

Removal of Nickel(II) from Wastewater: Activated Carbons from Oilcakes

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Activated carbons prepared from agro industrial waste by products such as coconut and neem oilcake, by thermal activation at 800 °C, were used as efficient sorbents for the removal of nickel ion from wastewater. The sorption conditions, such as pH, adsorbent dose and concentration of nickel(II) were examined. The coconut oilcake activated carbon (COCAC) shows more adsorption efficiency than neem oilcake activated carbon (NOCAC). The kinetic processes of Ni(II) adsorption on to activated carbons were described by applying pseudo-first-order, pseudo-second-order and reversible pseudo-first-order rate equations. The kinetic data was found to follow pseudo-second-order rate equation for both carbons. The equilibrium data were studied by Freundlich, Langmuir and Temkin isotherm. Based on regression coefficient, Temkin isotherm model was found to be more suitable for these carbons.

Key Words: Ni(II) removal, Coconut oilcake carbon, Neem oilcake carbon, Kinetics, Isotherm models.

INTRODUCTION

Heavy metals are more hazardous to the environment due to their stability and mobility. Nickel is an essential element at trace level only but it becomes toxic at higher concentration for both plants and animals. World Health Organization¹ has suggested that the maximum amount of nickel in drinking water should not more than 0.01 mg/L. Nickel(II) is introduced as a pollutant from wastewater of silver refineries, electroplating, zinc based casting industries, storage battery industries². High level exposure of nickel causes cancer of lungs, nose and bone, dermatitis (nickel itch), dizziness, headache, nausea, vomiting, chest pain, dry cough and shortness of breath, rapid respiration, cyanosis, extreme weakness and DNA damage³.

Various conventional methods have been proposed for removing heavy metal ion such as Ni(II) include chemical precipitation⁴, reverse osmosis⁵, ion-exchange^{6,7}, complexation, sequestration⁸, electrochemical operation⁹, biological treatment¹⁰ and adsorption on activated carbon¹¹. However, these processes have considerable disadvantages including incomplete metal removal, requirements for expensive equipment, chemicals and monitoring system, high reagent and energy requirements and generation of toxic sludge or other waste products that require disposal.

The costs of activated carbons prepared from agricultural waste byproducts are comparatively cheap than commercial activated carbon¹². The properties of the activated carbon are mainly based on the source materials. Activated carbon prepared from low cost waste materials by both physical and chemical activation show maximum removal of heavy metals from water and wastewater^{13,14}. Numerous reports have been published involving the low cost activated carbon adsorbents produced from readily available agricultural waste materials such as almond husk¹⁵, rice husk¹⁶, cotton seeds¹⁷, tamarind nuts¹⁸, peanut hulls¹⁹, for the removal of heavy metals from water and wastewater.

Cocos nucifera (coconut) tree is Arecaceae family (palmae), which is grown around the world in lowland tropical and subtropical habitats and widely distributed in Tamil Nadu, Rajasthan, Maharashtra and Kerala in India. Its fruits are highly nutritious and extracted oil from its fruit meal is one of the important components of Indian diet, cosmetic and medicinal purposes, however coconut oilcake is left as solid waste. Similarly *Azadirachta indica* (neem) is a tree in the mahogany family (meliaceae) which is native to India and Burma growing in tropical and semi-tropical regions. The plant parts root, fruits, leaf, gum and oil, flower and wood have medicinal application, however oilcake is left as solid waste.

Coconut and neem oilcakes are the crude solid residues obtained from pressing the coconut meal and neem seeds for oil extraction. These residues are generally used as cattle feed, bio pesticides^{20,21} and biofertilizer²². However the consumption rate of oilcakes is found to be very small when compared with production rate. Hence enormous residues are dumped in to the environment without any usage in India.

Rao and Khan^{23,24} reported the removal and recovery of Cu(II), Cd(II) and Pb(II) by neem oilcake is better by column operation as compared to batch process in single metal and multi metal systems. Activated carbon prepared from *Cocos nucifera* oilcake by chemical treatment method studied earlier in our laboratory^{25,26} was found to be high adsorption capacity of sorbent for the removal of Ni(II) and Hg(II) from aqueous system.

In the present study, attempts have been made to prepare novel adsorbents by thermally activated, coconut oilcake (COCAC) and neem oilcake (NOCAC) carbons and the suitability of these carbons with respect to Ni(II) removal from plating industry wastewater has been investigated. The paper reports the results of adsorption of Ni(II) by NOCAC and COCAC in terms of kinetic and batch mode operations.

EXPERIMENTAL

Preparation of activated carbon: *Azadirachta indica* (neem) and *Cocos nucifera* (coconut) oilcakes were procured from oil industries as waste products, washed, dried in hot air-oven at 100-110 °C for 24 h and then subjected to pyrolysis and activation in *Muffle furnace* (Shivans, Gujarat). Pyrolysis of oilcakes is carried out at temperature range of 500-600 °C in the absence of air, volatile products were

removed and the residue was converted into a char. The chars were then subjected to thermal activation in the absence of air at elevated temperatures (800-900 °C)²⁷. The resulting activated carbon particles were ground in a mill and sieved to 120-200 mesh size and stored in a desiccator. The characteristics of the COCAC and NOCAC are given in Table-1.

