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Uptake of toxic metals from wastewater by activated carbon from agro industrial by-product

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Activated carbon prepared from neem oilcake, by pyrolysis accompanied with microwave oven activation is evaluated for the adsorption of Cd(II) and Ni(II) from wastewater. Parameters such as pH, agitation time, metal ion concentration and adsorbent dose are studied. The percent removal increased with pH from 2.0 to 7.0. The adsorption data fit well with Langmuir, Freundlich and Temkin isotherm models. The adsorption capacity (q_e) calculated from Langmuir isotherm are 54.95 mg Ni(II)/g and 23.70 mg Cd(II)/g at an optimal pH of 7.0 at 30°C for the particle size 0.120-0.075 mm. Adsorption of Cd(II) and Ni(II) by activated carbon from neem oilcake follows pseudo-second-order kinetic model. Desorption studies with dilute hydrochloric acid indicate that quantitative recovery of cadmium and nickel ions are possible. The mechanism of adsorption seems to follow ion exchange process. As neem oilcake is discarded as waste from oil processing industries, the carbon could be exploited for metal ions recovery from wastewater.

Keywords: Activated carbon, Toxic metal, Wastewater, Neem oilcake

Increasing industrialization has led to rapid disposal of heavy metals in to the environment. It is well known that some heavy metals are harmful and lead to toxic effects in human beings and disturb ecological environment. Both cadmium and nickel, are present in wastewater from several industries¹⁻³. Acute exposure of cadmium and nickel causes potential hazards due to its bioaccumulations in food chain⁴⁻⁶ and has led to stricter environmental regulations on wastewaters for dischargeable purpose. In India, the permissible limit for cadmium and nickel for discharge into inland surface⁷ is 2.0 mg/L and for drinking water^{8,9} is 0.01 mg/L. This necessitates the removal of cadmium and nickel from wastewater before its discharge into the environment. Distillation, precipitation, ion exchange, filtration, reverse osmosis, adsorption on activated carbon were used for removal of heavy metals in aqueous solution¹⁰.

Adsorption of heavy metals by using activated carbon has absolutely been the most popular method used in wastewater treatment. The cost of activated carbon prepared from agricultural waste by-products is comparatively lower than commercial activated carbon¹¹. Several research groups have anticipated and studied^{5,12-16} the removal of heavy metals from water and wastewater using low cost activated carbon

adsorbents prepared from different agricultural byproducts. Rao and Khan^{17,18} reported that the removal and recovery of Cu(II), Cd(II) and Pb(II) by neem oilcake which is better by column operation as compared to batch process in single metal and multi metal systems.

Since limited studies have been repoted with respect to activated carbons of these materials for the removal of other metals, attempts were made to study the removal of Cd(II) and Ni(II) from wastewaters, using microwave activated carbon prepared from Azadirachta indica (neem) oilcake. Microwave energy is recently used as heating source for activating the carbonized materials; resulting activated carbon shows better results¹⁹⁻²².

In this study, microwave activated neem oilcake carbon was prepared by treated with microwave energy using domestic microwave oven for heavy metal removal from wastewater. The effect of parameters such as pH, contact time, adsorbent dose and initial metal ion concentration, adsorption kinetics and isotherms were also studied.

Materials and Methods

Procedure for adsorbent preparation and activation

After extracting oil from Azadirachta indica (neem) seed, the residual matter called oilcake was washed with water and dried in hot air-oven at 100-110°C for

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24 h. After drying, the oilcakes were subjected to pyrolysis process. During slow carbonization of the raw material in the absence of air at a temperature range of $500-600^{\circ}C^{23}$, volatile products were removed and the residue was converted into a char. The char was then subjected to microwave activation in domestic microwave oven. The input power of microwave equipment was set at 360 W for 5 min²⁴. The resulting activated carbon particles were ground in a mill, and sieved in a 120 - 200 ASTM mesh size and stored in a desiccator.

Instrumentation

Muffle furnace (Shivans, Gujarat) was used for carbonization of the oilcake. Domestic microwave oven (LG MC - 7648 WSH) was used for activation of the adsorbents. Atomic absorption spectrophotometer (Elico SL 163) was used for determining metal ions concentration. An Elico (LI -120) pH meter was used for pH measurements. The pH meter was standardized using buffer solution of a pH value of 7.0. A thermostatically controlled mechanical shaker was used for equilibrating 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.

