Removal of Ni(ii) form water by agricultural waste: Oil removed coconut residues

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ABSTRACT

Activated carbon prepared form coconut residues (CORC), and agricultural waste by-product obtained after oil extraction was used for the adsorption of Ni(II) form aqueous solution. The process of uptake obeys both Freundlich and Langmuir adsorption isotherms. Kinetic studies indicate that it obeys Lagergram kinetic model. Quantitative removal of Ni(II) from 100mL aqueous solution containing 10mg/L of Ni(II) was observed over a P^H range 4.0 to 10.0. The suitability of this material for trating nickel-plating industry wastewater was also examined. A comparative study with a commerical granular activated carbon (CAC) showed that CORC is 6 times more efficient compared to CAC based on Langmuir adsorption capacity(Q_o).

Key words: Activated Carbon, Ni(II) removal, Adsorption isotherms.

INTRODUCTION

Reasonable quantities of nickel containing wastewater are introduced into natural water bodies from the effluents of nickel-plating units, silver refineries, zinc based casting industries and storage batteries[1]. The tolerance levle of nickel in drinking water is 0.01 mg/L[2]. Nickel has been noticed to give cancer of lungs, nose and bones, "Nickel itch" is the most frequent effect of exposure to nickel, such as coins and costume jewellry. Acute Ni(II) poisoining causes dizziness, headache, nausea and vomiting, chest pain, dry cough and shortness of breath, rapid respiration, cyanosis, cyanosis and extreme weakeness[3,4]. These harmful effects of Ni(II) necessitate its removal from wastewater before it is released to natural bodies of water.

Methods are available for Ni(II) removal form wastewater, which include precipitation[5,6], coagulation and floculation[7], Ion exchange[8], Complexation/sequestration[9] electrochmical operation[10] biological treatment[11] and adsorption on activated carbon[12] Many reports have appeared on the development of activated carbon from cheaper and readily available materials[13]. Activated carbons derived form rise husk[14], coconut shell[15] and peanut hulls have been used for the removal of heavy metals form aqueous solutions. Activated carbons prepared form rice husk, tamarind nut and peanut hulls have been sucessfully employed for the removal or Cr(VI), Hg(II) Cd(II) and Ni(II) form aqueous solution[16-19]. Coconut residue, which is obtained after the extraction of oil, and agricultural waste product, is generally utilized in India as a fuel or cattel feed. The investigation reported here deals with a comparative stduy of CORC and CAC for the removal of NI(II) form aqueous solution and from a nickel plating industry wastewater.

EXPERIMENTAL

CORC was preapared as reported before[19]. The particle of 0.575mm (20-50 Mesh ASTM) was used. The CAC obtained form M/s SD Fine Chemicals, Baroda, India, was ground and sieved to the same size. The characteristics of CORC and CAC have been reproted in Table -1.

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Batch Mode Studies

A stock solution of 1.0 g/L of Ni(II) was prepared by dissolving 0.4479g or nickel sulphate {$NiSO_4 \cdot 6H_2O$} in distilled water containing 1.0ml or concentrated nitric acid to prevent hydrolysis and diluted to 1000mL. The stock solution was diluted as required to obtain standard solution of 10mg/L Ni(II). 100mL. of Ni(II) solutions of a desired concentration, adjusted ot a desired pH were taken in reagent bottels of 350mL capacity and known amounts of CORC and CAC were added. The pH was adjusted using dilute HNO_3 or Na0H solutions. All the chemical used were of analytical reagent grade and were obtained from BDH, Emerk, SDS and Ranbaxy. The solutions wre agitated for a predetermined period at 30°C in a rotary mechanical shaker. The bottels were removed and the carbons were separted by centrifugation and Ni(II) in the centrifugate was analysed spectrophotometrically using dimethyl glyoxime[20]. Adsoprtion isotherms were drawn with different intial concntration of Ni(II) while maintaining the carbon dosage at constant level. For pH effect, 10mg/L Ni(II) and CORC dose of 100mg/100ml was used. In order to correct for any adsorption of Ni(II) on the containers, control experiments were carried out without adsorbent and there was negligiblle adsorption by the container walls.

