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Evaluation of Coconut Oilcake Carbon as Absorbent for Nickel Ion: Equilibrium and Kinetic Studies

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The adsorption behaviour of coconut oilcake activated carbon (COCAC) for nickel ion removal from wastewater has been investigated, as a function of appropriate equilibrium time, amount of adsorbent, concentration of adsorbate and pH using a batch system. The efficiency of COCAC was compared with commercial activated carbon (CAC). Studies showed that pH of wastewater affected nickel adsorption because of removal efficiency increased with increasing solution pH but after 5, the removal efficiency remains constant. The adsorption of Ni(II) was found to be maximum for COCAC (96.83 %) than CAC (74.8 %), at pH 7, contact time 30 min and initial Ni(II) concentration of 63 mg/L. The adsorption data fit well with Temkin isotherm model, the adsorption capacity 'b' calculated from the Langmuir isotherm was 555.56 and 30.77 mg/g for COCAC and CAC, respectively. The Freundlich constant N_f indicates beneficial adsorption. Kinetic studies show better applicability of second-order-kinetic model. Desorption studies were performed with dilute hydrochloric acid. Quantitative recovery of the metal ion is possible. The mechanism of adsorption seems to be ion exchange.

Key Words: Activated carbon, Ni(II) adsorption, Isotherm, Kinetics, Wastewater.

INTRODUCTION

Heavy metals are toxic to aquatic flora and fauna even in trace amounts. Nickel is a commonly occurring toxic metal in natural ecosystems due to the effluents of, silver refineries, zinc based casting industries, storage batteries and nickel-plating plants[1]. The tolerance limit[2] of nickel in drinking water is 0.01 mg/L. Higher concentrations of nickel cause cancer of lungs, nose and bone. Dermatitis (nickel itch) is the most frequent effect of exposure to nickel, such as coins and costume jewelry. Acute Ni(II) poisoning causes dizziness, headache, nausea and vomiting, chest pain, dry cough and shortness of breath, rapid respiration, cyanosis, extreme weakness and DNA damage[3]. These harmful effects of Ni(II) necessitate its removal from wastewater before release in to streams.

Various methods have been proposed for the treatment of wastewater containing nickel wastes such as chemical precipitation[4], reverse osmosis[5], ion exchange[6,7], sequestration[8], electrochemical operations[9], biological treatment[10] and adsorption on activated carbon[11]. These methods are not cost-effective in the Indian context. However, adsorption on to the surface of activated carbons is the most widely used method, but the cost of commercial carbon is very high. Hence, there is a growing need to develop low cost activated carbon adsorbent materials from cheaper and locally available agricultural by-products. The cost of activated carbon prepared from agricultural waste by-products is comparatively lower than the commercial activated carbon[12]. Activated carbon prepared from low cost adsorbents by both physical and chemical activation show maximum removal of heavy metals from water and wastewater[13,14].

Coconut is probably the most important plants in the tropics. *Cocos nucifera* (coconut) tree belongs to Arecaceac family and its fruits are highly nutritious. Extracted oil from its fruit meal, find wide usage as a food production, cosmetic and medicinal purposes. Oil cakes generated after removing oils are disposed as a solid waste in oil industries, though small amount of its oilcakes are used as cattle feed in rural India. Activated carbon prepared from *Cocos nucifera* oilcake by chemical treatment method studied earlier in our laboratory was found to be high adsorption capacity of sorbent for the removal of Ni(II) and Hg(II) from water and wastewater[15,16].

In the present investigation, a thermally activated coconut oil cake carbon was prepared and its capacity for Ni(II) removal from plating wastewater has been investigated. The results of batch and kinetic studies on the removal of Ni(II) from plating wastewater by adsorption technique were reported. The effect of various parameters like equilibration time, pH, adsorbent dosage, initial metal ion concentration has been studied. Various kinetics and isotherm models were tested with experimental data. Simultaneously the performance of COCAC was evaluated with commercial activated carbon (CAC) procured from market.

EXPERIMENTAL

Procedure for adsorbent preparation and activation: After extracting oil from coconut (*Cocos nucifera*) meal, waste matter left after extraction is known as coconut oilcake. The oilcake was washed with water, dried in hot air-oven at 100-110 °C for 24 h. After drying, the oilcake was subjected to pyrolysis process. Pyrolysis is a process consisting of dehydration and carbonization of the raw material followed by activation in the absence of air. Slow heating of the starting material does carbonization, over the temperature range 500-600 °C in the absence of air. During carbonization, volatile products are removed and the residue remaining is referred to as char. The chars are subjected to thermal activation at elevated temperatures (800-900 °C)[17]. The resulting activated carbon particles was ground in a mill and sieved to 120-200 mesh size and stored in a desiccator. Comparative studies were simultaneously carried out with commercial activated carbon (CAC) of same particle size (SD fine). The characteristics of COCAC and CAC are given in Table-1

Muffle furnace (Shivans, Gujarat) was used for carbonization and activation of the adsorbents. Atomic absorption spectrophotometer (Elico SL 163) was used for determining Ni(II) concentration. An Elico (LI-120) pH meter was used for pH measurements. The pH meter was standardized using buffer solution of pH value 7.0. A thermostatically controlled mechanical shaker was used for agitating the samples. Fourier transform infrared spectrometry (Shimaduz 84005 FT-IR) was used to analyze the organic functional groups of the adsorbents. Scanning electron microscopy (JOEL JSM 6360) was used to analyze the surface of the adsorbent.

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. All the chemicals used to analyze the characteristic of carbon was of analytical reagent grade from E-Merck, Himedia, Ranboxy, Sd's Fine. The characteristic of wastewater before and after treatment was analyze and summarized in Table-2.