Reagents

Working standards were prepared by progressive dilution of stock solutions of cadmium and nickel (1000 mg/L) from E-Merck, AR reagent grade HCl, NaOH, buffer solution (E-Merck) were used to adjust the solution pH. Analytical reagent grade chemicals from E-Merck, Hi-media, Ranbaxy and SD-Fine were used for experimental studies. The characteristics of wastewaters were analyzed before and after treatment and results are given in Table 3.

Adsorption studies

Removal of Cd(II) and Ni(II) using activated carbon was carried out by batch method. 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 stoppered 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 $(30 \pm 1^{\circ}\text{C})$ 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 by filtration using wahtman filter paper number 41 and the final concentration of metal ions were 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 batch adsorption study was replicated thrice for each of the adsorbents. The experimental conditions for these studies are given in Table 1. Desorption studies were carried out with 100 mL of (0.025-0.15 M) concentrated HCl solution,

Table	Table 1- Experimental conditions for batch adsorption studies								
S.No	Optimization study	Constants	Variables						
01	Agitation time	 Metal ion concentration (75 mg/L for Cd(II) and 63 mg/L for Ni(II)). Adsorbent weight (500 mg/ 100 mL) pH 7± 0.2 	Time (5, 10, 15, 20, 25 and 30 min)						
02	рН	 Metal ion concentration (75 mg/L for Cd(II) and 63 mg/L for Ni(II)). Adsorbent weight (500 mg/ 100 mL) contact time (30 min) 	pH ranges from 2 to 7 ± 0.2						
03	Concentration of initial metal ion	 Adsorbent weight (500 mg/ 100 mL) pH 7±0.2 Agitation time 30 min 	Concentration of metal ions For Cd(II) 75, 60, 45, 30, 15, and 9 mg/L For Ni(II) 63, 50, 44, 35, 25 and 18 mg/L						
04	Adsorbent weight	 Metal ions concentration (75 mg/L for Cd(II) and 63 mg/L for Ni(II) pH 7± 0.2 Agitation time 30 min 	Adsorbent weight (0.1, 0.25, 0.5, 0.75, 1.0, 1.25 and 1.50 g/100 mL)						

and the bottles were shaken for 30 min at room temperature $(30 \pm 1^{\circ}C)$ using a mechanical shaker. The solutions were then filtered by using whatman filter paper number 41. The filtrates were analyzed for Cd(II) and Ni(II) desorbed.

Kinetics

The kinetics of the interactions were studied by determining the amount adsorbed at different agitation times for various concentrations of the metal ions (45, 30 and 15 mg/L for Cd(II) and 20, 15 and 10 mg/L for Ni(II)) at constant adsorbent dosage (100 mg/100 mL) and 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 kinetic²⁵.

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

$$\ln (q_{\rm e} - q_{\rm t}) = -K_{\rm l}t + \ln q_{\rm e} \qquad \dots (1)$$

where q_e is the amount of metal ions adsorbed at equilibrium per unit weight of adsorbent (mg/g), q_t is the amount of metal ions adsorbed at any time (mg/g) and K_1 (h⁻¹) is the adsorption rate constant.

As indicated by Eq. (1) 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 $\ln q_e$.

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

$$t/q_{\rm t} = 1/K_2 q_{\rm e}^2 + 1/q_{\rm e} t$$
 ... (2)

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 also be considered as reversible reaction with an equilibrium state between two phases²⁶. 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

$$\ln (1 - U_{(t)}) = -Kt \qquad \dots (3)$$

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

As indicated by Eq. (3), a plot of $\ln (1 - U_{(t)})$ versus t would give a straight line with a slope of K the overall rate constant. Both forward rate constant and backward rate constant k_1 and k_2 are obtained from K (h⁻¹)

 $K = k_1 + k_2 = k_1 + k_1/K_c = k_1 (1 + 1/K_c) \qquad \dots (4)$

$$K_1 = [K/1 + 1/K_c]$$
 ... (5)

$$K_{\rm c} = X_{\rm e}/a - X_{\rm e} \qquad \dots \tag{6}$$

$$X_{\rm e} = C_0 - C_{\rm e} \qquad \qquad \dots \tag{7}$$

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.

