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Nickel(II) Removal by Phosphorylated Tamarind Nut Carbon

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Activated carbon prepared from phosphorylated tamarind nut (PTNC) has been used for the removal of Ni(II) from aqueous system by batch and column experiments. The efficiency of PTNC was compared with commercial granular activated carbon (CAC). The equilibrium adsorption capacity was determined as a function of the solution pH, adsorbent dosage and contact time for both carbons and found to follow Freundlich and Langmuir isotherms. Kinetic studies indicated that the removal process followed reversible first order equation and adsorption of Ni(II) governed by film diffusion process. Desorption of Ni(II) from carbons were also done by 0.3 N HCl. Column studies were conducted in 2.5 cm diameter columns. Under optimum conditions of flow rate and bed height, breakthrough capacities were found out. PTNC was found to be 6 times superior to CAC in the removal of Ni(II). The mechanism of adsorption for Ni(II) on to PTNC was found to follow ion exchange process predominantly and supported by FT-IR. Nickel(II) removal was also confirmed by XRD and SEM studies.

Key Words: Activated carbon, Phosphorylated tamarind nut carbon, Freundlich isotherm, Kinetic studies.

INTRODUCTION

Industrial wastewater often contains considerable quantities of heavy metals that would endanger public health and the environment if discharged without complete treatment. Considerable quantities of nickel containing effluents are introduced into the water bodies from nickel-plating units, silver refineries, zinc based casting industries, storage batteries and nuclear power plant coolant water[1]. The tolerance limit of nickel in drinking water is 0.01 mg/L[2]. Higher concentration of nickel causes cancer of lungs, nose and bones. Dermatitis (nickel itch) is the frequent effect of exposure to nickel such as coins and costume jewelry. Nickel carbonyl has been observed[3] as lethal in humans at atmospheric exposures of 30 ppm for 0.5 h. Acute Ni(II) poisoning causes dizziness, headache, nausea and vomiting, chest pain, dry cough and shortness of breath, rapid respiration, cyanosis and extreme weakness[4]. Hence these harmful effects of Ni(II) make its removal from wastewater mandatory.

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Ni(II) has been removed from wastewater by various conventional methods like chemical precipitation[5,6], coagulation and flocculation[7], ion-exchange[8], complexation/sequestration[9], electrochemical operation[10], biological treatment[11] and adsorption on activated carbon[12]. Reports are available on the development of the activated carbon from cheaper and readily available materials[13]. Activated carbon derived from rice husk[14], coconut shell[15], peanut hulls[16], oil-removed coconut residues[17] and cotton seed[18] have been successfully used for the removal of heavy metals from aqueous solutions. Quantitative removal of Ni(II) was observed from aqueous solutions by bicarbonate treated rice husk carbon modified by sulphuric acid over the pH range of 4.0- 5.0[19]. In present studies, it was proposed to make use of the nuts (seeds) of *Tamarindus indica* a tropical tree which has high mechanical strength, low cost and hardness for the preparation of activated carbon. Phosphorylation has been mentioned as a method to produce activated carbon from date pits[20] and cellulose[21]. It has been suggested that phosphoric acid is able to modify the structure of biosorbents by penetration, particle swelling, and partial dissolution of the biomass, bond cleavage and reformation of the structure resistant to thermal decomposition[20]. The micro porosity of the carbon is also enhanced by phosphoric acid impregnation[22]. Since no studies have been done with respect to treatment of tamarind seed with phosphoric acid, it was decided to prepare an activated carbon, which could be applied to heavy metal removal such as Ni(II). Batch, kinetic and column studies on the removal of Ni(II) were conducted from aqueous solution by adsorption technique using phosphorylated tamarind nut carbon (PTNC) and performance of this carbon was simultaneously evaluated with commercial activated carbon (CAC) procured from market.

EXPERIMENTAL

Preparation of carbon: Tamarind nuts (seeds) procured from the market was washed with distilled water, dried and pulverized to 20-50 (ASTM) mesh size. Then it was treated with phosphoric acid under a weight ratio of 1:1 and heated in the hot air oven at 160 ± 5 °C for 24 h. The carbonized material was washed with distilled water to remove the excess acid and dried at 100 ± 5 °C. Then the carbon was soaked in 1 % sodium carbonate solution for 24 h to remove any free acid. It was washed with distilled water to remove excess sodium carbonate and dried at 100 ± 5 °C. Studies were then carried out with this bicarbonate washed carbon (PTNC). Comparative studies were simultaneously carried out with granular commercial activated carbon (CAC) of the same particle size (SD fine). The carbon characteristics are summarized in Table-1. All the chemicals used for this study were of analytical reagent grade obtained from E. Merck and BDH.

Batch mode experiments: A stock solution of Ni(II) 1000mg/L was prepared by dissolving 4.479 g of $NiSO_4.6H_2O$ in distilled water and 1 mL of conc. HNO_3 diluted to 1000 mL. The stock solution was diluted as and when required to obtain solutions containing 10-50 mg/L Ni(II). 100 mL of Ni(II) solutions of a desired

TABLE-1
CARBON CHARACTERISTICS

Parameter	PTNC	CAC
Bulk density (g/mL)	0.619	0.668
Moisture (%)	5.736	15.84
Ash (%)	4.400	0.900
Solubility in water (%)	1.761	0.594
Solubility in acid (%)	6.365	6.725
pH	6.98	9.40
Decolorizing power (%)	1.8	1.05
Phenol number	20	40
Ion exchange capacity (meq/g)	0.4172	Nil
Surface area (m^2/g)	316.21	214
Iron (%)	0.18	0.44

concentration adjusted to desired pH was taken in polythene reagent bottles of 300 mL capacity and known amount of PTNC and CAC were added. The pH of the working solutions was adjusted using dilute hydrochloric acid and sodium hydroxide. Nickel(II) solutions were agitated for a predetermined period at 32 ± 0.5 °C in a horizontal mechanical shaker. The carbons were separated by centrifugation and solutions were analyzed by spectrophotometric method at wavelength 470 nm for Ni(II) content (AWWA, APHE 1973). For time and pH optimization 10 mg/L Ni(II), carbon dose of 100 mg/100 mL of PTNC and CAC were used. For optimization of carbon dose, 10 mg/L Ni(II), with dose varying from 25-550 mg for PTNC and CAC were used. Control experiments were carried out without adsorbent and there was negligible adsorption of Ni(II) ions by the container walls.