Adsorption studies: Removal of Ni(II) using activated carbon was carried out by batch method and the influence of various parameters such as effect of pH, agitation time, adsorbent dose and initial metal ion concentrations were studied. For each experimental run 100 mL of wastewater of known concentration of metal ion was taken in 300 mL stoppard polyethylene reagent bottles, pH was adjusted 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, supernatant solution was separated from activated carbon (COCAC/CAC) by filtration using Whatman filter paper number 41 and final concentration of metal ion was determined in the filtrate by atomic absorption spectrophotometer (AAS). Blank solutions were treated similarly (without adsorbent) and the concentration was taken as initial concentration. The removal percentage (R %) is determined as the ratio of difference in metal concentration before and after adsorption (C_0-C_e) to the initial concentration of Ni(II) in the wastewater (C_0) was calculated using eqn. 1.

$$R\ \% = (C_0 - C_e)/C_0 \times 100 \qquad (1)$$

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

Effect of pH: Effect of pH was studied in the range of 2-8 ± 0.2 by adjusting pH with the addition of dilute aqueous solution of HCl or NaOH and buffer solutions. 100 mL of wastewater (63 mg/L of Ni(II)) was taken in reagent bottle and treated with 500 mg of adsorbent and after equilibrium, the final concentration of Ni(II) was determined.

Effect of agitation time: A series of 300 mL stoppard polyethylene container, each having 500 mg adsorbent and 100 mL wastewater [63 mg/L of Ni(II)] were shaken in mechanical shaker at room temperature (30 ± 1 °C). At the predetermined intervals, the solution of the specified flask was taken out and filtered. The concentration of Ni(II) in the filtrate was determined by AAS. The amount of Ni(II) adsorbed in each case was then determined as described earlier.

Effect of adsorbent and adsorbate concentrations: A series of 300 mL stoppard polyethylene container, each containing 100 mL of wastewater were treated with fixed amount of adsorbate (63 mg/L of Ni(II)) and varying amount of adsorbent (100-1500 mg). In another experiment, wastewater was treated with fixed amount of adsorbent (optimum dosage of 500 mg) and varying amount of adsorbate (63-18 mg/L). The flasks were shaken in mechanical shaker at room temperature (30 ± 1 °C) and after equilibrium, solution were filtered. The amount of Ni(II) in filtrate was then determined by AAS, amount of Ni(II) adsorbed in each case was calculated as above.

Desorption studies: Desorption studies help in recycling of the adsorbent and recovery of metals. After equilibrium, adsorbent saturated with nickel was removed from solution 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 30 min at room temperature (30 ± 1 °C) using a mechanical shaker. The solutions were then filtered and analyzed for metal concentration.

Kinetics: The kinetics of the interactions were studied by determining the amount adsorbed at different agitation times for various concentration of the Ni(II) (20, 15 and 10 mg/L) at constant adsorbent dosage (100 mg/100 mL) at optimum pH. Various kinetic models pseudo-first-order, pseudo-second-order and reversible-first-order have been applied for the experimental data to predict the adsorption kinetic[18].

The pseudo-first-order-kinetic can be expressed as

$$dq_t/dt = K_1\ (q_e - q_t) \qquad (2)$$

where q_e is the amount of nickel adsorbed at equilibrium per unit weight of adsorbent (mg/g), q_t is the amount of nickel adsorbed at any time (mg/g) and K_1 (h^{-1}) is the adsorption rate constant.

By integrating eqn. 2 and rearranging the resultant equation, the pseudo-first-order-kinetics can be rewritten as

$$\ln\ (q_e - q_t) = -K_1t + \ln\ q_e \qquad (3)$$

As indicated by eqn. 3 a plot of $\ln\ (q_e - q_t)$ *versus* 't' would give a straight line with a slope of $-K_1$ and an intercept of lnqe.

The pseudo-second-order-kinetic equation can be written as

$$dq_t/dt = K_2(q_e - q_t)^2 \qquad (4)$$

Integration of eqn. 4 yields

$$1/q_e - q_t = 1/q_e + K_2t \qquad (5)$$

Eqn. 5 can be rearrange into a linear form as follows

$$t/q_t = 1/K_2q_e^2 + 1/q_et \qquad (6)$$

where K_2 (g/mg h) is the rate constant. K_2 and q_e can be obtained from the intercept and slope of plotting t/q_t *versus* 't'.

The sorption of metal ion from liquid phase to solid may be considered as reversible reaction with an equilibrium state between two phases[19]. A simple first-order reaction model can be used to correlate the rate of the reaction. The liquid film diffusion equation can be expressed as

$$\ln [1-U_{(t)}] = -Kt \qquad (7)$$

where $U_{(t)}$ is fractional attainment of equilibrium (q_t/q_e) and K (h^{-1}) the overall rate constant.

As indicated by eqn. 7, a plot of ln [1 - $U_{(t)}$] *versus* 't' would give a straight line with a slope of K (h^{-1}) the overall rate constant. Both forward rate constant $\mathbf{k_1}$ and backward rate constant $\mathbf{k_2}$ is obtained from K (h^{-1})

$$K = k_1 + k_2 = k_1 + k_1/K_c = k_1(1 + 1/K_c) \qquad (8)$$

$$K_1 = [K/1 + 1/K_c] \qquad (9)$$

$$K_c = X_e/a-X_e \qquad (10)$$

$$X_e = C_0 - C_e \qquad (11)$$

where K_c is the equilibrium rate, C_0 and 'a' is initial metal ion concentration, C_e is the concentration of metal ion at equilibrium.

In order to understand the nature of diffusion process responsible for the adsorption of nickel on COCAC and CAC, attempts were made to calculate the pore and film diffusion coefficient for various concentrations of Ni(II) using the following equations[20].

$$D_p = 0.03 \times r_o^2/t_{1/2} \qquad (12)$$

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

$$D_f = 0.23 \times r_o\delta \times C^*/C.t_{1/2} \qquad (13)$$

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.