TABLE-1
CHARACTERISTICS OF THERMALLY ACTIVATED COCONUT OILCAKE CARBON (COCAC) AND NEEM OILCAKE CARBON (NOCAC)

Control test	COCAC	NOCAC
Bulk Density(gmL ⁻¹)	0.67	1.15
Moisture (%)	4.29	0.46
Solubility in water (%)	15.93	5.42
Solubility in 0.25M HCl (%)	23.73	50.08
pH	9.84	8.96
Surface area (m ² g ⁻¹)	618.02	252.66
Ash (%)	15.67	72.85
Ash analysis (%)		
(i) CaO	2.80	2.86
(ii) MgO	7.64	1.22
(iii) Fe ₂ O ₃	1.10	3.67
(iv) Na ₂ O	2.25	2.06
(v) K ₂ O	41.88	2.10
(vi) Al ₂ O ₃	15.35	5.85
(vii) SiO ₂	12.56	81.60

Adsorption studies: Batch adsorption experiments were carried out for removing Ni(II) from plating industry wastewater in terms of pH effect, adsorbent and adsorbate dose. For each experimental run, 100 mL of wastewater of known concentration of metal ion was taken in 300 mL stoppard polyethylene reagent bottles. Then pH was adjusted (Elico-LI-120) to the desired value and a known amount of the activated carbon was introduced. The solutions in bottles were agitated at room temperature (30 ± 1 °C) using a mechanical shaker for a prescribed time to attain equilibrium. At the end of the predetermined time intervals, the samples were taken out, solutions were separated from the activated carbon (COCAC and NOCAC) by filtration using Whatman filter paper No. 41 and final concentration of metal ion was determined in the filtrate by atomic absorption spectrophotometer (AAS) (Elico SL 163) with air-acetylene fuel. Adsorption isotherm and kinetic studies were carried out with different initial concentration of nickel(II) at optimum pH and at fixed carbon dosage (100 mg/100 mL). For pH effects, both NOCAC and COCAC were used at a dosage of 0.5 gm/100 mL with higher nickel concentration (63 mg/L).

Control experiments were carried out without adsorbent in bottles and there was negligible adsorption of metal ion by the container walls.

The removal percentage (R %) is determined as the ratio of difference in metal concentration before and after adsorption (C₀-C_e) to the initial concentration of Ni(II) in the wastewater (C₀) was calculated using the following equation:

$$R \% = C_0 - C_e/C_0 \times 100$$

The batch adsorption study was replicated thrice for each of the adsorbents (COCAC and NOCAC).

Desorption studies help to elucidate the nature of adsorption and to recover the precious metals and spent carbon. After equilibrium, carbon saturated with nickel was removed and washed with double distilled water to eliminate unadsorbed metal ions. The adsorbent after washing was treated with 100 mL of (0.05-0.35 M) concentrated HCl solution and the bottles were shaken for 0.5 h at room temperature (30 ± 1 °C) using a mechanical shaker. The solutions were then filtered and analyzed for metals desorbed.

Working standards were prepared by progressive dilution of stock nickel solution (1000 mg/L) from E-Merck, AR reagent grade HCl, NaOH and buffer solution (E-Merck) were used to adjust the solution pH. Analytical reagent grade chemicals from E-Merck, Hi-media and Ranbaxy, SD's Fine were used for experimental studies. The characteristic of wastewater was analyzed before and after treatment, results were summarized in Table-2.

TABLE-2
CHARACTERISTICS OF PLATING INDUSTRY WASTEWATER

Parameter	Values		
	Before treatment (mg/L)	After treatment (mg/L)	
		COCAC	NOCAC
pH (except pH)	6.30	8.5-9.0	8.6-9.0
Basicity	80.00	12.00	39.0
Total solids	1850.00	80.00	289
Suspended solids	270.00	14.00	158
Cyanide	0.60	0.20	0.25
Copper	6.00	0.01	0.01
Nickel	63.00	2.45	17.0

RESULTS AND DISCUSSION

By examining the characteristics of both carbons, COCAC show more moisture content than NOCAC. The higher moisture content of COCAC suggested that the thermal activation has made the carbon more porous. NOCAC has higher ash content than COCAC which indicates that the former material contains large amount of inorganics. The presence of ash inhibits surface area development because inorganic may fill or block some portions of existing micro pore volume. This may be the reason for the lower surface area observed in carbons with high ash contents²⁸.

Effect of pH: The pH is an important controlling parameter in all the adsorption processes. The effect of initial pH on the removal of Ni(II) by COCAC and NOCAC were shown in the Fig. 1. COCAC was found to be effective for the maximum removal of Ni(II) ion over the pH range $4.0-7.0 \pm 0.2$ whereas NOCAC was effective for the maximum removal in the pH range $5.0-7.0 \pm 0.2$. It could be seen that

COCAC shows a wider pH range in the removal of metal ion when compared to NOCAC. Under this optimum range of pH conditions, the Ni(II) ion removal by COCAC was found to be 1.41 times superior to NOCAC.

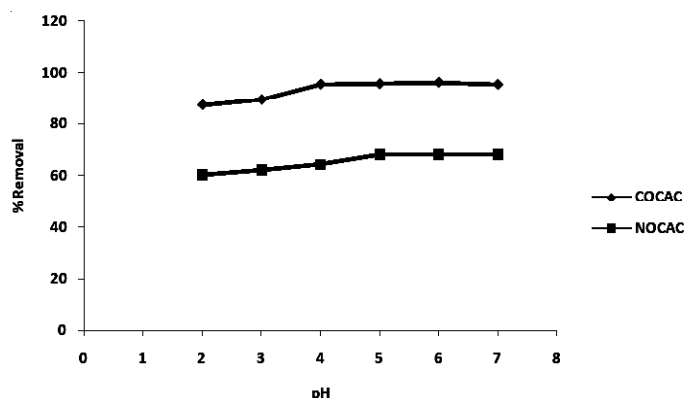
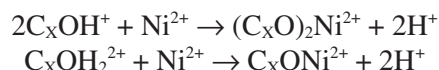


Fig. 1. Effect of initial pH on the removal of Ni(II) ion by both COCAC and NOCAC, [63 mg/L]