Adsorption isotherms studies were carried out with different initial concentration of Ni(II) while maintaining the carbon dosage at constant level. Kinetic studies were performed by withdrawing the samples after regular intervals of time, each sample containing a fixed carbon dose of 100 mg/100 mL and concentration varying from 3 to 10 mg/L. The rate constants were calculated by using the convention rate expression[11].

To make the adsorption process more economical, it would be necessary to regenerate the spent carbon. After adsorption experiments with 10 mg/L of Ni(II) and 100 mg of PTNC and CAC, the carbons were separated, gently washed with distilled water. The carbons were then agitated with 100 mL of dilute hydrochloric acid of various strengths ranging from 0.05 to 0.5 N for 3 h in the case of PTNC and 5 h in the case of CAC and the amount of Ni(II) desorbed was estimated.

Column studies: Nickel(II) stock solution was diluted to obtain 200 mg/L of Ni(II) and used for column studies. Cylindrical glass column of 2.5 cm diameter and 30 cm height with a Teflon stopper valve to control the flow of solution was used for this study. Optimum weights of carbon under proper flow rate and bed height conditions were used for column studies. For PTNC, Ni(II) of concentration

200 mg/L at an optimum flow rate of 5 mL/min with optimum bed height of 12.1 cm was employed to assess the potential. For CAC, 20 mg/L of Ni(II) at an optimum flow rate of 3 mL/min and bed height of 8.7 cm was maintained. Percolation of Ni(II) solution was stopped as soon as Ni(II) concentration in the effluent exceeded the permissible limit[23] at 0.1 mg/100 mL, which is the break point. Lot volumes of 100 mL were collected and analyzed for Ni(II) by DMG method[24] using suitable aliquots.

Regeneration and recycling of PTNC was done by treating with dilute solution of 0.3 N HCl (optimum concentration) followed by soaking in 1 % sodium carbonate. The commercial granular activated carbon (CAC) was also regenerated with 0.3 N HCl, thoroughly washed and reloaded in the column under wet conditions.

Break through capacities pertaining to Ni(II) adsorption in the presence of common impurities such as bicarbonates, chloride, sulphate, calcium and magnesium were done under optimum bed height and flow rate conditions for both the carbons.

RESULTS AND DISCUSSION

Effect of agitation time: The effects of agitation time on the removal of Ni(II) by PTNC and CAC are shown in Fig. 1. It could be seen that the extent of removal increases with time and attains equilibrium at 3 h for PTNC and 5 h for CAC for 10 mg/L of Ni(II) used. This indicates that the optimum time for maximum Ni(II) removal by PTNC was 1.6 times less than that required by CAC.

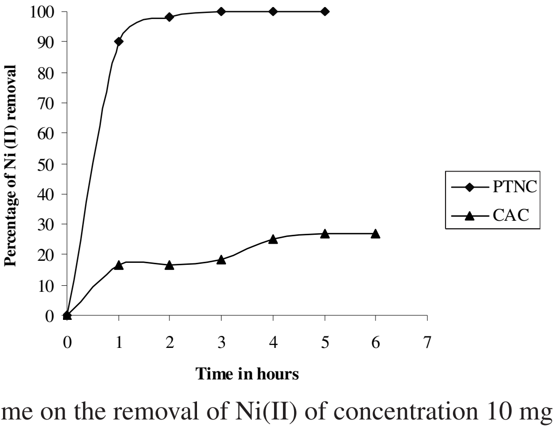

Fig. 1. Effect of time on the removal of Ni(II) of concentration 10 mg/L by PTNC and CAC-carbon dose 100 mg/100 mL; pH 5.0

Effect of pH: The effect of initial pH on the removal of Ni(II) by PTNC and CAC were shown in Fig. 2. Quantitative removal of Ni(II) by PTNC could be seen with increase in pH. Maximum removal was observed over the pH range of 5.0-9.0 for this carbon. However, CAC was effective to an extent of 35 % removal only over the pH range of 8.5-9.0. It was also noticed that at higher pH conditions the adsorption capacity decreased for both the carbons.

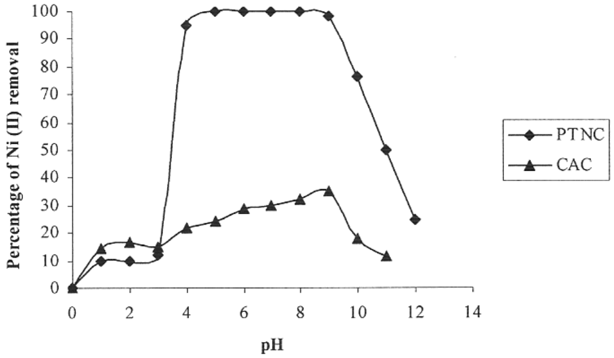

Fig. 2. Effect of pH on the removal of Ni(II) of concentration 10 mg/L; PTNC: dose 100 mg/100 mL, agitation time 3 h, CAC: dose 100 mg/100 mL, agitation time 5 h

The influence of pH on the removal of Ni(II) may be explained as follows. At lower pH, a higher concentration of H^+ ions present in the mixture competes with the positively charged Ni(II) ions for the adsorption sites results in reduced uptake of metal ion. As the pH increases, the concentration of H^+ ion decreases and the concentration of Ni(II) ions remains constant and therefore the uptake of metal ions can be explained as an H^+-Ni^{2+} exchange reaction. At higher pH, the decrease in Ni(II) uptake by PTNC and CAC was expected due to the precipitation of Ni(II) as $Ni(OH)_2$ in the presence of NaOH[25].