Isotherm

Adsorption isotherm was studied by varying initial metal ion concentration (9 mg/L to 75 mg/L for Cd(II) and 18 mg/L to 63 mg/L for Ni(II)) 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 models²⁷.

The Langmuir sorption isotherm equation can be expressed as.

$$1/q_{\rm e} = 1/b + 1/ab^* 1/C_{\rm e}$$
 ... (8)

where C_e is the metal ion concentration in the solution at equilibrium (mg/L), q_e is the metal ion concentration on the sorbent at equilibrium (mg/g), *b* and *a* are Langmuir constant which 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

$$R_{\rm L} = 1/(1+a\ C_0) \qquad \dots (9)$$

where 'a' is the Langmuir constant and C_0 is the initial concentration of metal ions. The R_L value indicates the type of the isotherm according to the following adsorption characteristics: $R_L = 1$ (linear adsorption), $R_L = 0$ (irreversible), $R_L > 1$ (unfavorable) and $0 < R_L < 1$ (favorable). If the value of R_L is considerably less than 1.0 the adsorption is considered to be favorable²⁸.

The Freundlich isotherm equation can be written as

$$\log q_{\rm e} = \log K_{\rm f} + 1/N_{\rm f} \log C_{\rm e}$$
 ... (10)

where q_e and C_e are the equilibrium concentrations of cadmium and 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 $q_{\rm e}$ versus log $C_{\rm e}$.

The Temkin isotherm equation can be rearranged as follows

$$q_{\rm e} = a_{\rm t} + 2.3 \ b_{\rm t} \log C_{\rm e} \qquad \dots (11)$$

where a_t and b_t are Temkin isotherm constant and it can be calculated from the intercept and slope of the linear plot with $q_{\rm e}$ versus log $C_{\rm e}$.

Results and Discussion

Characteristics of the adsorbent

Physicochemical characteristics of the adsorbent NOCAC are given in Table 2. The raw neem oilcake is expected to contain numerous organic compounds such as alkaloids, terpenoids and other heterocyclic compounds, which up on treatment with HCl extracts

Table	e 2- Characteristics of activated c	carbon (NOCAC)
S.No	Parameter	NOCAC
01	Bulk density (g/mL)	1.15
02	Moisture (%)	0.40
03	Solubility in water (%)	5.42
04	Solubility in acid (%)	50.08
05	pH	9.26
06	Surface area (m^2/g)	252.90
07	Ash (%)	72.85
08	Ash analysis (%)	
	(i) CaO	2.86
	(ii) MgO	1.22
	(iii) Fe ₂ O ₃	3.67
	(iv) Na ₂ O	2.06
	(v) K ₂ O	2.10
	(vi) Al ₂ O	5.85
	(vii) SiO ₂	81.60

a large amount of soluble organics and hence a higher value of solubility is noted. The high pH of the carbon is due to the presence of alkali and alkaline earth metal oxides associates with ash. The higher bulk density of the carbon may be due to the presence of high silica content. Silica may be available in amorphous or crystalline form. The presence of higher ash content inhibits surface area development because inorganics may fill or block some portions of existing micro pore volume. This may be the reason for the lower surface area observed in this carbon with high ash content^{29,30}.

In order to know the structure of adsorbent, morphological analysis of the NOCAC was performed by scanning electron microscopy. Figure 1 shows the structure of adsorbent obtained by scanning electron microscopy (SEM). This figure indicates that NOCAC have a large number of steps, kinds and broken edges in them and these show extensive surface area and active centers and may be used as a sorbent material.