The influence of pH on Ni(II) removal by COCAC and NOCAC is due to the formation of some carbon-oxygen complexes at the carbon surface, which render the surface polar. Since there is no satisfactory method for determining the polar character of the surface quantitatively, the above statement is relative²⁹. As the pH decreases, the positive characteristics of the carbon surface intensify which prevents the adsorption of positive species such as Ni(II) ion, due to electrostatic repulsion. Besides this, a higher concentration of H⁺ ions present in the reaction mixture competes with Ni(II) ions for the adsorption sites (as the proton to nickel ratio is more at low pH) resulting in the reduced uptake of metal ion. On the contrary, as the pH increases the adsorbent surface becomes more and more negatively charged and the adsorption of Ni(OH)⁺ species is more favored as reported on hydrous oxide of gels of iron³⁰ and goethite³¹. The following adsorption mechanism is suggested for the adsorption of Ni(II) on COCAC and NOCAC surfaces. The surface oxide groups³² present on carbon can undergo hydrolytic reactions with the result proton exchangeable sites such as C_xOH₂²⁺, C_xOH⁺ may be formed. These groups may play a significant role in removing nickel ions as follows:



It may be stated in this connection that the presence of -OH groups on the surface of carbons are also indicated by FT-IR spectrum.

Effect of carbon dosage: The effect of adsorbent concentration on Ni(II) uptake by adsorbents was shown in Fig. 2. From these figures it is clear that, a minimum carbon dosage of 500 mg/100 mL (COCAC) and 750 mg/100 mL (NOCAC) is required for 96 and 72 % removal of nickel(II), respectively from wastewater under optimum (pH = 7.0) conditions. Therefore it could be seen that COCAC is 1.33

times superior to NOCAC. It could further be noticed that even at higher carbon dosages, both carbons did not produce any significant removal of nickel(II) with higher concentrations of metal ion (63 mg/L).

Effect of initial Ni(II) concentration: In batch adsorption, the initial concentration of metal ions in the solution plays a key role as a driving force to overcome the mass transfer resistance between the aqueous and solid phases. Therefore, the amount of metal ions adsorbed was expected to be higher with a higher initial concentration. The effect of initial nickel concentration in the wastewater on the removal of Ni(II) by two adsorbents COCAC and NOCAC, is shown in Fig. 3. The removal capacity of all the adsorbents increased with increasing initial concentration, since transfer of metal ions from bulk to the surface of the sorbent increases with increase in concentration of metal ions. The removal of Ni(II) increases from 2.02-12.2 mg/g for COCAC and from 3.12-8.12 mg/g for NOCAC when initial concentration of Ni(II) was increased from 18-63 mg/L, respectively. The fact that the adsorption capacity increased with increasing the metal ion concentration, indicates a great potential application of COCAC and NOCAC as a sorbent, to the treatment of wastewater containing metal ions at higher concentrations. At optimum conditions activated carbons COCAC (500 mg/100 mL of adsorbent, pH 7.0) and NOCAC (750 mg/100 mL of adsorbent, pH 7.0) were also able to remove other metal ions (Table-2) completely from wastewater.

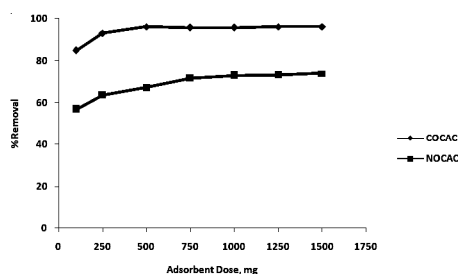


Fig. 2. Effect of adsorbent dosage on the removal of Ni(II) ion by COCAC and NOCAC at optimum pH-7.2, (63 mg/L)

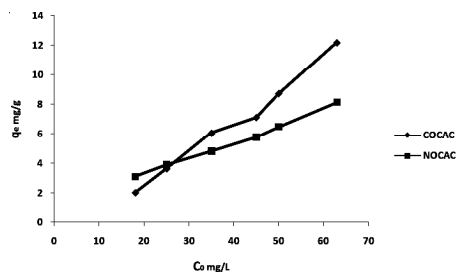


Fig. 3. Effect of initial metal ion concentration on the removal of Ni(II) by COCAC and NOCAC (63 mg/L)

Desorption studies: In order to make the adsorption process more economical, it is important to desorb the spent adsorbents. Desorption studies were carried out by batch process using HCl at different concentration ranging from 0.05-0.35 M. The per cent recoveries of nickel(II) from COCAC were found to be 56.12, 68.59, 74.82, 81.06, 93.53, 99.9 and 99.9 by 0.05, 0.10, 0.15, 0.20, 0.25, 0.30 and 0.35 M HCl, respectively. In the case of NOCAC, the corresponding values were 74.88, 86.71, 94.59, 99.9, 99.9, 99.9 and 99.9 % for the same concentration of HCl as mentioned above. In highly acidic medium, H^+ ions displaces the nickel(II) ions by ion exchange process.

Adsorption isotherm: The adsorption equilibrium of nickel(II) on COCAC and NOCAC, as a function of initial ions concentrations (63-18 mg/L) at optimum pH conditions are shown in Figs. 4-6. The Freundlich, Langmuir and Temkin isotherm models³³ are the simple and most frequently applied to explain the sorption process of nickel(II) by COCAC and NOCAC.

The relation between the metal uptake capacity $\log q_e$ (mg g^{-1}) of adsorbent and the residual metal ion concentration C_e (mg L^{-1}) at equilibrium conditions is given by

$$\log q_e = \log K_f + 1/N_f \log C_e$$

where the intercept $\log K_f$ (mg g^{-1}) is a measure of adsorbent capacity and the slope N_f is the sorption intensity. Fig. 4 shows the isotherm data fit with Freundlich model. The values of the constants K_f and N_f for both activated carbons were calculated from the plots and shown in Table-3. High value of N_f (greater than one) and K_f suggests that the adsorption capacity of adsorbent was high at higher concentration of metal ion in solution.