Effect of carbon dosage: The effect of carbon dosage on the removal of Ni(II) by PTNC and CAC are shown in Fig. 3. Carbon dosage was varied over the range 25-550 mg and equilibrated to 3 h for PTNC and 5 h for CAC. It was observed that for the quantitative removal of 10 mg/L Ni(II) in 100 mL solution, a minimum carbon dosage of 100 mg of PTNC was required for 97 % removal and 300 mg of CAC for 65 % removal. This shows that approximately PTNC was 3 times more efficient than CAC.

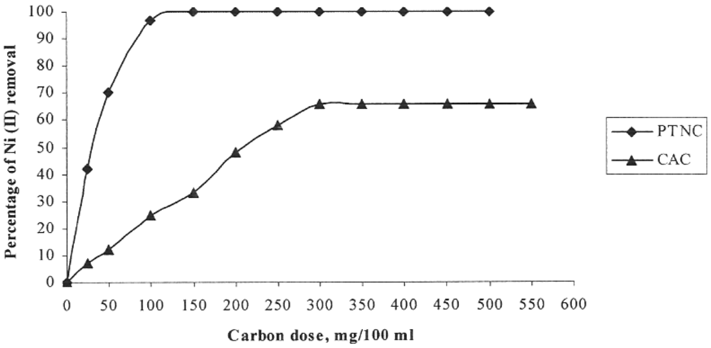

Fig. 3. Effect of carbon dose on the adsorption of Ni(II) of concentration 100 mg/L; PTNC: pH 5.0, agitation time 3 h, CAC: pH 8.5; agitation time 5 h

Desorption studies: Experiments were conducted to desorb Ni(II) from the spent carbon. 100 mg samples of PTNC and CAC were equilibrated with 10 mg/L of Ni(II). Each sample after adsorption was equilibrated using HCl of various strengths ranging from 0.05 to 0.5 N. The results of Ni(II) recovery for PTNC are given in Table-2. It could be seen that 0.3 N HCl was required for the desorption of Ni(II) from PTNC and also for CAC. It may be stated that in the acid medium protons compete with Ni(II) ions and displace the maximum amount of adsorbed nickel and ion-exchange mechanism was important in connection with desorption.

TABLE-2
DESORPTION OF Ni(II) FROM CARBON

Concentration of HCl (N)	Percentage of Ni(II) desorbed	
	PTNC	CAC
0.05	87.8	73.9
0.10	86.9	75.8
0.15	92.8	83.7
0.20	98.9	83.8
0.25	98.9	85.2
0.30	99.9	87.2
0.35	99.9	87.1
0.40	99.9	87.2
0.45	99.9	87.2
0.50	99.9	87.2

Adsorption isotherms: The equilibrium removal of Ni(II) was mathematically expressed in terms of adsorption isotherms. The Freundlich adsorption isotherm is represented by the equation[26].

$$\log x/m = \log k + 1/n (\log C_e)$$

where C_e is the equilibrium concentration (mg/L) and x/m is the amount adsorbed per unit weight of PTNC and CAC (mg/g). The constant k and n represents the adsorption capacity and intensity of adsorption, respectively. Plots of log (x/m) *versus* log C_e are linear for PTNC and CAC. Figs. 4 and 5 show the Freundlich adsorption isotherms for PTNC and CAC in distilled water and tap water respectively. The straight-line nature of the plots indicates that the processes followed were of Freundlich adsorption type. The k and n values for both the carbons were calculated from the intercepts and slopes, respectively and are shown in Table-3. The values of $1 < n < 10$ show favourable adsorption of Ni(II) on both PTNC and CAC[27].

The Langmiur equation[28] was applied for adsorption equilibrium for both PTNC and CAC.

$$C_e/q_e = 1/Q_o b + C_e/Q_o$$

TABLE-3
k AND n VALUES OF FREUNDLICH ADSORPTION ISOTHERM

Carbon	Distilled water		Tap water	
	k	n	k	n
PTNC	10.00	4.75	3.80	2.88
CAC	6.61	5.50	2.09	2.50

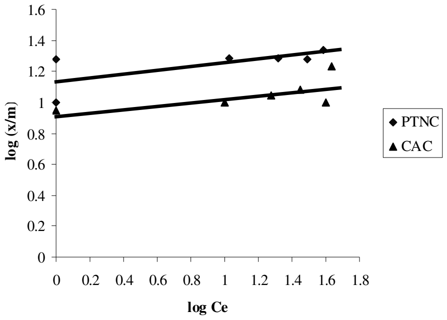

Fig. 4. Freundlich's adsorption isotherm for PTNC and CAC in distlled water

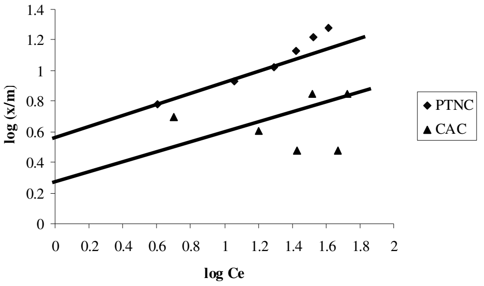

Fig. 5. Freundlich's adsorption isotherm for PTNC and CAC in tap water

where C_e is the equilibrium concentration mg/L, q_e is the amount adsorbed at equilibrium (mg/g) and Q_o and b are Langmiur constants related to adsorption capacity and energy of adsorption, respectively. The linear plots of C_e/q_e *versus* C_e show that the adsorption obeys the Langmiur model for both PTNC and CAC (Figs. 6 and 7). In distilled water Q_o and b were determined from the Langmiur plots and found to be 22.3713 mg/g and 0.447 mg/L, respectively for PTNC and 7.8616 mg/g and 0.4240 mg/L, respectively for CAC. In tap water Q_o and b were determined from the Langmiur plots and found to be 68.02 mg/g and 0.00918 mg/L, respectively for PTNC and 7.5018 mg/g and 0.2666 mg/L respectively for CAC.