Isotherm: Adsorption isotherm was studied by varying initial metal ion concentration of Ni(II) from 18-44 mg/L at constant adsorbent dosage (100 mg/100 mL). The adsorption was allowed to proceed until equilibrium between the amount of metal ions adsorbed on the adsorbent and that in solution was reached. Equilibrium adsorption isotherms are usually used to determine the capacity of an adsorbent. The experimental adsorption equilibrium data were analyzed in terms of Langmuir, Freundlich and Temkin isotherm models[21].

Langmuir sorption isotherm equation can be expressed as eqn. 14.

$$1/q_e = 1/b + 1/ab^*1/C_e \qquad (14)$$

where C_e and q_e is the metal ion concentration in the solution (mg/L) and sorbent at equilibrium (mg/g). Langmuir constant 'b' and 'a' are related to sorption capacity and energy of sorption, respectively and can be calculated from the intercept and slope of the linear plot, $1/q_e$ *versus* $1/C_e$.

The essential characteristics of the Langmuir isotherm can also be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L which is defined as

$$R_L = 1/(1 + aC_0) \tag{15}$$

where 'a' is the Langmuir constant and C_0 is the initial concentration of nickel. The R_L value indicates the type of isotherm, according to the following adsorption characteristics, $R_L = 1$ (linear adsorption), $R_L = 0$ (is irreversible), $R_L > 1$ (is unfavorable) and $0 < R_L < 1$ (is favorable). If the value of R_L is considerably less than 1.0 the adsorption is considered to be favorable[22].

Freundlich isotherm equation can be written as

$$\log q_e = \log K_f + 1/N_f \log C_e \tag{16}$$

where q_e and C_e are the equilibrium concentrations of nickel in the adsorbent and liquid phases in mg/g and mg/L, respectively, K_f and N_f are the Freundlich constants that are related to the sorption capacity and intensity and it can be calculated from the slope and intercept of the linear plot with log q_e *versus* log C_e.

Temkin isotherm equation can be rearranged as follows

$$q_e = a_t + 2.3b_t \log C_e \tag{17}$$

where a_t and b_t are Temkin isotherm constant and can be calculated from the intercept and slope of the linear plot with q_e *versus* log C_e.

RESULTS AND DISCUSSION

Characteristics of COCAC and CAC (Table-1) show that COCAC has higher moisture content than CAC. The higher moisture content of COCAC suggested that the thermal activation has made the carbon more porous. Coconut oilcake activated carbon has higher ash content than CAC, which indicates less carbon content.

TABLE-1
CHARACTERISTICS OF COCONUT OILCAKE CARBON (COCAC)
AND COMMERCIAL ACTIVATED CARBON (CAC)

Control test	COCAC	CAC
Bulk density (g mL^{-1})	0.67	0.76
Moisture (%)	4.29	0.49
Ash (%)	15.67	2.17
Solubility in water (%)	15.93	1.31
Solubility in 0.25 M HCl (%)	23.73	3.53
pH	9.84	6.59
Ion exchange capacity (m equiv g^{-1})	Nil	Nil
Surface area (m^2 g^{-1})	618.02	194.84
Iron (%)	0.02	0.08

Effect of agitation time: The effect of agitation time at pH 7.2 for four different concentrations of Ni(II) over the range 5-20 mg/L with adsorbents dosage of 100 mg/100 mL is shown in Fig. 1 (A and B). Equilibrium condition on COCAC was established within 60 min for 20 and 15 mg of Ni(II)/L. An equilibration time of 75 min was observed with 10 and 5 mg Ni(II)/L. It could be seen that nickel removal increases with time and remains constant after 75 min (90-96 %) over the above concentration range examined. In the case of CAC the removal of nickel was found to be 75-81 % only at 180 min for the same concentration range studied. Fig. 1(C) and 2 show equilibrium adsorption was established within 20 min for Ni(II) removal (63 mg/L) by increasing a dose of 500 mg/100 mL of adsorbent (COCAC-97 % or CAC-76 %). It is clear from these results that for maximum uptake of metal ions by carbon, equilibration time was dependent on both adsorbent and adsorbate concentration.

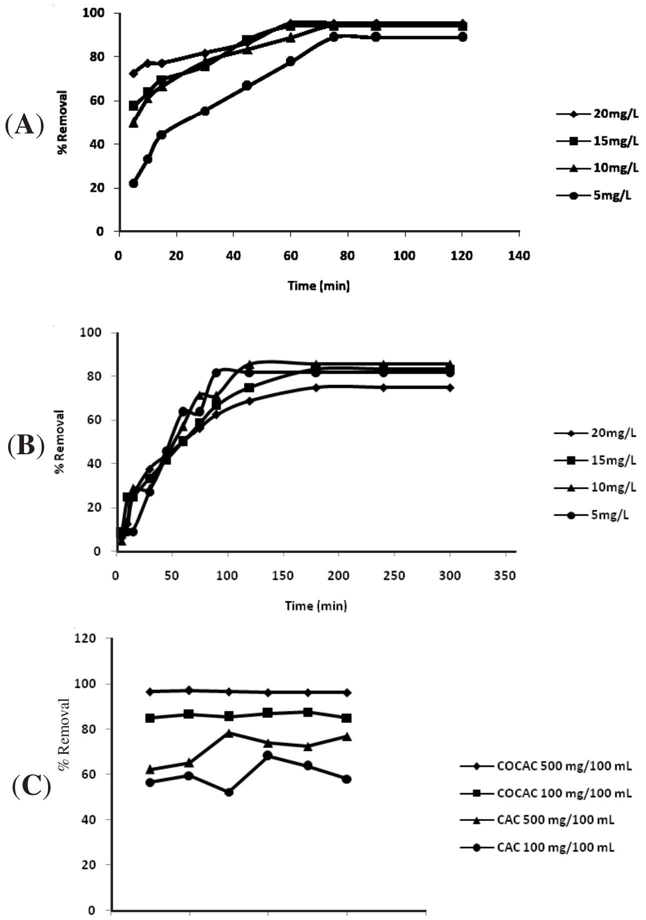

Fig. 1. Effect of contact time for the removal of Ni(II); (**A**) By COCAC; (**B**) By CAC; (**C**).Both COCAC and CAC (500 mg and 100 mg/100 mL of adsorbents, equilibration time = 30 min, concentration of Ni(II) = 63 mg/L)