Fig. 1- SEM photograph of NOCAC

Table 3– Characteristics of plating industry wastewaters of Ni and Cd plating units							
Sl.No	Parameter	Before t	reatment	After treatment			
		Cd	Ni	Cd	Ni		
01	pH	2.30	6.30	8.0-8.5	8.6-9.0		
02	Basicity (mg/L)	Nil	80.00	12.00	39.00		
03	Total solids (mg/L)	250.00	1850.00	90.00	189.00		
04	Suspended solids (mg/L)	40.00	270.00	10.00	58.00		
05	Cyanide (mg/L)	Nil	0.60	Nil	0.25		
06	Copper (mg/L)	15.00	6.00	0.10	0.01		
07	Nickel (mg/L)	21.00	63.00	6.00	17.00		
08	Zinc (mg/L)	20.00	Nil	0.10	Nil		
09	Cadmium (mg/L)	75.00	Nil	3.88	Nil		

The functional groups on NOCAC and the corresponding infrared absorption bands are shown in Table 4. As shown in Table 4, the spectra shows a number of absorption peaks, indicating the complex nature of NOCAC. Some inference can be drawn about the surface functional groups from FTIR spectra. The surface structures of carbon-oxygen (functional groups) are by far the most important structures in influencing the surface characteristics and surface behavior of carbon³¹⁻³³.

Effect of pH on removal of cadmium and nickel

The effect of pH on removal of Cd(II) and Ni(II) by the adsorbent NOCAC was carried out in the pH range 2.0-7.0 \pm 0.2 and the results are shown in Fig. 2. It can be noticed that the removal of metal ions increased with increasing pH of aqueous solution and reached maximum value at pH 5 for Ni(II). It is evident that the carbon is effective for the maximum removal of Ni(II) over the pH range 5-7. However, in the case of Cd(II), the maximum removal was

Table 4– The FTIR spectral characteristics of NOCAC							
FTIR peak	Adsorption bands (cm ⁻¹)	Assignment					
1	2920, 2852	(C–H) stretching doublet in alkyl group					
2	2375	(N–H) stretching in amino acid					
3	1594 - 1383	(C=O) formation of carboxylic functional group in surface of carbon					
4	1500-1400	$(-CH_2)$ stretching in aromatic skeletal					
5	1116	(S=O) stretching in sulphur compound					
6	1033	(-C–O) stretching in alcohols and phenols contain OH group					



Fig. 2- Effect of pH on removal of cadmium and nickel

observed at pH 7.0. At pH below 3, the H^+ ions compete with metal ions for the surface of the adsorbents. This could be due to the excess of H^+ ions surrounding the binding sites making sorption unfavorable. By taking into account these considerations, the optimum pH for removal of both Ni(II) and Cd(II) was fixed as 7.0. However at pH beyond 8.0 the tendency of metal ions to precipitate as metal hydroxide was predominant and hence no further studies were conducted at pH beyond 8.0.

Effect of contact time on the removal of cadmium and nickel

Equilibrium time is one of the parameters for economical wastewater treatment plant applications. The results of the removal of Cd(II) and Ni(II) by NOCAC as a function of contact time at initial concentration of Cd(II) and Ni(II) is 75 mg/L and 63 mg/L are shown in Fig. 3. Equilibrium adsorption was established within 20 min for Ni(II) and 25 min for Cd(II). It could be seen that the removal was found to be 75% for Ni(II) and 97% for Cd(II) at optimum pH conditions. The higher removal of cadmium is probably due to the hydration energy of cadmium when compared to Ni(II). According to these results, the agitation time was fixed at 30 min for the rest of the batch experiments to make sure that equilibrium was reached.

Effect of adsorbent dosage on removal of cadmium and nickel

The removal of metal ions as a function of carbon dosage is shown in Fig. 4. It was observed that with increasing adsorbent dosage from 100 mg to 1500 mg/100 mL the percent removal of metal ion increased up to 96.8% for Cd(II) (under optimum dose of 1.0 g) and 73.71% for Ni(II) (under optimum dose of 0.75 g). Further increasing dosage has no effect on metal ion removal. The removal efficiency



Fig. 3– Effect of contact time on removal of cadmium and nickel (pH 7.0)

of NOCAC increases with adsorbent due to increase of number of active sites. Hence, higher dosage of adsorbents has a positive effect on the initial rate of metal ion removal. However, there was a decrease in adsorption density/capacity (Table 5) which may be due to the fact that some adsorption sites may remain unsaturated during the adsorption process³⁴.