Langmuir equation relates solid phase adsorbate concentration q_e and uptake of the equilibrium liquid concentration C_e as follows.

$$1/q_e = 1/b + 1/ab \times 1/C_e$$

where 'a' and 'b' are the Langmuir equilibrium constant to the energy of sorption, amount of metal ions required to form a monolayer, respectively. The isotherm plot is shown in Fig. 5. The values of 'a' and 'b' for COCAC and NOCAC were determined from graph and their values were summarized in Table-3.

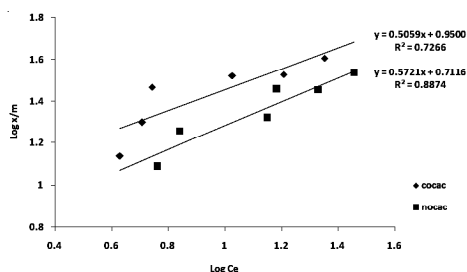


Fig. 4. Freundlich isotherm equation fit for both COCAC and NOCAC under optimum pH conditions

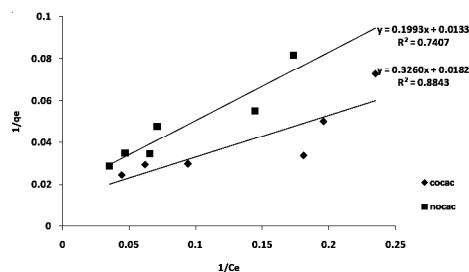


Fig. 5. Langmuir isotherm equation fit for both COCAC and NOCAC under optimum pH conditions

TABLE-3
ADSORPTION ISOTHERM PARAMETER FOR Ni^{2+} ION
ADSORPTION BY COCAC AND NOCAC

Adsorbent	Langmuir model (mg g^{-1}) (L mg^{-1})				Freundlich model (mg g^{-1}) (L mg^{-1})			Temkin model (mg g^{-1}) (L mg^{-1})		
	b	a	ab	R^2	K_f	N_f	R^2	a_t	b_t	R^2
COCAC	75.758	0.066	5.010	0.742	8.913	1.977	0.727	0.110	13.044	0.811
NOCAC	54.945	0.056	3.067	0.884	5.148	1.748	0.887	8.202	12.425	0.901

The value of b indicates that 1 g of both adsorbents (COCAC and NOCAC) required 75.19 and 54.95 mg of Ni(II), respectively to form a monolayer on the surface of the adsorbent. It could be seen once again that the COCAC was 1.5 times more efficient than NOCAC for the removal of Ni(II) from wastewater.

The essential characteristics of Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter (R_L). Then R_L values indicates the isotherm shape according to the following adsorption characteristics, $R_L > 1$ (is unfavorable), $R_L = 1$ (linear adsorption), $R_L = 0$ (is irreversible) and $0 < R_L < 1$ (is favorable). It has been expressed as

$$R_L = 1/L + aC_0$$

where 'a' and C_0 are the Langmuir constant and initial concentration of nickel(II)³⁴. The correlation between isotherm shape and R_L values (Table-4) suggest that, the favorable adsorption of nickel(II) on activated carbons (COCAC, NOCAC) at room temperature 30 ± 1 °C.

TABLE-4
EQUILIBRIUM PARAMETER R_L VALUES UNDER OPTIMUM pH = 7.2 CONDITIONS

Concentration of initial metal ion (mg/L)	R_L Values	
	COCAC	NOCAC
63	0.1939	0.2208
50	0.2326	0.2632
44	0.2561	0.2887
35	0.3021	0.3378
25	0.3774	0.4167
18	0.4570	0.4980

Temkin equation has generally been applied in the following linearized form

$$q_e = a_t + 2.3b_t \log C_e$$

where a_t and b_t are Temkin isotherm constants. Temkin adsorption isotherm model using the data is shown in Fig. 6. The values of a_t and b_t for both carbons were determined from the plots and listed in Table-3.

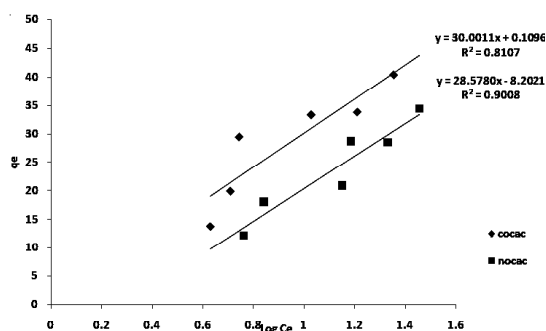


Fig. 6. Temkin isotherm equation fit for both COCAC and NOCAC under optimum pH conditions

The coefficient determination (R^2) values were calculated for all the isotherm models and the values are summarized in Table-3. From the values of coefficient of determination (R^2), it has been found that Temkin isotherm model fit well for both COCAC and NOCAC.

Adsorption kinetics: Kinetic models^{35,36} of pseudo-first-order, pseudo-second-order and reversible first-order kinetic rate equations are used for the purpose of investigating the sorption mechanism of nickel on COCAC and NOCAC.

The pseudo-first-order kinetic model may be expressed as

$$\ln(q_e - q_t) = -K_1 t + \ln q_e$$

where q_e and q_t are the amount of metal adsorbed (mg g^{-1}) at equilibrium and at time t , respectively and K_1 is the pseudo first order equilibrium rate constant ($1/\text{h}$). A plot of $\ln(q_e - q_t)$ versus t gives straight line (Fig. 7A and 7B). The applicability of the rate equation was confirmed by using their R^2 values.

