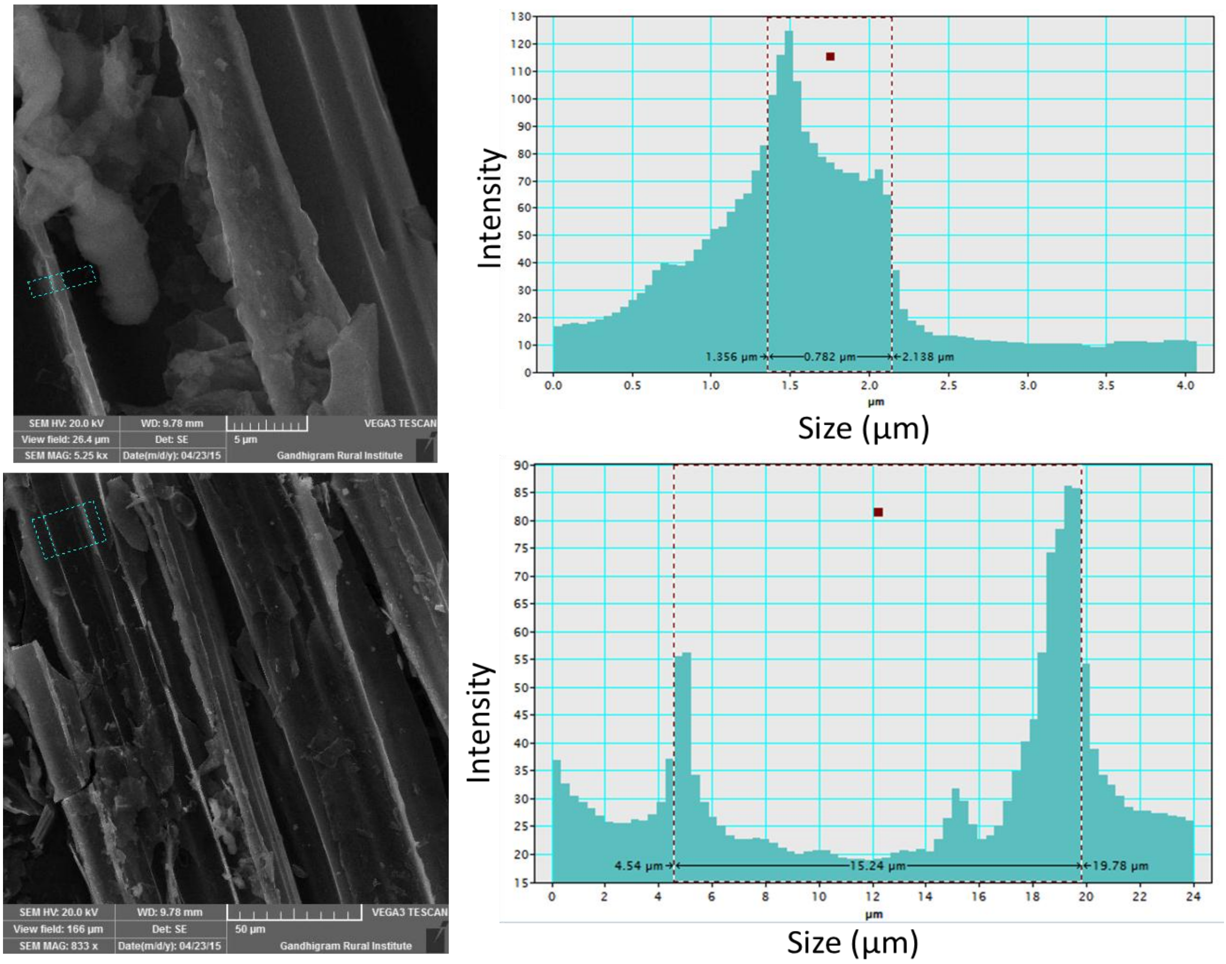

Fig. 12 Cell wall thickness and cell diameters measured for PTC using Gatan Micrograph

Besides the visual measurements of cell wall thickness and cell diameters, Energy dispersive spectroscopy (EDX) were conducted inside the SEM on different samples of PTC before and after the removal of Ni^{2+} ions. The cell wall thickness for PTC before and after adsorption is 743 nm and 903 nm. So the difference in cell wall thickness analysed and EDX spectra(Fig.13) in synergy provide the evidence for the adsorption process. It is further confirmed by the presence of Nickel in the EDX spectrum of PTC after the adsorption study.