Desorption studie were carried out as follows. After adsorption experiments with 10mg/L of Ni(II) and 100mg of CORC of CAC, the nickel loaded carbons were separted, gently washed with distilled water. The carbons were then agitated with 100ml of HCl of various strengths for 3 h in the case of CORC and 5 in the case of CAC and the amount of desorbed nickel was estimated as before.

The nickel-plating industry wastewater collected from Salem, India was diluted to 10 times for study with CORC and CAC. For pH effects, 100mL each of the respective sample with 500mg of CORC or 1000mg CAC was agistated for 3 h in the case or CORC and 5 h in the case of CAC. For the study of the effect of carbon dosage, the sample pH was adjusted to 5.0 and agitated with different dosages of CORC for 3h or CAC for 7h.

RESULTS AND DISCUSSION

Effect of Agitation time

Figs. 1 and 2 shows the effect of agitation time on the removal of Ni(II) by CORC and CAC. The percentage of removal increases with time and attains equilbrium at 3h for CORC and 5h for CAC for all the concentratrions of Ni(II) used. This indicates that the optimum time required for maximum Ni(II) removal by CORC would be 1.6 times less than that required by CAC.

Effects of carbon dosage

Figures 3 presents the removal of Ni(II) as a function of carbon dosage by CORC and CAC. It shows that for the quantitative removal of Ni(II) form 100mL solution containing 10mg/L Ni(II),a minimum carbon dosage of 50gm of CORC is required.

Table -1: Carbon characteristics

S. No.	Parameters	CAC	CORC
1.	Bulk density g/mL	0.66	0.79
2.	Moisture %	0.61	5.24
3.	Ash %	0.91	22.60
4.	Solubility in water %	0.32	10.54
5.	Solubility in acid %	1.05	11.95
6.	pH	7.66	4.25
7.	Decolourising power mg/g	0.6	4.50
8.	Phenol number	37.47	50.84
9.	Ion exchange capacity meq	nil	0.29
10.	Surface area m² /gm	210	312
11.	Iron %	1.18	2.26

Table -2: Characteristics of Nickel plating industry waste water

pH	1.45
conductivity, mS/cm	16.78
Total solids, mg/ml	8560
Turbidity, NTU	1.5
COD, mg/L	10
Chloride, mg/L	541
Sulphate mg/L	4356
Iron, mg/L	50.2
Total iron, mg/L	165
Nickel, mg/L	1020
Sodium, mg/L	224
Calcium, mg/L	62

However, for the same solution a maximum removal of only 80% was observed for a CAC dosage of 250mg/100mL. This shows that approximately CORC is five times more efficient than CAC.

Effect of pH

Figures 4 presents the effect of intial pH on the removal of Ni(II) by CORC and CAC. For comprasion, Ni(II) removal by precipitation as Ni(OH)$_2$ in the absence of any adsorbent it also shown in the figure. Significantly Ni(II) removal by both the carbon inceases with increase in pH and attains 99.9% and 80% for CORC and CAC respectively at pH 4.0.CORC is effective for the maximum removal of Ni(II) over the pH range 4.0-10.0 and CAAC is effective for the maximum removal

Table -3: Rate constants/hr

Ni (II) mg/L	CORC			CAC		
	k	k1	k2	k	k1	k2
3	1.75	1.69	0.06	0.93	0.90	0.03
5	1.97	1.93	0.04	1.00	0.96	0.04
7	2.64	2.56	0.08	0.98	0.94	0.04
10	2.10	1.98	0.12	1.32	1.24	0.08

Table - 4: Diffusion coefficients of the adsorbents for the removal of Ni(II)