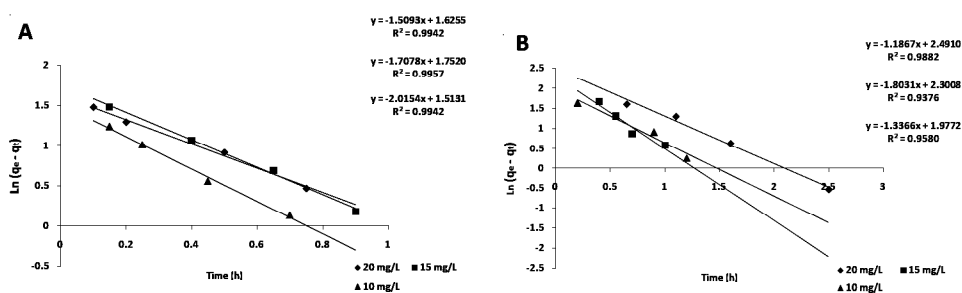


Fig. 7. Pseudo first-order-kinetic equation fit for Ni(II) removal by COCAC (A) and NOCAC (B), (pH-7.0)

Pseudo-second-order adsorption rate equation may be expressed as

$$t/q_t = 1/K_2 q_e^2 + 1/q_e \times t$$

where K_2 is the pseudo-second-order adsorption rate constant (g/mg h). A plot of t/q_t versus t produces straight line and indicates the applicability of pseudo-second-order model (Fig. 8A and 8B). Constants of rate equations are given in Table-5.

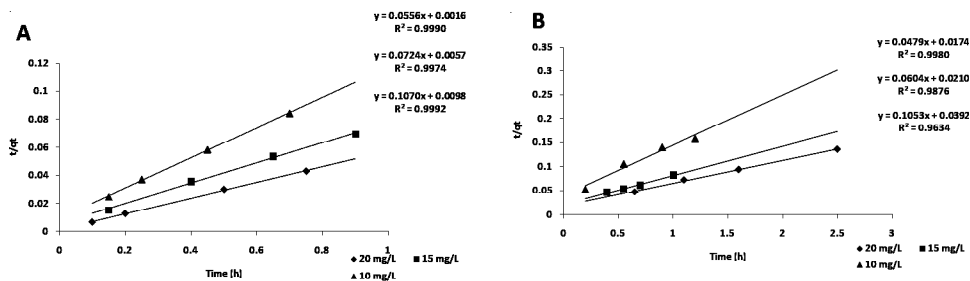


Fig. 8. Pseudo second-order-kinetic equation fit for Ni(II) removal by COCAC (A) and NOCAC (B), (pH-7.0)

TABLE-5
PSEUDO-FIRST-ORDER, REVERSIBLE-FIRST ORDER AND PSEUDO-SECOND-ORDER
KINETIC CONSTANTS AND DIFFUSION COEFFICIENTS FOR THE ADSORPTION OF
Ni²⁺ ION ON COCAC AND NOCAC AT OPTIMUM pH CONDITIONS

Carbon	Ni(II) (mg/L)	Pseudo-first-order kinetic				Pseudo-second-order kinetic			
		k ₁	Film diffusion	Pore diffusion	R ²	k ₂	Film diffusion	Pore diffusion	R ²
		(h ⁻¹)	(cm ² s ⁻¹)			(g/mg h)	(cm ² s ⁻¹)		
COCAC	20	1.509	6.4768×10 ⁻⁹	4.3124×10 ⁻⁸	0.9942	1.932	1.1493×10 ⁻⁷	7.6525×10 ⁻⁷	0.9990
	15	1.708	7.2158×10 ⁻⁹	4.8812×10 ⁻⁸	0.9957	0.920	4.0402×10 ⁻⁸	2.7330×10 ⁻⁷	0.9974
	10	2.015	8.5127×10 ⁻⁹	5.7585×10 ⁻⁸	0.9942	1.168	3.4196×10 ⁻⁸	2.3132×10 ⁻⁷	0.9992
NOCAC	20	1.187	5.0387×10 ⁻⁹	3.3922×10 ⁻⁸	0.9882	0.132	7.7662×10 ⁻⁹	5.2284×10 ⁻⁸	0.9980
	15	1.803	7.5037×10 ⁻⁹	5.1526×10 ⁻⁸	0.9376	0.174	7.5275×10 ⁻⁹	5.1690×10 ⁻⁸	0.9876
	10	1.337	5.3420×10 ⁻⁹	3.8209×10 ⁻⁸	0.9580	0.283	7.8359×10 ⁻⁹	0.6047×10 ⁻⁸	0.9634

Carbon	Ni(II) (mg/L)	Reversible-first order					
		K (h ⁻¹)	k ₁ (h ⁻¹)	k ₂ (h ⁻¹)	Film diffusions	Pore diffusion	R ²
					(cm ² s ⁻¹)		
COCAC	20	1.509	1.441	0.0679	6.4768 × 10 ⁻⁹	4.3124 × 10 ⁻⁸	0.9942
	15	1.708	1.606	0.1025	7.2158 × 10 ⁻⁹	4.8812 × 10 ⁻⁸	0.9958
	10	2.015	1.894	0.1209	8.5127 × 10 ⁻⁹	5.7585 × 10 ⁻⁸	0.9942
NOCAC	20	1.187	1.121	0.0659	5.0387 × 10 ⁻⁹	3.3922 × 10 ⁻⁸	0.9882
	15	1.803	1.670	0.1334	7.5037 × 10 ⁻⁹	5.1526 × 10 ⁻⁸	0.9377
	10	1.337	1.189	0.1484	5.3420 × 10 ⁻⁹	3.8209 × 10 ⁻⁸	0.9580

Reversible first-order rate equation may be considered for the sorption of metal ion from liquid phase to solid, as follows

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

where K = overall rate constant, U_t = the fractional attainment of equilibrium.

$$U_t = q_t/q_e$$

A plot of $\ln(1-U_t)$ versus t gives a straight line (Fig. 9A and 9B). From this equation forward rate constants (k₁) and backward rate constants (k₂) were calculated, using the following equations.

$$K = k_1 + k_2$$

$$K_c = k_1/k_2$$

$$K = k_1(1 + 1/K_c)$$

where K_c is the equilibrium constant.