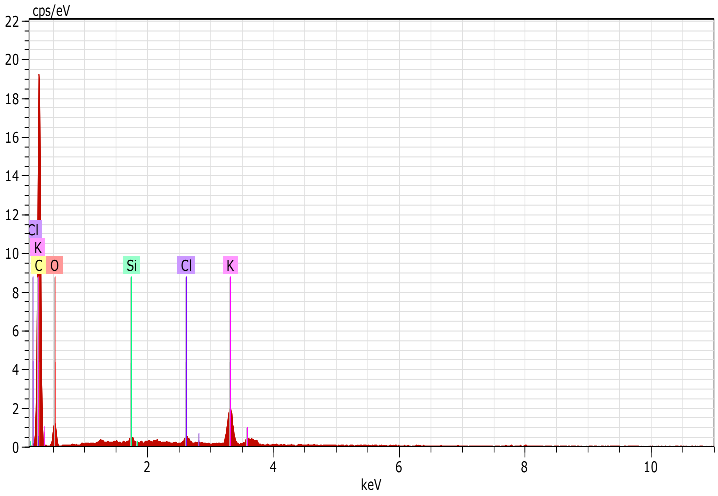

Fig.13 EDX spectrum for PTC

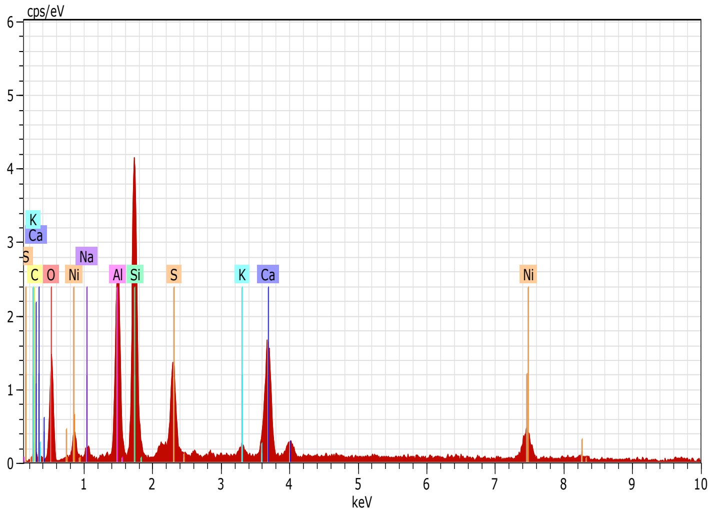

Fig. 14 EDX spectrum for PTC after the adsorption of Ni^{2+} ions

2. ADSORPTION ISOTHERM

Analysis of adsorption equilibrium data is important for optimizing the design of an adsorption system. Adsorption isotherm expresses the relationship between metal ions adsorbed onto the adsorbents and metal ions in the solution. Also it provides important design parameters for adsorption system. Several isotherm models have been widely used to model the equilibrium of adsorption system. Langmuir and Freundlich models were used in the case of the adsorption of Ni(II) ions onto PTC.

The formation of a monolayer adsorbate on the adsorbent was represented by the Langmuir isotherm model.[16]

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 equation in to 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 Ni^{2+} (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. 15. The essentialfeaturesof the Langmuir isotherm may be expressed in terms of equilibrium parameter R_L, which is a dimensionless constant mentioned as separation factor or equilibriumparameter.

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

This isotherm is used to describe the adsorption characteristics for the heterogeneous surface. These data often fit the empirical equation proposed by Freundlich.[17]

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

Where K_f = Freundlich isotherm constant

n = adsorption intensity

C_e = equilibrium concentration of adsorbate

Q_e = amount of Ni^{2+} ions adsorbed per gram of the 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 are independent of the concentration. If the value of 1/n is below one it indicates a normal adsorption. On the other hand, 1/n being above one indicates cooperative adsorption.