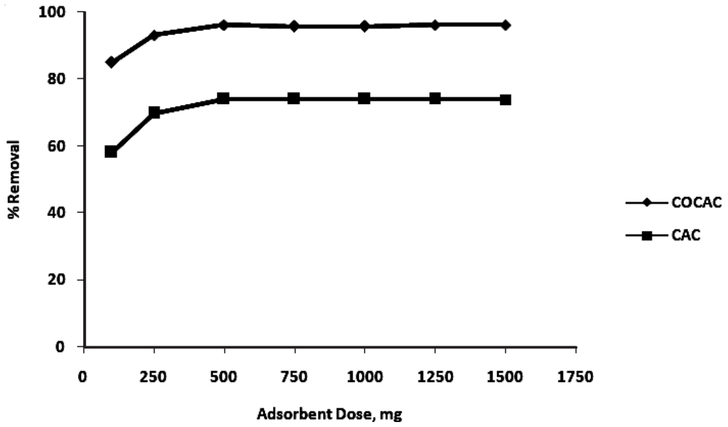

Fig. 2. Effect of carbon dosage on the removal of Ni(II) by COCAC and CAC

Effect of initial metal ion concentration: The equilibrium sorption capacities of sorbents obtained from experimental data at different initial concentration of nickel was shown in Fig. 3. As seen from the results, the sorption capacities of the sorbent increased with increasing nickel concentration; since the initial metal ion concentration provided an important driving force to overcome all mass transfer resistance. This would results in increasing adsorption capacity of all the adsorbents increased with initial metal ion concentration. The removal of Ni(II) increases from 2.02-12.2 mg/g for COCAC and from 1.31-9.74 mg/g for CAC when initial concentration of Ni(II) was increased from 18-63 mg/L, respectively. At optimum conditions (500 mg/100 mL of adsorbent and pH 7 for COCAC and CAC) other metal ions present in wastewater was effectively removed by activated carbons, values were shown in Table-2.

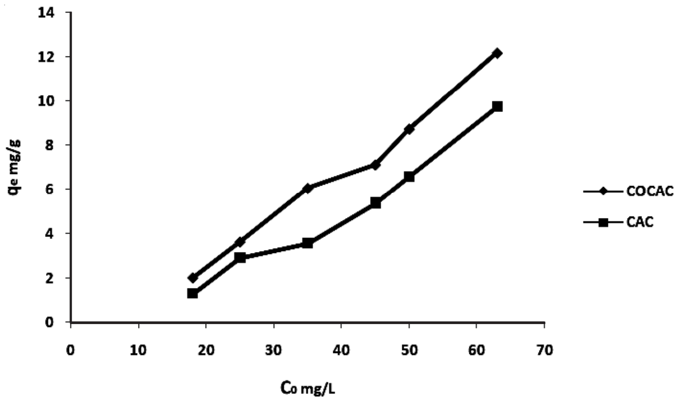

Fig. 3. Effect of initial metal ion concentration for the removal of Ni(II) by COCAC and CAC

Effect of initial pH: The effect of initial pH on the removal of Ni(II) by COCAC and CAC are shown in the Fig. 4. The Ni(II) removal by COCAC and CAC increased with increasing pH and attained values of 97 and 74 %, respectively at an initial pH of 5 and 6. It is evident that the COCAC was effective for the maximum removal of nickel ion over the pH range 5-8 ± 0.2, whereas CAC was effective for the maximum removal in the pH range 6-8 ± 0.2.

TABLE-2
CHARACTERISTICS OF PLATING INDUSTRY WASTEWATER

Parameter	Before treatment (mg/L)	After treatment (mg/L)	
		COCAC	CAC
pH	6.30	8.0-8.5	6.3 to6.5
Bsicity	80.00	10.00	15.00
Total solids	1850.00	92.00	260.00
Suspended solids	270.00	9.00	14.00
Cyanide	0.60	0.40	0.55
Copper	6.00	0.01	0.05
Nickel	63.00	0.01	14.30

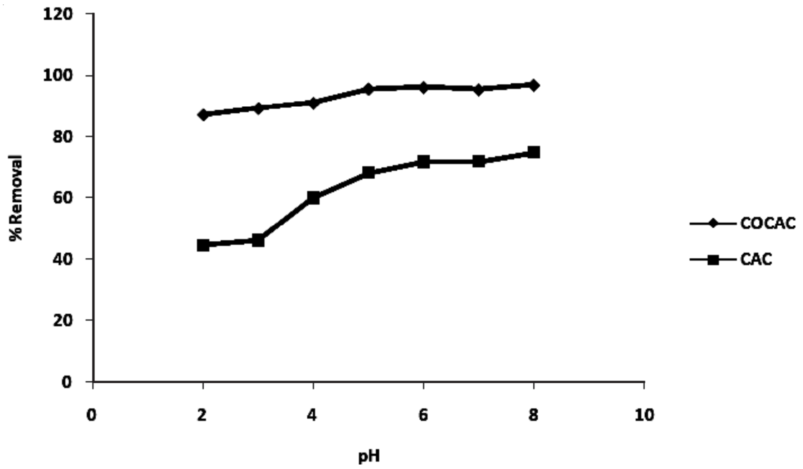

Fig. 4. Effect of initial pH on the removal of Ni(II) by COCAC and CAC

The influence of pH on Ni(II) removal by COCAC and CAC 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 relative[23]. As the pH decreases, the positive characteristics of the carbon surface intensify. Since the species to be adsorbed at low pH is Ni(II), which is also positive, the adsorption of Ni(II) is not favored. 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 Ni(II). 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 favorable. Similar results were reported for the adsorption of Ni(II) on hydrous oxide of gels of iron[24] and goethite[25]. The following reaction mechanism is suggested for the adsorption of Ni(II) on the COCAC surface. Based on the work of Frumkin[26] the surface oxide groups present on carbon can undergo hydrolytic reactions with the result proton exchangeable sites such as $C_XOH_2^{2+}$, C_XOH^+ may be formed. These groups may play a significant role in removing nickel ions as follows:

$$2C_XOH^+ + Ni^{2+} \rightarrow (C_XO)_2Ni^{2+} + 2H^+$$
$$C_XOH_2^{2+} + Ni^{2+} \rightarrow C_XONi^{2+} + 2H^+$$

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

Desorption studies: Desorption studies were carried out to further elucidate the mechanism of adsorption of Ni(II). Attempts were made to desorbs Ni(II) from the spent carbons using hydrochloric acid of various strength ranging from 0.05-0.35 M. The per cent recoveries of Ni(II) for COCAC were found to be 56.12, 68.59, 74.82, 81.06, 93.53, 99.99 and 99.99 % by 0.05, 0.10, 0.15, 0.20, 0.25, 0.30 and 0.35 M hydrochloric acid, respectively. In the case of CAC, the corresponding values were 94.53, 98.83, 99.99, 99.99, 99.99, 99.99 and 99.99 % for the same concentration of HCl. In highly acidic medium protons (H^+ ions) compete with Ni(II) ions and displace the same. Hence, it could be suggested that ion exchange mechanism involving, replacement of proton is an important aspect to be considered in the adsorption processes by both carbons.

Adsorption kinetics: The kinetic of adsorption of nickel was studied using three kinetic models, such as pseudo-first-order, pseudo-second-order and reversible-first-order kinetic models at low initial concentration of nickel.

Pseudo-first-order model: The adsorption kinetics was investigated for better understanding of the dynamics of adsorption of metal ion onto COCAC and CAC, also obtaining predictive models that allow estimations off the amount adsorbed with the treatment time. This information could be used for scale-up to a larger system.

Pseudo-first-order kinetic was applied, to the obtained experimental data. The kinetic plots were drawn for two activated carbon adsorbents and the adsorption rate constants (K_1), adsorption capacity (q_e) were calculated from the slope and intercepts of the plots of ln (q_e - q_t) against t (Fig. 5). The value of q_e (theo) calculated from kinetic models are compared with experimental values q_e (exp) in Table-3. It is found that the sorption of Ni(II) by CAC follows pseudo-first-order-kinetic, for the reason that the values of q_e (theo) are found to be very close to q_e (exp) and also high values of coefficient (R^2) factor.

Pseudo-second-order model: The relationship with t/q_t and't' is linear with a slope of $1/q_e$ and intercept of $1/K_2\ q_e^2$ (Fig. 6). These can be obtained from a plot of t/q_t *versus* 't' shown in Fig. 8. The values of q_e (theo) are found to be close to q_e (exp) and also very high values of coefficient (R^2) factor (Table-3) conforms adsorption of Ni(II) by COCAC follows pseudo-second-order kinetic model well[27].

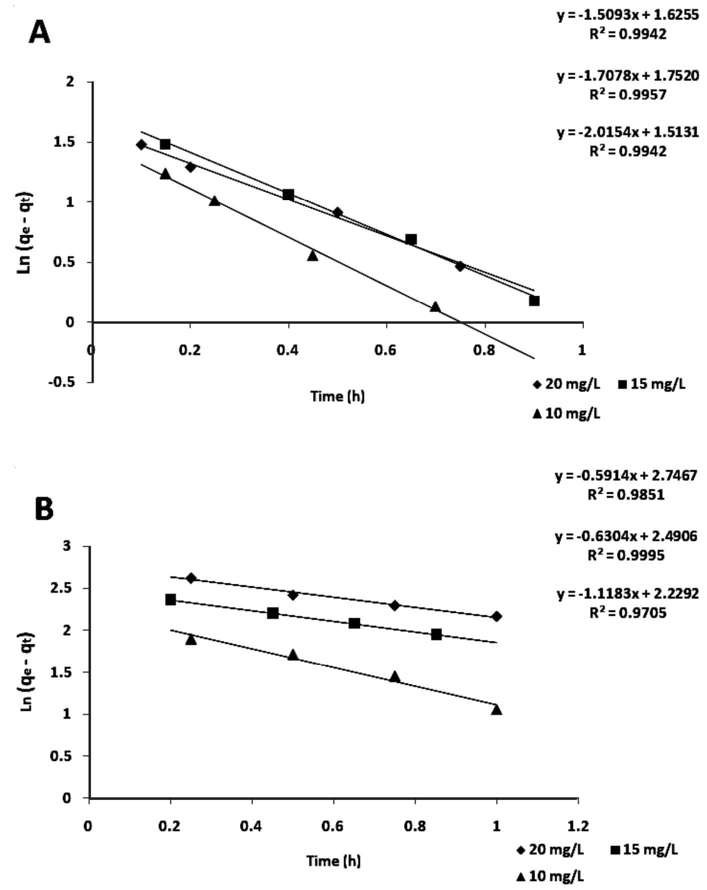

Fig. 5. Pseudo-first-order-kinetic fits for the adsorption of Ni(II) in COCAC (A) and CAC (B)