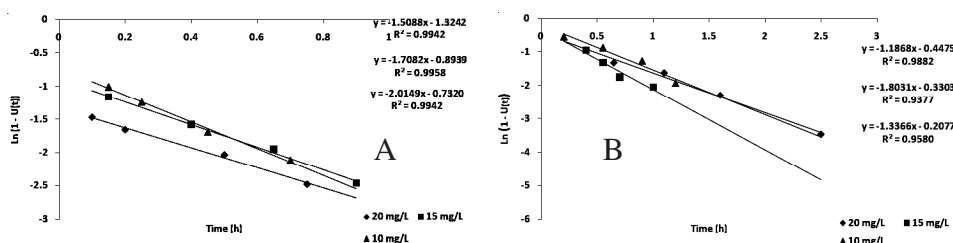


Fig. 9. Reversible-first-order-kinetic equation fit for Ni(II) by COCAC (A) and NOCAC (B), (pH -7.0)

The kinetic data for activated carbons are presented in Table-5. It could be seen that the forward rate constants were found to be higher than backward rate constants, suggesting, the rate of adsorption is clearly dominant for COCAC and NOCAC.

In order to understand the nature of the diffusion process responsible for the adsorption of nickel(II) on COCAC and NOCAC, attempts were made to calculate the pore and film diffusion coefficient for various concentrations of Ni(II) using the following equation³⁷.

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

where D_p is the pore diffusion coefficient expressed in cm^2s^{-1} , r_0 is the radius of the sorbent expressed in cm and $t_{1/2}$ is the half life period in sec.

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

where D_f is the film diffusion coefficient expressed in cm^2s^{-1} , δ is the film thickness expressed in cm and C^*/C is the equilibrium loading of the sorbent. According to Michelsen *et al.*³⁸ if film diffusion to be the rate determining process in the adsorption of heavy metals on a sorbent, the values of film diffusion coefficient (D_f) should be between 10^{-6} and $10^{-8} \text{ cm}^2\text{s}^{-1}$. If pore diffusion D_p is the rate determining process, its value should be in the range of 10^{-11} - $10^{-13} \text{ cm}^2\text{s}^{-1}$. It is evident from Table-5, that the removal of Ni(II) follows film diffusion process, since the co-efficient values are closer to the range of 10^{-6} - $10^{-8} \text{ cm}^2\text{s}^{-1}$.

Error analysis: In order to compare quantitatively the applicability of kinetic models in fitting to data, the per cent relative deviation (P), given by the following equation was calculated³⁹.

$$P = 100/N \times \Sigma \{ [q_e (\text{exp}) - q_e (\text{theo})] / q_e (\text{exp}) \}$$

where $q_e (\text{exp})$ is the experimental value of q_e at any value of C_e , $q_e (\text{theoret.})$ the corresponding theoretical value of q_e and N is the number of observations. It is found that lower the value of percentage deviation (P) better is the fit. It is generally accepted that when P value is less than 5, the fit is considered to be excellent. The value of $q_e (\text{theoret.})$ calculated from these models are compared with experimental values of $q_e (\text{exp.})$ in Table-6. Higher the value of P indicates that the calculated q_e values were not equal to intercept of the plot of $\ln (q_e - q_t)$ against t and lower the P value indicates that the q_e value calculated from graph of t/q_t against t was much closer to experimental q_e values.

The another method of finding deviation based on the $t_{1/2}$ values which can be calculated by both theoretical as well as experimental methods for first order, second order and reversible first order rate equations. The experimental $t_{1/2}$ values were calculated by using the graph, plotted between amount of metal ion remaining in solution and time in minutes.

Theoretical calculations of $t_{1/2}$ values for reversible, pseudo first order and second order kinetics are as follows:

$$t_{1/2} = 0.693/K$$

$$t_{1/2} = 1/K \cdot C_0$$

where K and C_0 are the overall rate constant and initial concentration of the metal ion. The difference (D) between theoretical and experimental $t_{1/2}$ values were higher in the case of first order kinetics for COCAC and NOCAC. However lower values (less than five) of D in pseudo second order kinetics indicates the best fit of experimental data (Table-6).

TABLE-6
PSEUDO-FIRST-ORDER, REVERSIBLE-FIRST ORDER AND PSEUDO-SECOND-ORDER
KINETIC DEVIATIONS FOR THE REMOVAL OF Ni(II) ION ON COCAC AND NOCAC