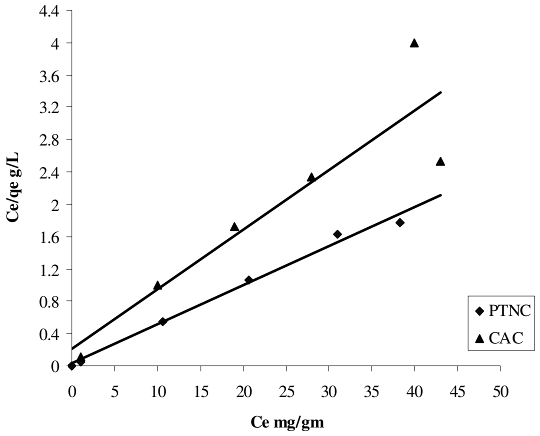

Fig. 6. Langmuir adsorption isotherm for Ni(II) with PTNC and CAC systems in distilled water

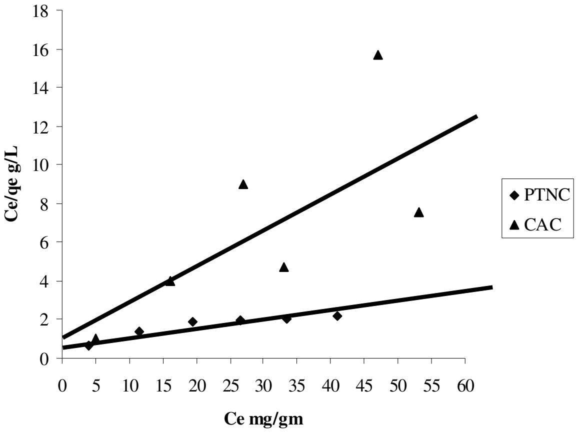

Fig. 7. Langmuir adsorption isotherm for Ni(II) with PTNC and CAC systems in tap water

TABLE-4
R_L VALUES AND ISOTHERMS

R_L value	Type of isotherm
$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$0 < R_L < 1$	Favourable
$R_L = 0$	Irreversible

The essential characteristics of Langmuir isotherms were expressed in terms of a constant separation factor or equilibrium parameter R_L, which is defined by $R_L = 1/(1+bC_0)$, where b is the Langmuir constant and C_0 is the initial concentration of Ni(II)[26]. The parameter indicates that the isotherm shapes as in Table-4. R_L values observed between 0 and 1 indicate favourable adsorption of Ni(II) on both PTNC and CAC as in Table-5.

TABLE-5
EQUILIBRIUM PARAMETER, R_L

Initial Ni(II) concentration	PTNC		CAC	
	DW	TW	DW	TW
10	0.0691	0.0098	0.0702	0.0789
20	0.0345	0.0049	0.0351	0.0394
30	0.0230	0.0032	0.0234	0.0263
40	0.0172	0.0024	0.0175	0.1973
50	0.0138	0.0019	0.1404	0.0157
60	0.0115	0.0016	0.0117	0.0131

Adsorption kinetics: The Kinetics of nickel adsorption on both PTNC and CAC follow the first order rate expression[29].

$$\ln(1-U_t) = -Kt$$

where $U_t = (C_o-C_t)/(C_o-C_e)$.

C_o, C_t and C_e are the concentrations of Ni(II) in mg/L initially, at time t and at equilibrium, respectively. The straight line plot of ln $(1-U_t)$ *vs.* time t indicates the adsorption process follows first order kinetics as shown in Figs. 8 and 9. The slope values of the straight-line portions give the overall rate constant K of the process. The forward (K_1) and backward (K_2) rate constants are calculated using the following equation:

$$K = K_1 + K_2$$
$$K_2 = K_1 / K_c$$
$$K = K_1 [1+1/K_c]$$
$$K_c = K_1 / K_2$$

where K_c is the equilibrium constant. The kinetic data are furnished in Table-6. It is evident that the forward rate constant is much higher than the backward rate constant suggesting that the rate of adsorption is dominant for PTNC. For CAC backward rate constant is higher than forward rate constant indicating that rate of desorption is dominant. The ΔG values were also calculated for PTNC and CAC using the equilibrium constant values of the adsorption process (k_1/k_2) for each concentration of the metal ions. It was found that for PTNC and CAC the average values of ΔG were worked out to be -9962.75 and +1066.8 calories, respectively. The values indicated clearly that the adsorption on PTNC was found to be more spontaneous when compared with CAC.

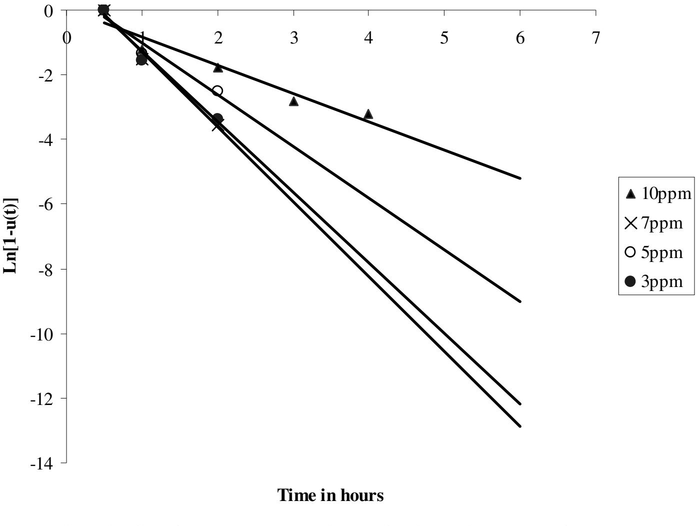

Fig. 8. Kinetic fits for the adsorption of Ni(II) in case of PTNC system

In order to assess the nature of the diffusion process responsible for the adsorption of nickel on PTNC and CAC, attempts were made to calculate the pore and film diffusion coefficients for various concentrations of nickel(II) using the following equations[30].