TABLE-3
ADSORPTION KINETICS FOR NICKEL

Adsorbent	Concentration of Ni(II) (mg/L)	q_e (exp) (mg/g)	Pseudo-first-order			Pseudo-second-order			Reversible-first-order			
			k_1 (h^{-1})	R^2	q_e (theo) (mg/g)	k_2 (g/mgh)	R^2	q_e (theo) (mg/g)	K (h^{-1})	k_1 (h^{-1})	k_2 (h^{-1})	R^2
COCAC	20	19.10	1.509	0.9942	5.08	1.932	0.9990	17.99	1.509	1.4411	0.0679	0.9942
	15	14.10	1.708	0.9957	5.77	0.920	0.9974	13.81	1.708	1.6055	0.1025	0.9958
	10	9.44	2.015	0.9942	4.54	1.168	0.9992	9.35	2.015	1.9022	0.1128	0.9942
CAC	20	18.75	0.591	0.9851	15.59	0.136	0.9983	14.84	0.591	0.5541	0.0369	0.9851
	15	13.75	0.630	0.9995	12.07	0.191	0.9791	10.38	0.630	0.5775	0.0525	0.9995
	10	8.57	1.118	0.9705	9.29	0.024	0.7561	17.99	1.118	0.9581	0.1599	0.9705

Reversible-first-order model: Plot for reversible-first-order reaction model was made for COCAC and CAC (Fig. 7). Approximate linear fit was generally observed for all concentration of nickel ion. Correlation coefficients, overall rate constant K, forward rate constants k_1 and backward rate constant k_2 were calculated and summarized in Table-3. The values of coefficient (R^2) factor comparatively lower than other two kinetics model.

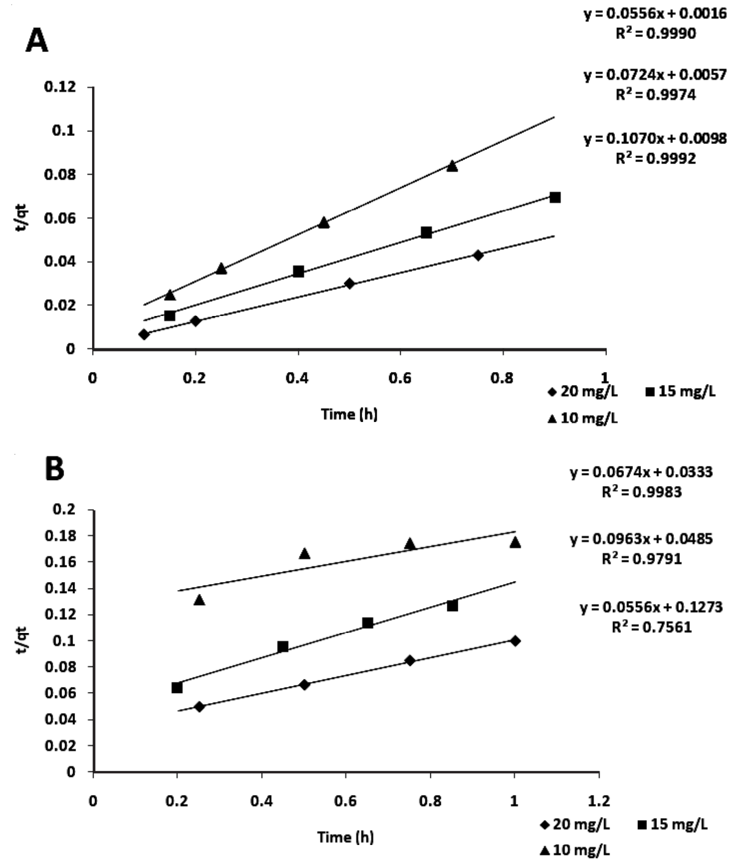

Fig. 6. Pseudo-second-order-kinetic fits for the adsorption of Ni(II) in COCAC (A) and CAC (B)

Diffusion coefficient: According to Michelsen *et al.*[28] 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} 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}-10^{-13} cm^2 s^{-1}. It is evident from the Table-4 that the removal of Ni(II) follows film diffusion process, since the coefficient values are closer to the range of 10^{-6}-10^{-8} cm^{2}s^{-1}.

Adsorption isotherms: Freundlich, Langmuir and Temkin isotherm models are the most frequently employed models to explain the adsorption process.

Based on Freundlich adsorption model the relation between the metal uptake capacity x/m (mg/g) of adsorbent and the residual metal ion concentration "C_e"

(mg/L) at equilibrium[22] is shown in Fig. 8. The values of intercept log K (adsorbent capacity) and slope 1/n (sorption intensity) were calculated from the plots and summarized in Table-5 for COCAC and CAC, respectively. The value of 1 < n < 10 indicates a favorable adsorption of Ni(II) on both COCAC and CAC[25].

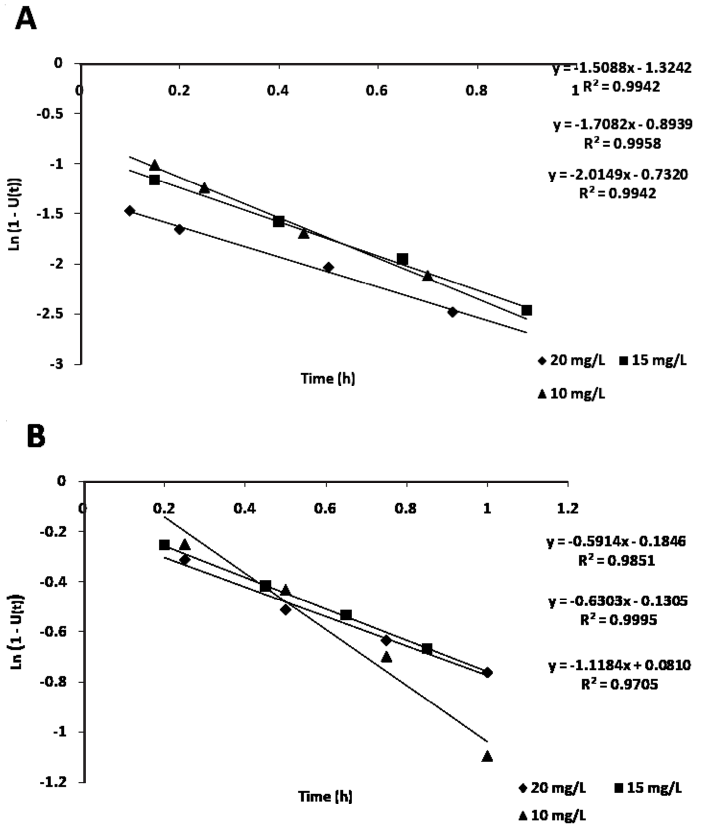

Fig. 7. Reversible-first-order-kinetic fits for the adsorption of Ni(II) in COCAC (A) and CAC (B)