Effect of initial metal ion concentration on removal of cadmium and nickel

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 due to the transfer of metal ions from bulk to the surface of the sorbent. The effect of initial metal ion concentration in the wastewater on the removal of Cd(II) and Ni(II) by NOCAC, is shown in Fig. 5. The removal of metal ions increases from 0.83 to 7.12 mg/g for Cd(II) and 1.91 to 5.57 mg/g in the case of Ni(II) when initial concentration of Cd(II) and Ni(II) was increased from 9 mg/L to 75 mg/L and 18mg/L to 63 mg/L, respect-

Table 5–Adsorption capacities of adsorbent for Ni and Cd at different adsorbents doses							
Adsorbent dose (g/100 mL) Adsorption capacity (mg/g)							
	Ni	Cd					
0.1	35.86	35.50					
0.25	16.06	23.60					
0.50	8.46	13.10					
0.75	6.02	9.36					
1.00	4.59	7.10					
1.25	3.69	5.78					
1.50	3.10	4.86					



Fig. 4– Effect of adsorbent dose for the removal of cadmium and nickel

tively. The fact that the adsorption capacity increased with increasing metal ion concentration, indicates the potential application of NOCAC as a sorbent, to the treatment of wastewater containing cadmium and nickel at higher concentrations. Incidentally, NOCAC was also able to remove other metal ions (Table 3) apart from cadmium and nickel, completely from wastewaters.

Adsorption kinetics

In order to study the kinetics of Cd(II) and Ni(II) adsorption by NOCAC, pseudo-first-order-kinetics, reversible-first-order and pseudo-second-order-kinetic models were employed. The kinetic plots were drawn for two metal ions and the adsorption rate constants $(K_1 \text{ and } K_2)$, and adsorption capacity (q_e) were calculated from the slope and intercepts of the plots of log $(q_e - q_t)$ against 't' for the pseudo-first-order and t/q_t against 't' for the second-order (Figs 6a & 6b). Rate constants K_1 and K_2 and the model prediction of q_e along with the experimental q_e values are shown in Table 6.



Fig. 5- Effect of initial metal ion concentration on removal of cadmium and nickel



Fig. 6a– Pseudo-second-order-kinetic for the removal of cadmium onto activated carbon (NOCAC)

Table 6– Adsorption kinetics for NOCAC												
Metal	Concen-	$q_{\rm e} ({\rm exp})$	Pse	udo-first-c	order	Pseud	o-second-	order	R	eversible	-first-ord	er
ion	tration (mg/g)	(mg/g)	k_1 (h ⁻¹)	R^2	q _e (theo) (mg/L)	k ₂ (g/mg h)	R^2	$q_{\rm e}$ (theo) (mg/g)	<i>K</i> (h ⁻¹)	$k_1 (h^{-1})$	k ₂ (h ⁻¹)	R^2
Cd	45	34.94	0.711	0.9916	4.63	1.520	0.9998	33.11	0.711	0.552	0.159	0.9916
	30	25.19	2.068	0.9812	3.47	2.000	0.9996	25.00	2.068	1.736	0.332	0.9812
	15	10.79	0.506	0.9944	4.46	0.807	0.9975	9.28	0.506	0.364	0.142	0.9944
Ni	20	18.89	1.187	0.9882	12.07	0.132	0.9980	20.87	1.187	1.121	0.066	0.9882
	15	13.89	1.803	0.9376	09.98	0.174	0.9876	16.56	1.803	1.670	0.133	0.9377
	10	08.89	1.337	0.9580	07.22	0.283	0.9634	09.50	1.337	1.189	0.148	0.9580

Table 7– Isotherm constants for NOCAC										
		Langmui	r model		Fre	eundlich mod	el	Т	emkin mode	1
Adsorbents	$b \pmod{(\text{mg g}^{-1})}$	$a (L mg^{-1})$	ab	R^2	$\frac{K_{\rm f}}{(\rm mg~g^{-1})}$	$N_{\rm f}$ (L mg ⁻¹)	R^2	a_{t} (mg g ⁻¹)	$b_{\rm t}$ (L mg ⁻¹)	R^2
Cd	23.70	0.0660	1.564	0.758	1.248	0.661	0.859	39.372	36.579	0.918
Ni	54.95	0.056	3.067	0.884	5.148	1.748	0.887	8.202	12.425	0.901



Fig. 6b– Pseudo-second-order-kinetic for the removal of nickel onto activated carbon (NOCAC)

The value of q_e (theo) calculated from kinetic models are compared with experimental values q_e (exp) in Table 6. It is found that values of q_e (theo) calculated from the pseudo-first-order-kinetic model differed appreciably from the experimental values q_e (exp). On the other hand values of q_e (theo) are found to be very close to q_e (exp) for pseudo-second-orderrate equation. The very high values of regression coefficient (R^2) factor confirm adsorption of Cd(II) and Ni(II) by NOCAC following the pseudo-secondorder kinetic model well¹⁷.