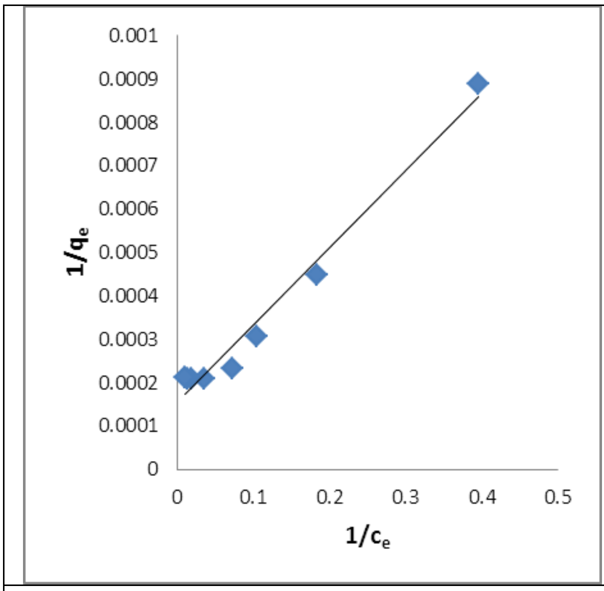

Fig. 15 Langmuir isotherm for Ni(II) ions removal by PTC

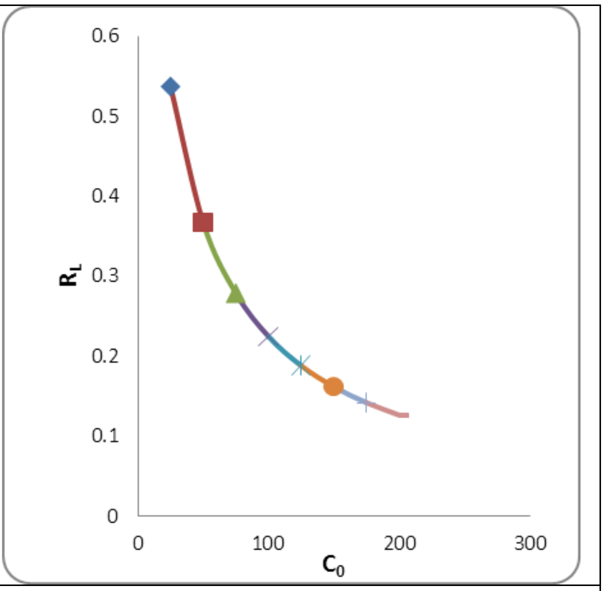

Fig. 16 R_L for Ni(II) ions removal by PTC

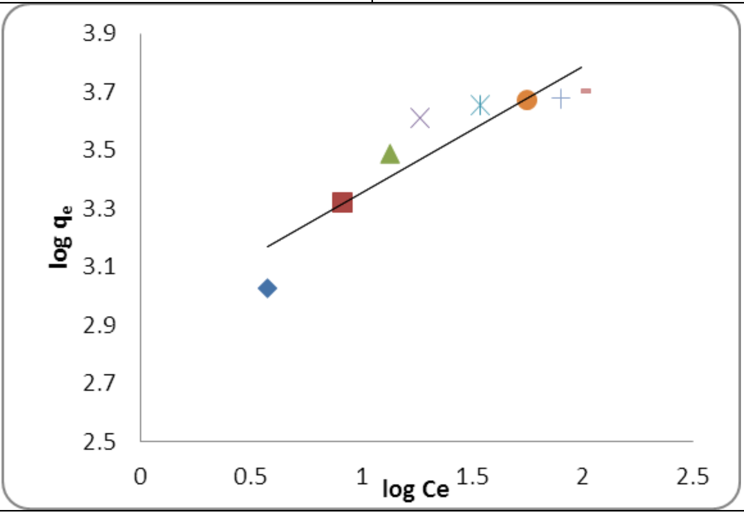

Fig. 17 Freundlich isotherm for Ni(II) ions removal by PTC

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 Langmiur isotherm model for the adsorption process.