TABLE-4
DIFFUSION COEFFICIENTS FOR THE ADSORPTION OF Ni(II) ION ON COCAC AND CAC

Carbon	Ni(II) (mg/L)	Pseudo-first-order kinetic ($cm^2 s^{-1}$)		Pseudo-second-order kinetic ($cm^2 s^{-1}$)		Reversible-first order ($cm^2 s^{-1}$)	
		Film diffusion	Pore diffusion	Film diffusion	Pore diffusion	Film diffusion	Pore diffusion
COCAC	20	6.4768×10^{-9}	4.3124×10^{-8}	1.1493×10^{-7}	7.6525×10^{-7}	6.4768×10^{-9}	4.3124×10^{-8}
	15	7.2158×10^{-9}	4.8812×10^{-8}	4.0385×10^{-8}	2.7319×10^{-7}	7.2158×10^{-9}	4.8812×10^{-8}
	10	8.5490×10^{-9}	5.7585×10^{-8}	3.4341×10^{-8}	2.3132×10^{-7}	8.5490×10^{-9}	5.7585×10^{-8}
CAC	20	2.4901×10^{-9}	1.6890×10^{-8}	7.9422×10^{-9}	5.3869×10^{-8}	2.4901×10^{-9}	1.6890×10^{-8}
	15	2.5955×10^{-9}	1.8004×10^{-8}	8.1797×10^{-9}	5.6740×10^{-8}	2.5955×10^{-9}	1.8004×10^{-8}
	10	4.3062×10^{-9}	3.1950×10^{-8}	6.4061×10^{-10}	4.7531×10^{-9}	4.3062×10^{-9}	3.1950×10^{-8}

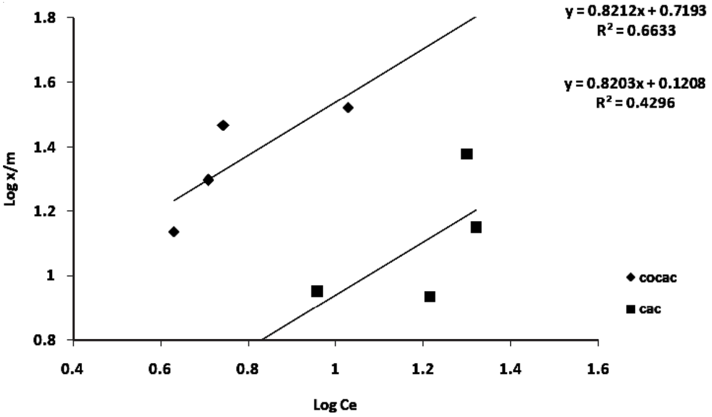

Fig. 8. Freundlich isotherm for nickel in COCAC and CAC system

TABLE-5
ADSORPTION ISOTHERM PARAMETER FOR Ni(II)
ION ADSORPTION BY COCAC AND CAC

Adsorbent	Langmuir model				Freundlich model			Temkin model		
	b	a	ab	R^2	K_f	N_f	R^2	a_T	b_T	R^2
	(mg g^{-1}) (L mg^{-1})				(mg g^{-1}) (L mg^{-1})			(mg g^{-1}) (L mg^{-1})		
COCAC	555.56	0.007	3.635	0.704	5.240	1.218	0.663	9.917	19.047	0.722
CAC	30.77	0.041	1.275	0.416	1.321	1.219	0.430	17.443	11.374	0.368

The Langmuir equation relates solid phase adsorbate concentration (q_e) and uptake to the equilibrium liquid concentration (C_e). Fig. 9 shows that isotherm data fits the Langmuir equation well, values of K_A and q_m were determined from the Langmuir plots were listed in Table-5 for activated carbons. R_L value indicates favorable adsorption of Ni(II) on COCAC and CAC (Table-6) at room temperature 30 ± 1 ºC.

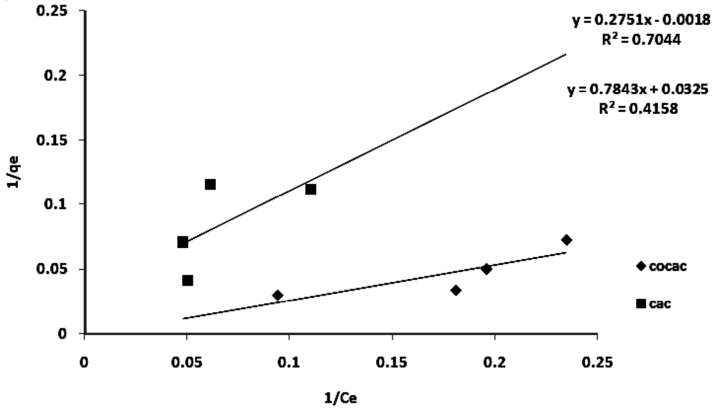

Fig. 9. Langmuir isotherm for nickel with COCAC and CAC system

TABLE-6
EQUILIBRIUM PARAMETER R_L VALUES UNDER OPTIMUM pH = 7.2 CONDITIONS

Concentration of initial metal ion	R_L Values	
	COCAC	CAC
63	0.6940	0.2791
50	0.7407	0.3279
44	0.7645	0.3566
35	0.8032	0.4107
25	0.8511	0.4938
18	0.8881	0.5754

Temkin isotherm based on the interaction of different adsorbates on the adsorbent, a plot of q_e *versus* log C_e was shown in Fig. 10 for both COCAC and CAC. The values of a_t and b_t from the Temkin isotherm (Table-5) suggests that the adsorption of Ni(II) on COCAC and CAC is favorable adsorption. Based on regression coefficient values Temkin model is found to be more suitable for adsorption process.