$$D_p = 0.03 \text{ X } r_0^2/t_{1/2}$$

TABLE-6
RATE CONSTANTS FOR THE REMOVAL OF Ni(II) BY
PTNC AT pH 5.0 AND CAC AT pH 8.5

Carbon	Ni(II) conc. (mg/L)	K overall rate constant (h^{-1})	k_1 Forward rate constant (h^{-1})	k_1 Backward rate constant (h^{-1})
PTNC	10	1.0580	1.0396	0.0104
	7	3.7500	3.6969	0.0531
	5	2.4285	2.3790	0.0495
	3	3.5000	3.383	0.1170
CAC	10	0.2777	0.0861	0.1916
	7	0.5454	0.1935	0.3519
	5	0.3636	0.1526	0.2110
	3	0.4666	0.2333	0.2333

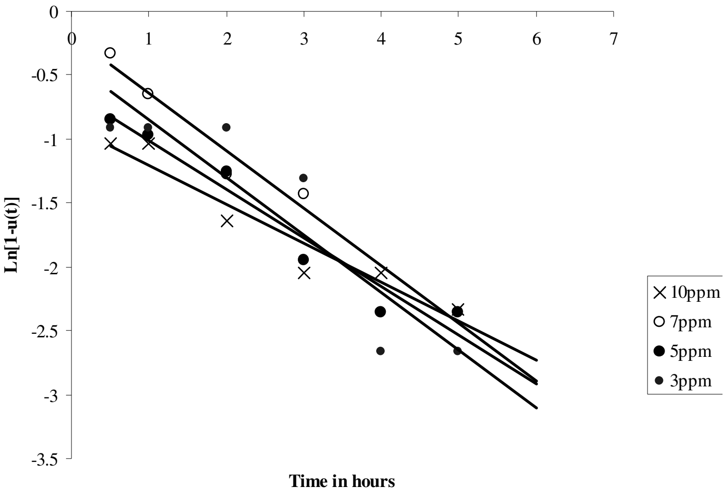

Fig. 9. Kinetic fits for the adsorption of Ni(II) in case of CAC system

where D_p is the pore diffusion coefficient expressed in $cm^2 s^{-1}$, r is the radius of the sorbent expressed in cm, and $t^{1/2}$ is the half-life period in second.

$$D_f = 0.23 \times r_0 \delta \times C^*/C \ t_{1/2}$$

where D_f is the film diffusion coefficient expressed in $cm^2 s^{-1}$, δ is the film thickness expressed in cm and C*/C is equilibrium loading of the sorbent. According to Michelson *et al.*[29] for the adsorption of heavy metals on the carbon surface, for film diffusion to be the rate determining process, the values of film diffusion coefficient (D_f) should be between 10^{-6} and 10^{-8} $cm^2 s^{-1}$. If pore diffusion D_p were to be rate determining process, its value should be in the range of 10^{-11} to 10^{-13} $cm^2 s^{-1}$. It is evident that the removal of Ni(II) follows film diffusion process, since the coefficients are very close to the range of 10^{-6} to 10^{-8} $cm^2 s^{-1}$ and these values are shown in Table-7.

TABLE-7
DIFFUSION COEFFICIENTS FOR THE REMOVAL OF Ni(II) BY PTNC AND CAC

Conc. of Ni(II) (mg/L)	Diffusion coefficient of PTNC ($cm^2 s^{-1}$)		Diffusion coefficient of CAC ($cm^2 s^{-1}$)	
	Pre diffusion	Film diffusion	Pre diffusion	Film diffusion
10	1.0515×10^{-8}	2.7758×10^{-9}	2.7604×10^{-9}	2.2817×10^{-10}
7	3.7279×10^{-8}	9.7977×10^{-9}	5.4212×10^{-9}	5.1622×10^{-10}
5	2.4141×10^{-8}	6.3080×10^{-9}	3.6129×10^{-9}	4.0476×10^{-10}
3	3.4792×10^{-8}	8.9613×10^{-9}	4.6364×10^{-9}	6.1835×10^{-10}

Column studies: In order to find out optimum flow rate and optimum bed height conditions for the removal of Ni(II) by PTNC and CAC, experiments were carried out with 200 mg/L Ni(II) solutions at pH of 6.0 and 8.5, respectively.

Table-8 indicates the breakthrough capacities of carbon under optimum flow rate and bed height conditions of PTNC and CAC from which it can be concluded that PTNC showed a higher removal capacity when compared to CAC.

TABLE-8
BREAKTHROUGH CAPACITIES OF CARBON
Optimum flow rate (PTNC) = 5mL/min; Optimum flow rate (CAC) = 3 mL/min; Optimum weight of carbon (PTNC) = 20 g (12.1cm); Optimum weight of carbon (CAC) = 20 g (8.7 cm)

Condition	Break through capacity (mg)	
	PTNC	CAC
Room temperature	280	60

Table-9 indicates the effect of common anions and cations available in water on the removal of Ni(II) by PTNC and CAC. Decrease in capacities was noted for both PTNC and CAC. The decrease in the removal of Ni(II) may be due to the competence of calcium, magnesium and sodium ions for the ion exchange sites during the adsorption process. However Ni(II) adsorption in column studies could not be carried out due to precipitation of $NiCO_3$[25].

TABLE-9
EFFECT OF COMMON ANIONS AND CATIONS ON THE REMOVAL OF Ni(II) UNDER OPTIMUM FLOW RATE AND BED HEIGHT CONDITIONS

Carbon	HCO_3^- 1000 mg/L	Cl^- 1000 mg/L	SO_4^{2-} 1000 mg/L	Ca^{2+} 1000 mg/L	Mg^{2+} 1000 mg/L
PTNC	Greater	180	120	60	40
CAC	40	40	20	20	40

PTNC showed constant breakthrough capacity values in distilled water under different regeneration cycles indicating that carbon is effective in the removal of Ni(II) over the number of cycles and it was not undergoing any significant degradation in particle size because of its hardness. However in CAC, the capacity was very much affected by the different cycles and also showed nil adsorption during the II cycle of regeneration as per Table-10.