Sorbent	Ni(II) concentration mg/L	Film diffusion coefficient cm^2 / sec	Pore diffusion coefficient cm^2 / sec
CORC	10	1.077×10^{-7}	6.685×10^{-8}
	7	6.787×10^{-7}	7.986×10^{-8}
	5	5.064×10^{-7}	5.959×10^{-8}
	3	4.499×10^{-7}	5.293×10^{-8}
CAC	10	3.376×10^{-9}	3.932×10^{-8}
	7	1.087×10^{-9}	1.300×10^{-8}
	5	2.544×10^{-9}	3.025×10^{-8}
	3	2.301×10^{-9}	2.813×10^{-8}

in the pH range 4.0-8.0. At higher pH conditions CAC is ineffective.

The influence of pH on Ni(II) removal may be explained as follows. A pure carbon surface is considered to be nonporous but in actual pratice some carbon-oxygen complexes are usually present, which render the surfacfe slightly polar[21]. As the pH decerases the surface of the carbon exhibits an increasing positive tendency. Since the

Table - 5: R$_L$ values and isotherms

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

Table - 6: Equilibrium parameter, R$_L$

Initial Ni (II) Conc.	CORC	CAC
10	0.0752	0.2963
20	0.0392	0.1742
30	0.0260	0.1233
40	0.0199	0.0954
50	0.0160	0.0778

species to be adsobed, Ni(OH) is also positive, the adsoption of NI (II) is not favored. Moreover, a higher concentration of H$^+$ ions present in the reduced uptake of Ni(II). As the pH is increased, the 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 Iron hydrous oxide gels[22] and geothite[23].

Desorption studies

Desorption studies indicate the nature of adsorption and recover valuable metals from wastewaters and the sorbent. Experiment were conducted to desorb Ni(II) from the spent carbons using HCI of various strengths ranging from 0.05 to 0.25M. The precent recoveries of Ni(II) for CORC were found 7.5, 85.0, 95.0, 95.0 smf 97.0 by 0.05, 0.10, 0.15, 0.20 and 0.25M HCI respectively. In the case of CAC the corresponding values were 73.0, 86.0, 93.8, 94.0 and 94.8. It may be stated that in the acid medium protons compete with Ni(II) ions and displace the maximum amount of adsorbed

nickel. Hence it can be stated that ions exchange mechanism is important in connection with adsorption process for both cabons.

Experiments with nickel plating wastewater

The characteristics of a nickel plating wastewater are shown in Table 2. As the wastewater has a very high concentration of nickel (1020mg/L) it was diluted 10 times for study with CORC and CAC respectively and then subjected to treatment.

Figure 5 represents the effect of pH on the adsorption of Ni(II) by CORC and CAC. It is evident that for the maximum removal of Ni(II) from wastewater, CORC is effective over the pH range 4.5 to 10.0 while for CAC the pH range is 5.0 to 9.0.

Figure 6 present the effect of adsorbent dosage on the removal of Ni(II) from wastewater. To get a quantiative removal of Ni(II) form 100mL
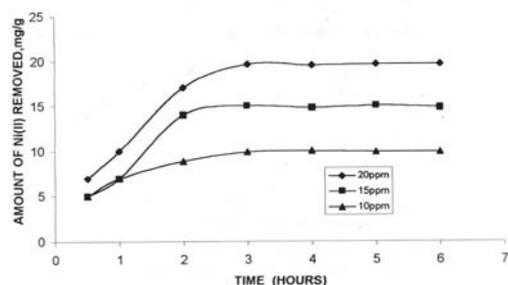