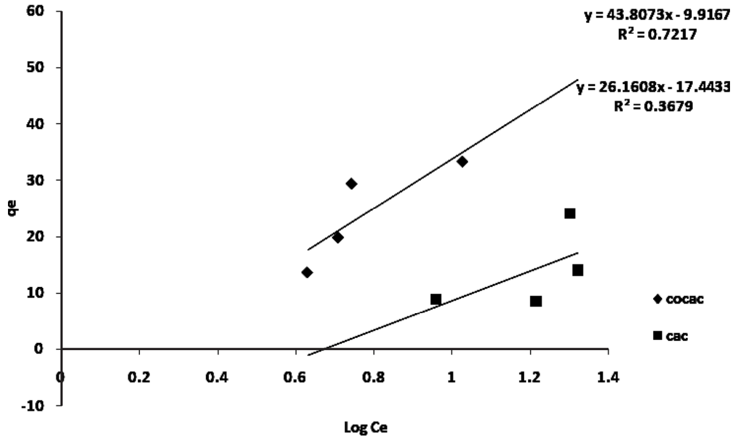

Fig. 10. Temkin isotherm for nickel with COCAC and CAC system

SEM and FT-IR studies: The scanning electron microscope (SEM) image of coconut oilcake activated carbon (COCAC) and commercial activated carbon (CAC) (Fig. 11 and 12) were recorded. The SEM image of activated carbons shows an irregular shape and size. Then COCAC particles have a large number of pores and broken edges than CAC, these are largely responsible for the extent of surface area and adsorptive capacity of carbon.

In order to determine the functional groups that are responsible for metal uptake, an FT-IR analysis in solid phase was performed on the activated carbons[29]. FT-IR spectra for COCAC has been obtained and shown in Fig. 13. Spectra displays a number of adsorption peaks, indicating the complex nature of the material examined. Fig. 13 shows that the peaks observed at 926 cm^{-1} can be assigned to the C-H group. The peaks observed at 1033 cm^{-1} can be assigned to the C-O stretching vibration of alcohols. The peak around 1116 cm^{-1} is due to the C-O-C stretching vibration of substituted ethers. The sharp band at 2360 and 2345 cm^{-1} can be assigned to the N-H group of amino acids.

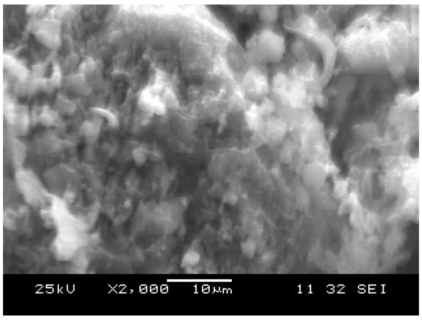

Fig. 11. SEM Photograph of COCAC

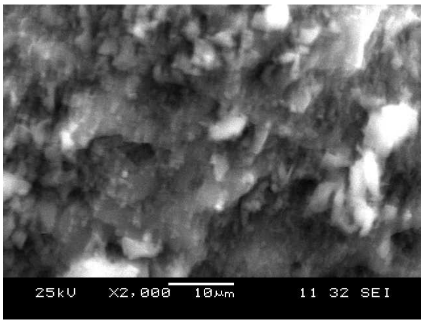

Fig. 12. SEM photograph of CAC

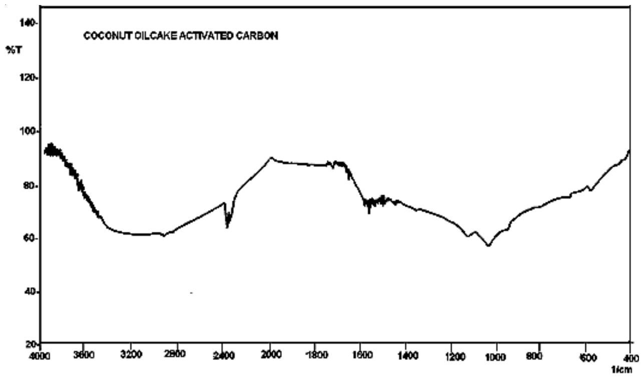

Fig. 13. FT-IR spectra of COCAC

Conclusion

Removal of nickel from wastewater is possible by using available low cost adsorbents. The present investigation shows that the activated carbon prepared from coconut oilcake, an agricultural by-product is able to remove Ni(II) effectively from wastewater. 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 greater adsorption capacity over a wide range of pH than CAC. Hence, other metal ions present in the wastewater were also effectively removed by COCAC than CAC. The kinetics of Ni(II) adsorption by COCAC follows the pseudo-second-order expressions, in the case of CAC it follows pseudo-first-order-kinetic, hence film diffusion being the essential rate-controlling step. The Temkin model was found to be linear indicating the applicability of classical adsorption isotherm to this adsorbate-adsorbent system.

Alternatively, agricultural by-product is used for activated carbon preparation, which can be processed in the place of commercial activated carbon. As coconut oilcake is discarded as waste from oil industries, activated carbon prepared from this oil cake shows better adsorption capacity, which is expected to be an economical product for metal ion remediation from wastewater. The reported data may be useful for designing an economically cheap treatment process using batched or 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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