The plot of ln $(1-U_{(t)})$ versus 't' as per the reversible first order kinetic model were also linear and the overall rate constant K, forward rate constant k_1 and backward rate constant k_2 were calculated and are given in Table 6. The plots however do not pass

Table 8– R_L values based on the Langmuir isotherm for both Cd and Ni

$C_0 (\mathrm{mg/L})$	Cd	$C_0 (\mathrm{mg/L})$	Ni
75	0.1681	63	0.2208
60	0.2016	50	0.2632
45	0.2519	44	0.2887
30	0.3356	35	0.3378
15	0.5025	25	0.4167
09	0.6274	18	0.4980

through the origin; thus, the reversible-first-orderkinetic model is not the predominant mechanism for Cd(II) and Ni(II) adsorption on NOCAC³⁵.

Isotherm

Three isotherm equations have been tested in the adsorption of Cd(II) and Ni(II) on to NOCAC adsorbent, namely, Langmuir, Freundlich and Temkin. The isotherm constants were determined from linear isotherm graphs for each of the isotherm equations tested. The values of the isotherm constant with the correlation coefficients are given in Table 7.

The adsorption capacities *b*, based on Langmuir isotherm for Cd(II) and Ni(II) by NOCAC adsorbent was 23.70 mg/g and 54.95 mg/g, respectively. The dimensionless separation factor R_L , were calculated by using '*a*' values and obtained R_L values were given in Table 8. For both metal ions, the values of R_L were between 0 and 1, pointing to the favorable adsorption of Cd(II) and Ni(II) on NOCAC.



Fig. 7- Temkin adsorption isotherms for cadmium and nickel

Table 9–Desorption data corresponding to NOCAC							
Concentration of HCl (M)	%Desorption of Ni	% Desorption of Cd					
0.025	80.09	94.76					
0.050	84.88	99.99					
0.075	96.71	99.99					
0.100	99.99	99.99					
0.125	99.99	99.99					
0.15	99.99	99.99					

Estimated adsorption parameters by the Freundlich models are shown in Table 6. High values of K_f and N_f suggest that the adsorption of Cd(II) and Ni(II) on NOCAC is a favorable adsorption.

Temkin isotherm is an empirical relationship which often gives a satisfactory model of experimental data (Fig. 7). The values of a_t and b_t from the Temkin isotherm (Table 7) suggest that the adsorption of Cd(II) and Ni(II) on NOCAC is favorable adsorption. Based on regression coefficient values, the Temkin model is found to be more suitable for adsorption process.

Desorption studies

Desorption of metal ions was studied by using different concentrations of hydrochloric acid (0.025-0.15 M). The recovery rate of Cd(II) increased with increase in concentration of HCl from 0.025 M to 0.05 M and then remained constant, in the case of Ni(II) maximum recovery was observed at 0.10 M (Table 9). The high level of desorption attained in these two cases could mean that surface adsorption was predominant on this adsorbent and that the ion exchange mechanism may be followed.

Conclusions

Neem oilcake activated carbon is an effective adsorbent for the removal of Cd(II) from wastewater.

The optimum conditions for the removal of cadmium is at pH 7.0, contact time 25 min and adsorbent dosage 1000 mg/ 100 mL. The optimum condition for the removal of nickel is at pH 7.0, contact time 20 min and adsorbent dosage 750 mg/100 mL. Langmuir adsorption capacity of cadmium and nickel is 23.7 mg/g and 54.95 mg/g for NOCAC. On the basis of R² values, Temkin isotherm shows good correlation for both Ni(II) and Cd(II) adsorption on NOCAC. Sorption of Cd(II) and Ni(II) by NOCAC follows pseudo-second-order-kinetic equation. Quantitative recovery of Cd(II) and Ni(II) is possible from NOCAC and it could be employed for effective treatment of wastewater containing Cd(II) and Ni(II) ions.

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