TABLE-10
REGENERATION CYCLES

Cycle	PTNC	CAC
I	320	20
II	319	–
III	280	–
IV	280	–
V	280	–

The experiments with synthetic wastewater and its characteristics similar to that of nickel plating industry are shown in Table-11. It could be seen that PTNC showed the adsorption capacity to an extent of 120 mg/20 g whereas CAC showed only 20 mg/20 g. The capacity of CAC was very poor even upon 10 times dilution of wastewater. Hence it may be concluded that PTNC could be effectively employed for the removal of Ni(II).

TABLE-11
Ni(II) WASTEWATER CHARACTERISTICS

Parameter	Amounts (mg/L)
Nickel	216.3
Chlorides	78.9
Sodium	411.3
Calcium	203.0
Magnesium	16.8

Surface chemistry studies: The IR spectra of the PTNC and CAC before and after adsorption of Ni(II) are shown in Fig. 10 and 11, respectively. The spectrum of these carbons is complex due to the numerous functional groups .The broad and strong band ranging from 3800 to 3200 cm^{-1} indicate -OH stretching frequency. It is observed that the frequencies corresponding to the functional groups >CH- (2968 cm^{-1}), >C=O (2271 cm^{-1}), -C=C- (1655 cm^{-1}), -C-O (1366 cm^{-1}), -POx (799 cm^{-1}) are also present for carbons and show a slight reduction after the adsorption of Ni(II). This clearly indicates that the adsorption of metal ions on the adsorbents is by physical force and not by chemical bonds.

It is observed from the Figs. 14 and 15 that EDAX analysis on the PTNC showed abundant oxygen content on the carbon surface and the weight percentage of oxygen was found to be high in PTNC (33.21 %) when compared to CAC (13.94 %). The increase in carbon-oxygen complexes on the surface of PTNC was mainly due to phosphoric acid treatment. These carbon-oxygen complexes such as C_xO, CO_x, C_xO_2, which makes the surface slightly polar[31]. The interaction of these groups with aqueous phase may lead to the following hydrolytic reaction.

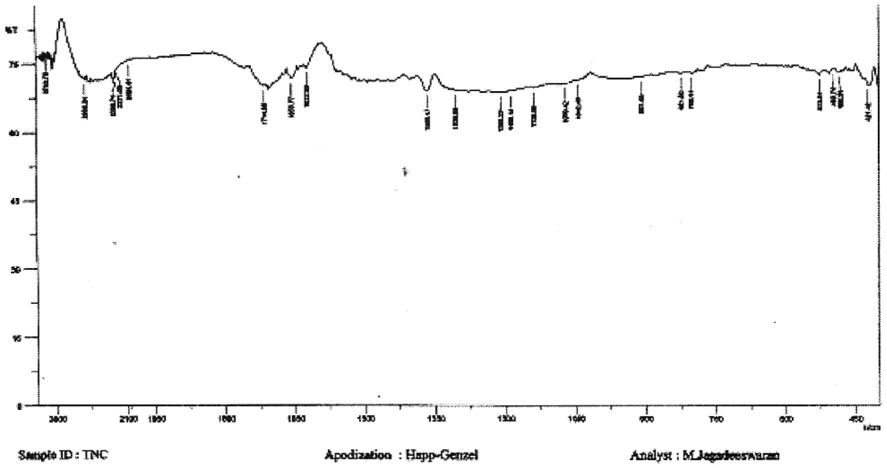

Fig. 10a. FT-IR spectrum of PTNC before Ni(II) adsorption

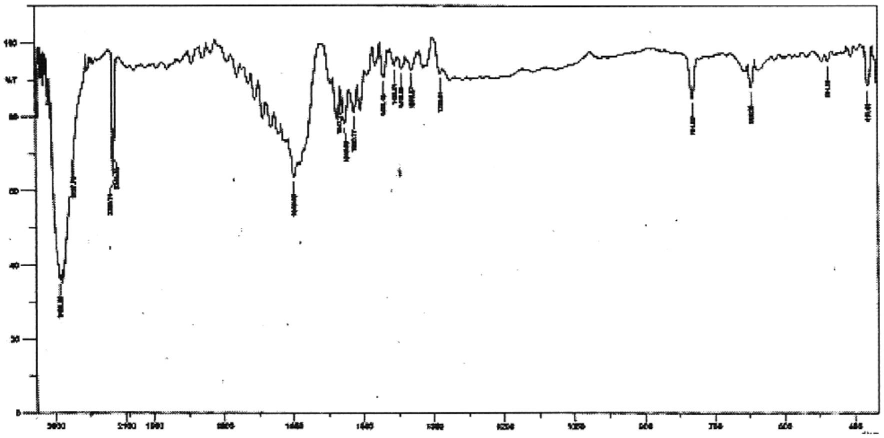

Fig. 10b. FT-IR spectrum of PTNC after Ni(II) adsorption

$$C_xO + 2H_2O \rightarrow C_xOH_2^{2+} + 2OH^-$$
$$CO_x + XH_2O \rightarrow C(OH)_x + XOH^-$$
$$C_xO_2 + H_2O \rightarrow C_xO^{2+} + 2OH -$$

Since PTNC was prepared upon treatment with phosphoric acid followed by sodium carbonate soaking, group such as C_xONa^+, $C_xONa_2^{2+}$, $C_xPO_3H_2$ and $C_xPO_3Na_2$ may be present. Hence it is expected that Na^+ and H^+ in the groups get exchanged with Ni(II).

$$2CxOH^+ + Ni^{2+} \rightarrow (CxO)_2Ni + 2H^+$$
$$CxOH_2^{2+} + Ni^{2+} \rightarrow CxONi^{2+} + 2H^+$$