Adsorbents	Con (mg/L)	$t_{1/2}$ (Exp) (min)	q_e (Exp) (mg g ⁻¹)	Reversible-first order				Pseudo-first order				Reversible-second order			
				$t_{1/2}$	D	q_e	P	$t_{1/2}$	D	q_e	P	$t_{1/2}$	D	q_e	P
				(Theoret.)	(Theoret.)	(Theoret.)	(Theoret.)	(Theoret.)	(Theoret.)	(Theoret.)	(Theoret.)	(Theoret.)	(Theoret.)	(Theoret.)	(Theoret.)
COCAC	20	-	19.10	-	-	-	-	-	-	5.08	73.40	-	-	17.99	5.81
	15	-	14.10	-	-	-	-	-	-	5.77	59.08	-	-	13.81	2.06
	10	-	09.40	-	-	-	-	-	-	4.54	51.70	-	-	09.35	0.53
NOCAC	20	-	18.89	-	-	-	-	-	-	12.07	36.10	-	-	20.87	10.48
	15	-	13.89	-	-	-	-	-	-	09.98	28.15	-	-	16.56	19.22
	10	-	08.89	-	-	-	-	-	-	07.22	18.79	-	-	09.50	6.86
COCAC	20	3.5	-	27.55	24.05	-	-	27.55	24.05	-	-	1.55	1.95	-	-
	15	4.5	-	24.34	19.84	-	-	24.34	19.84	-	-	4.35	0.15	-	-
	10	5.0	-	20.64	15.64	-	-	20.64	15.64	-	-	5.13	0.13	-	-
NOCAC	20	12.0	-	35.03	23.03	-	-	35.03	23.03	-	-	22.73	10.73	-	-
	15	20.5	-	23.06	0.256	-	-	23.06	02.56	-	-	22.99	2.49	-	-
	10	22.5	-	31.10	08.60	-	-	31.10	08.60	-	-	21.20	0.13	-	-

SEM and FT-IR studies: The scanning electron microscope (SEM) (JOEL JSM 6360) image of coconut oilcake activated carbon (COCAC) and neem oilcake activated carbon (NOCAC) before and after adsorption were recorded. The SEM images of raw COCAC and NOCAC show the presence of minute pores on the carbon surface (Figs. 10 and 12), which is largely responsible for the extent of surface area and adsorptive capacity of carbons. After the adsorption process the surfaces of the carbons are modified thereby clearly indicates the attachment of the metal ions, which could be seen from SEM image of COCAC and NOCAC Figs. 11 and 13.

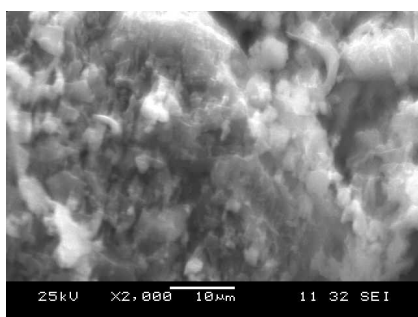


Fig. 10. SEM Photograph of COCAC before adsorption of Ni(II)

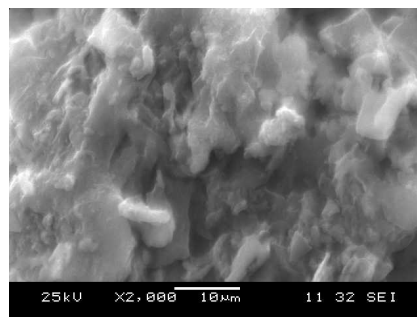


Fig. 11. SEM photograph of COCAC after adsorption of Ni(II)

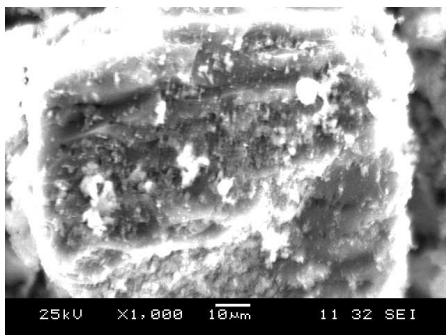


Fig. 12. SEM Photograph of NOCAC before adsorption of Ni(II)

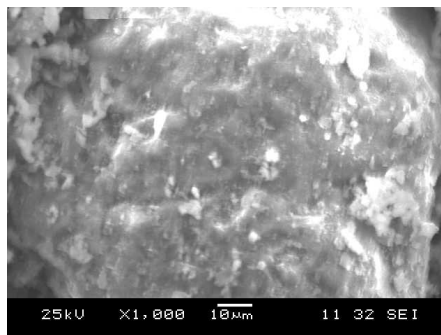


Fig. 13. SEM photograph of NOCAC after adsorption of Ni(II)

The functional groups which are responsible for metal uptake in COCAC and NOCAC were examined by using solid state FT-IR (Shimaduz 84005 FT-IRS) spectral analysis⁴⁰. FT-IR spectra for both COCAC and NOCAC, before and after adsorption process are shown in Figs. 14-17. Spectra displays a number of absorption peaks, indicating the complex nature of the material examined. The prediction of corresponding functional groups for the peaks obtained was listed in Table-7. It could be seen that all the peaks corresponding to those groups responsible for nickel adsorption, are shifted to lower absorbance value after the adsorption process (Figs. 15 and 17).