5.1 KINETIC STUDIES

The Lagergren pseudo-first order[18] rate expression is given as

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

Where,q_e and q_t are the amounts of Ni^{2+} ions adsorbed (mg/g) on PTC 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, used to determine the pseudo first order rate constant (k_1) and the theoretical amount of adsorbed ion per unit mass of adsorbent $q_e$respectively.

Pseudo first order plot showed reasonably good linearity till equilibrium time. This indicates that the adsorption follows first order kinetics and weak vanderwaal forces (physisorption).

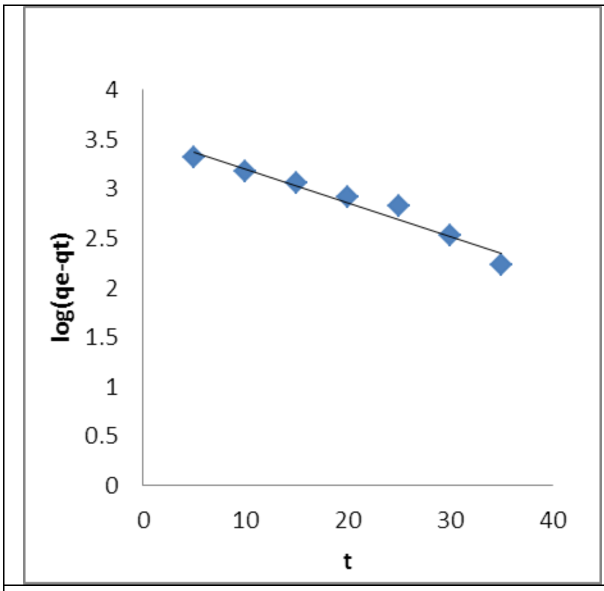

Fig. 18 Lagergren pseudo-first order model for Ni(II) ions removal by PTC

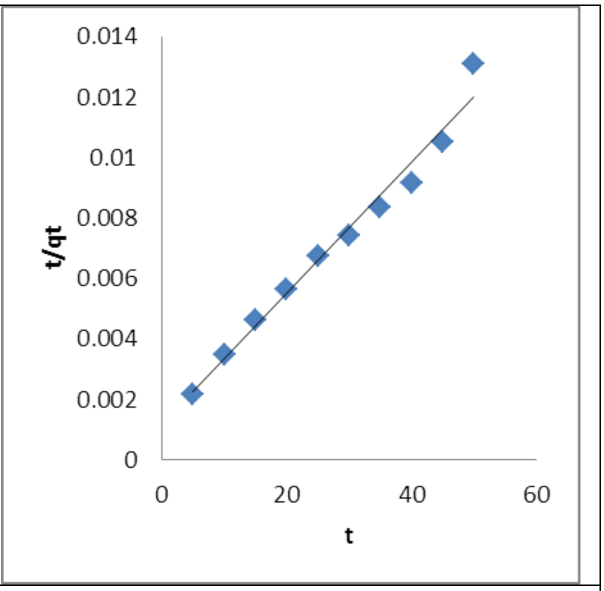

Fig. 19 Lagergren pseudo-second order model for Ni(II) ions removal by PTC

3. CONCLUSION

An attempt was made for the removal of the Ni^{2+} 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 Ni^{2+} ions. Hence, the present adsorption study can be considered as a green technique for the removal of Ni^{2+} ions. The testing of PTC as an adsorbent for removing of Nickel(II) ions from aqueous solution was done. The batch study parameters, pH of the solution, adsorbent dose, adsorbent concentration and contact time were found to be effective on the adsorption efficiency of Ni(II) ions. The experimental data obtained from kinetic and isotherm studies well fitted the kinetic model and Freundlich isotherm model. The thermodynamic study indicated that the adsorption of Ni(II) ions onto PTC is exothermic in nature. The results revealed that the preparations and use of PTC as an adsorbent is a simple and economic method. In addition, due to its biodegradability, it is considered as an eco-friendly adsorbent.

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