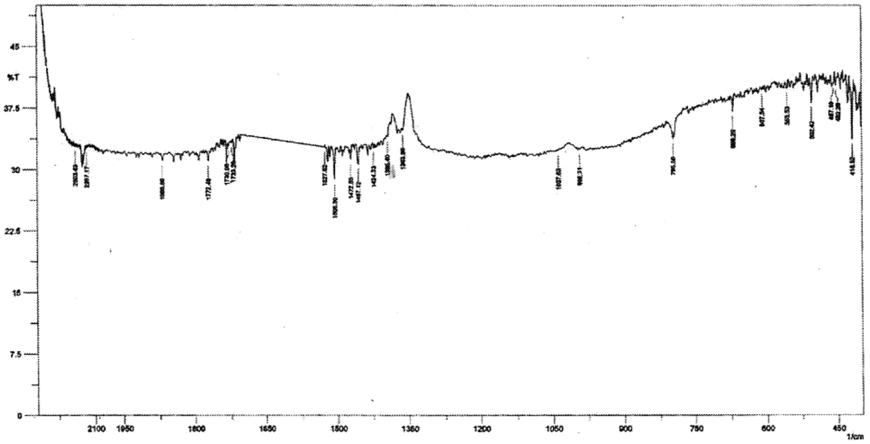

Fig. 11a. FT-IR spectrum of CAC before Ni(II) adsorption

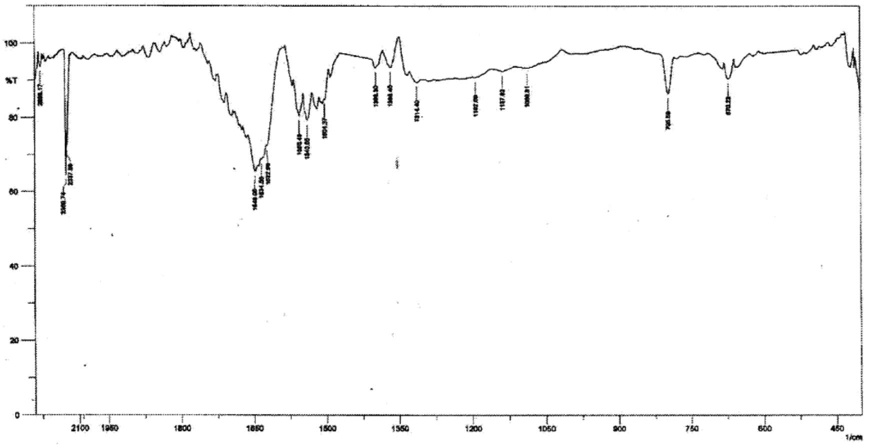

Fig. 11b. FT-IR spectrum of CAC after Ni(II) adsorption

$$2CxONa^{+} + Ni^{2+} \rightarrow (CxO)_2Ni^{2+} + 2Na^{+}$$
$$CxONa_2\ 2+ + Ni^{2+} \rightarrow CxONi^{2+} + 2Na^{+}$$
$$2CxPO_3H_2 + Ni^{2+} \rightarrow (CxPO_3)_2\ Ni^{2+} + 4H^{+}$$
$$2CxPO_3Na_2 + Ni^{2} \rightarrow (CxPO_3)_2\ Ni^{2+} + 4Na^{+}$$

SEM image of PTNC (Fig. 12a) reveals that the carbon surface is rough and porous in nature when compared to the image of CAC (Fig. 13a). It is evident that considerable Ni(II) adsorption had taken place as the SEM image of PTNC after adsorption (Fig. 12b) shows, an obvious density difference by the rough surface and the pores which were being entrapped with Ni(II) ions.