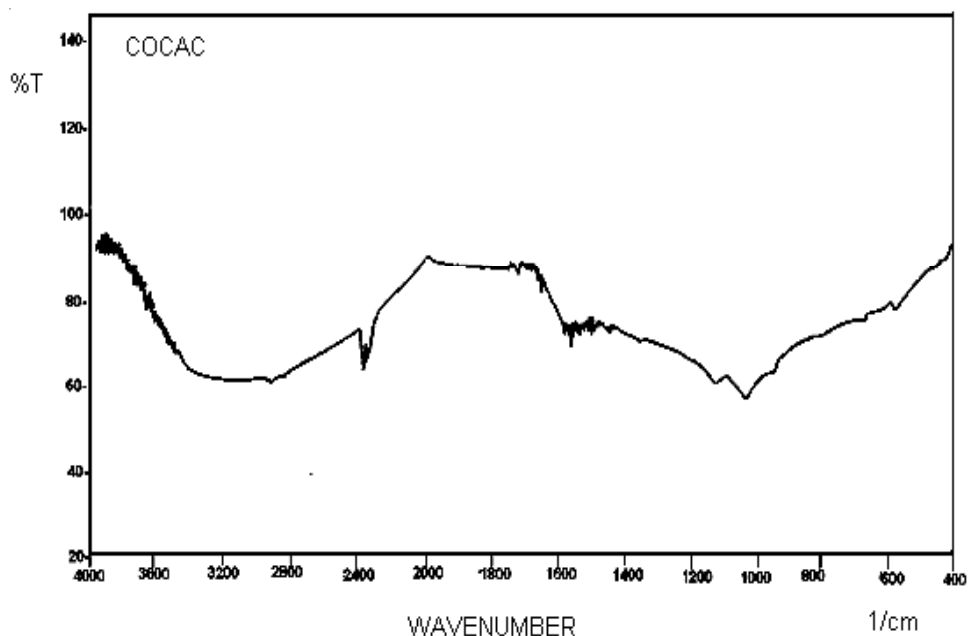


Fig. 14. FT IR spectra of COCAC

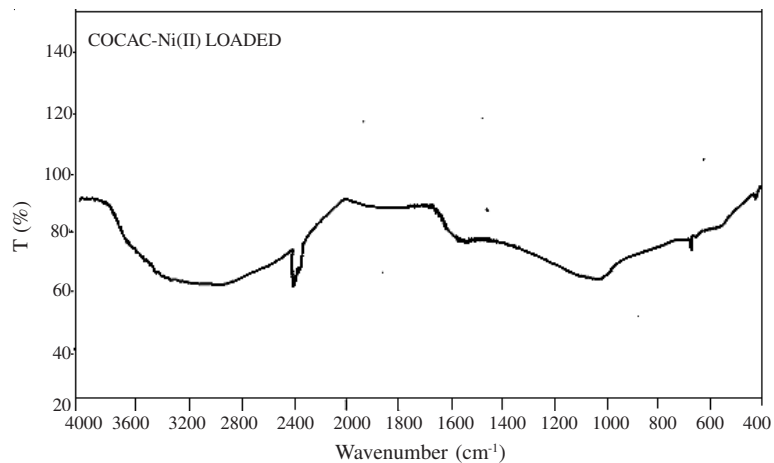


Fig. 15. FT-IR spectra of COCAC after adsorption of Ni(II)

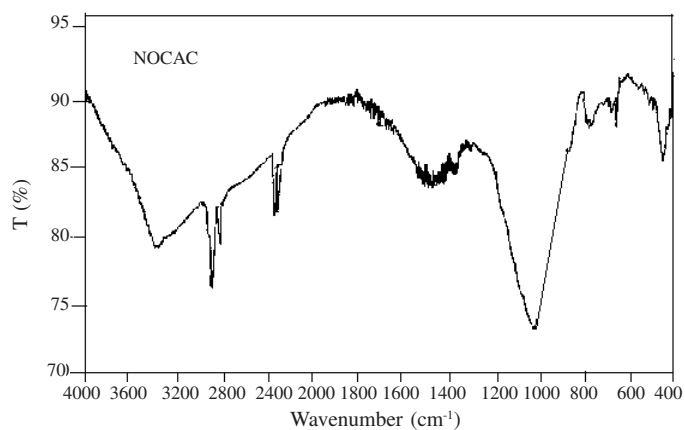


Fig. 16. FT-IR spectra of NOCAC

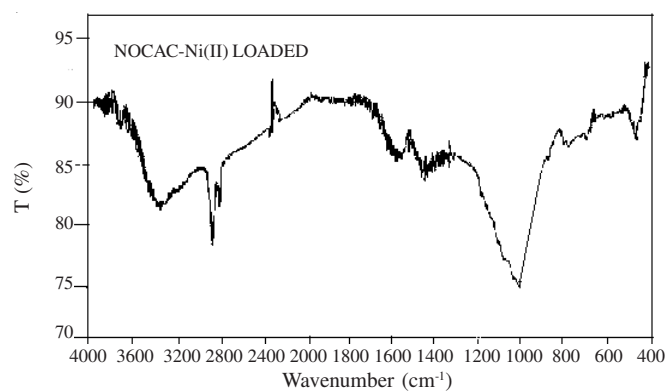


Fig. 17. FT-IR spectra of NOCAC after adsorption of Ni(II)

TABLE-7
PREDICTION OF FT-IR SPECTRAL BANDS (cm⁻¹) FOR
CORRESPONDING FUNCTIONAL GROUPS

Adsorbent	Band (cm ⁻¹)	Functional group
COCAC	926	C-H def for alkyl group
	1033	C-O stretching vibration of alcohols
	1116	C-O-C stretching vibration of substituted ethers
	2360 and 2345	N-H group of amino acids
NOCAC	1018	C-OH stretching vibration of alcohols
	2923 and 2852	C-H stretching vibration
	2364 and 2345	N-H group of amino acids
	3319	Intermolecular hydrogen bonded OH stretching vibration
	777 and 796	C-H vibration of aromatic hydrocarbons

Conclusion

Removal of nickel from wastewater is possible by using abundantly available low cost carbon adsorbents prepared from coconut and neem oilcakes. Detailed experimental investigation have been carried out for concentrations of Ni(II) over the range 18-63 mg/L, under various pH conditions and different carbon dosages indicated that COCAC shows 1.5 times greater adsorption capacity over a wider range of pH than NOCAC. SEM photographs indicate that surface of both carbons are modified by adsorption process. Based on P and D values the Ni(II) adsorption by both COCAC and NOCAC follow the pseudo second order expressions. Based on diffusion coefficient values Ni(II) sorption follows film diffusion process. The Freundlich, Langmuir and Temkin isotherm models are found to be linear indicating the applicability of classical adsorption isotherms to this adsorbate-adsorbent system. Based on the R² values of plots, it may be concluded that the adsorption process is governed predominantly by Temkin isotherm. The reported data may be useful for designing an economically cheap treatment process involving stirred tank flow reactors for the removal and recovery of Ni(II) from nickel containing wastewater from chemical and allied process industries.

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