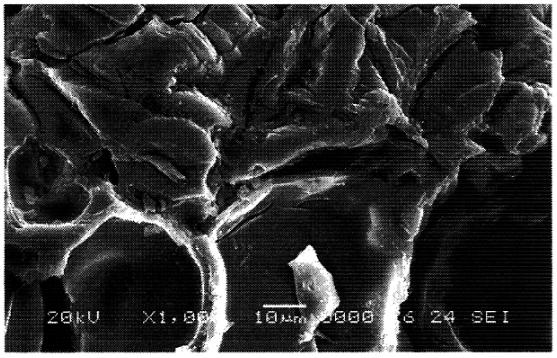

Fig. 12a. SEM image of PTNC before Ni(II) adsorption

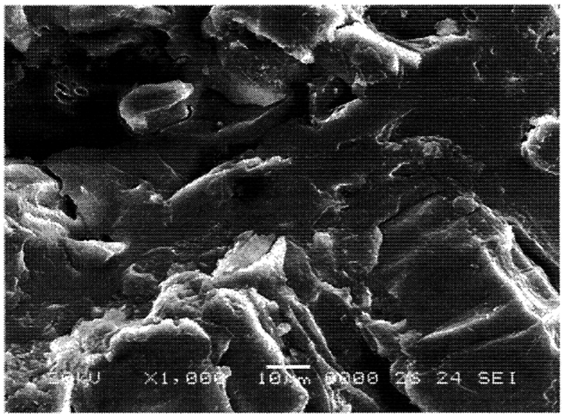

Fig. 12b. SEM image of PTNC after Ni(II) adsorption

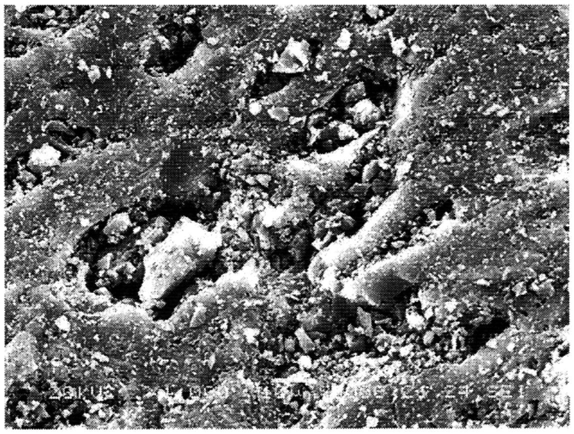

Fig. 13a. SEM image of CAC before Ni(II) adsorption

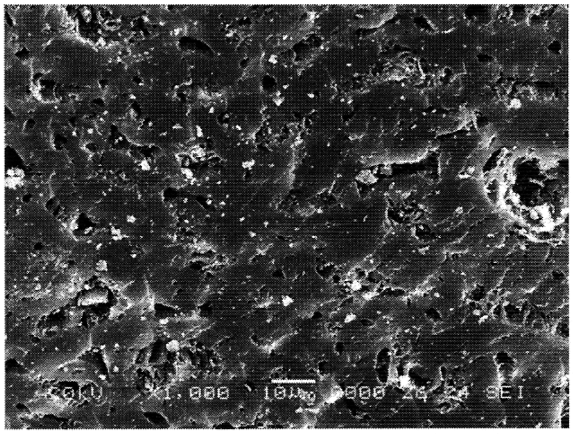

Fig. 13b. SEM image of CAC after Ni(II) adsorption

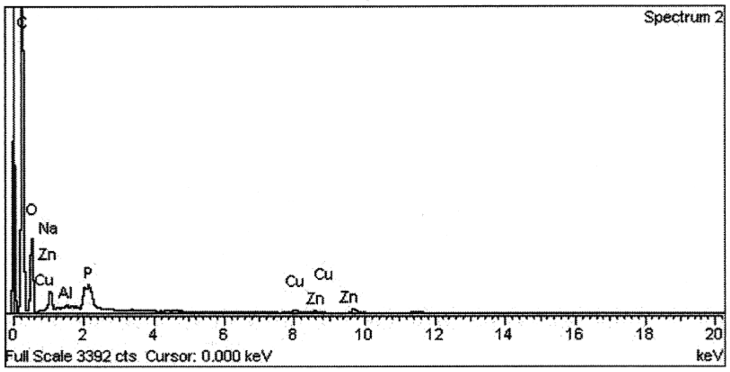

Fig. 14a. EDAX pattern of PTNC before Ni(II) adsorption

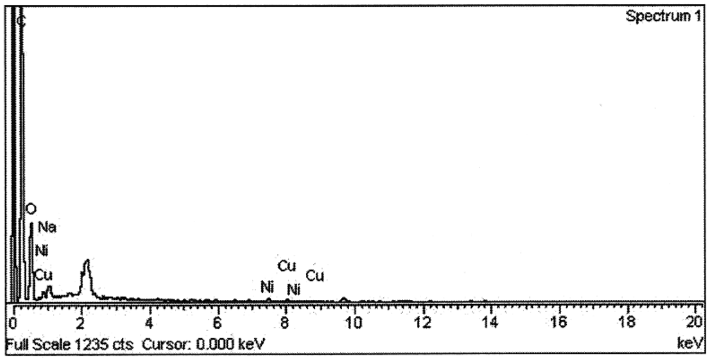

Fig. 14b. EDAX pattern of PTNC after Ni(II) adsorption

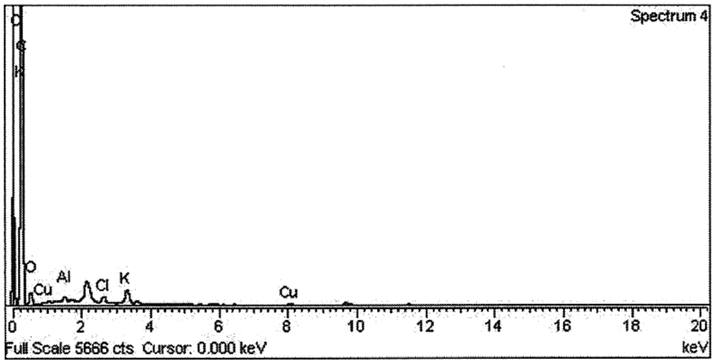

Fig. 15a. EDAX pattern of CAC before Ni(II) adsorption

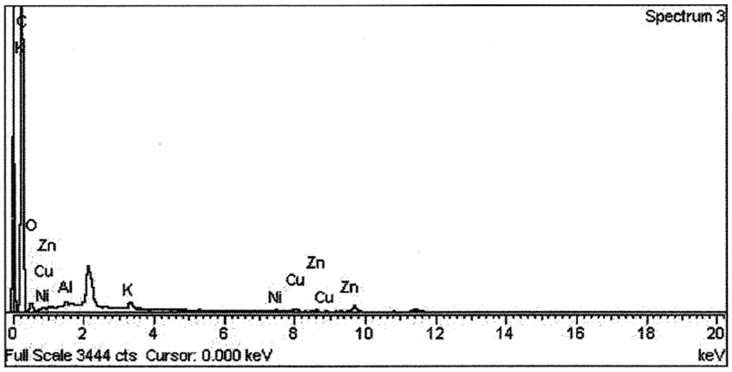

Fig. 15b. EDAX pattern of CAC after Ni(II) adsorption

Conclusion

Activated carbon prepared from Tamarind nuts, an agricultural waste is capable of removing Ni(II) from aqueous solution. Based on batch and column studies PTNC was found to have higher adsorption capacity compared to commercial activated carbon. The adsorption process obeys Freundlich and Langmuir adsorption isotherms. The ratio of weight percentage of Ni(II) adsorbed on PTNC (1.27 %) and on CAC (0.85 %) from EDAX analysis which is 1.49 and it is almost equivalent to the ratio of Freundlich adsorption capacity k for PTNC (K = 10) and CAC (K = 6.61). Since the ratios are equal it is confirmed that PTNC is found to have better adsorption capacity compared to CAC and the process is mainly governed by Freundlich adsorption type. Adsorption also followed reversible first order kinetics. Hence it is concluded that the activated carbon prepared from Tamarind nut could definitely be exploited as an alternative carbon material for the treatment of Ni(II) industrial effluents.

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