Fig. -1: Effect of agitation time on the removal of Ni(II) by CORC pH - 5.0, Carbon dosage, 100 mg/100 mL
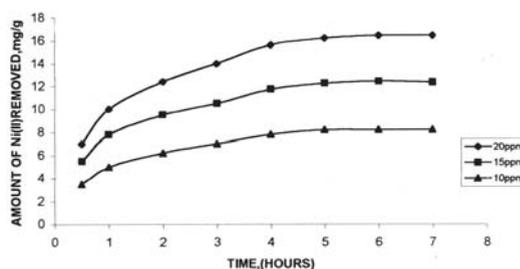
Fig. -2: Effect of agitation time on the removal of Ni(II) by CAC Carbon dosage, 200 mg/100 mL
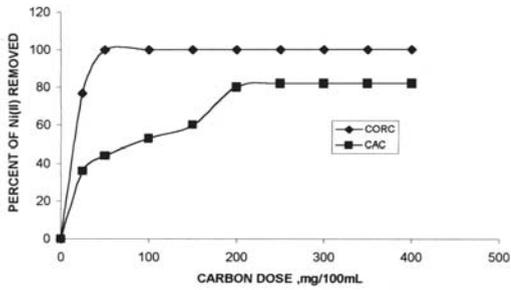
Fig. -3: Effect of carbon dosage on the adsorption of Ni(II) concentration 10m/L pH 6.0, CORC: Agitation time 3hr, CAC: Agitation time 5hr
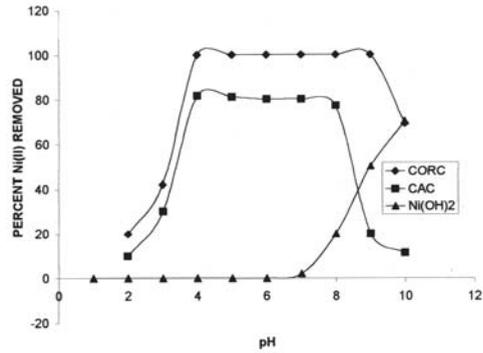

Fig. -4: Effect of pH on the removal of Ni(II); Conc. 10mg/L CORC dose 100mg/100mL; Agitation time 3hr; CAC dose 200mg/L. Agitation time 5hr; Ni(OH)$_2$ - Precipitation of Ni(II) as its hydroxide in the absence of adsorbent
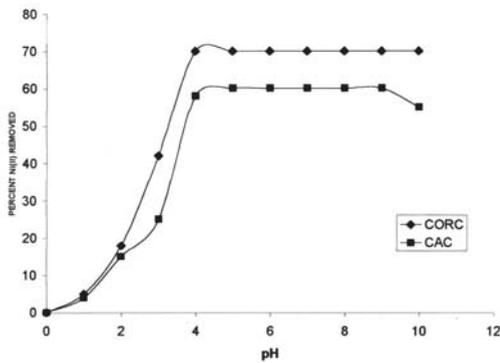

Fig. -5: Effect of pH on the removal of Ni(II) from Nickel plating industry waste water; CORC - Ni(II) conc. 102 mg/L; carbon dosage 500 mg/100mL; agitation time 3hr. CAC - Ni(II) concentration 102 mg/L; carbon dosage 1000 mg/mL; agitation time 5 hr
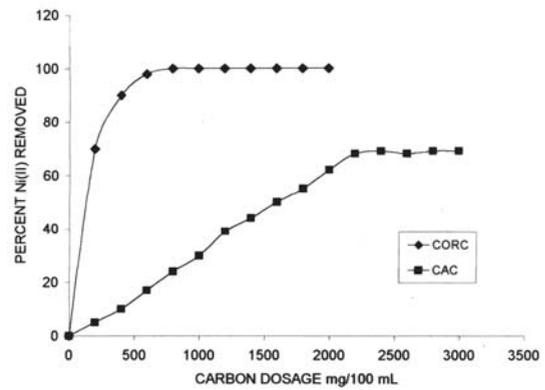

Fig. -6: Effect of carbon dose on the removal of Nickel (II) from plating waste water pH 5.0, Nickel concentration 102 mg/L, CORC - agitation time 3hr., CAC agitation time 5 hr
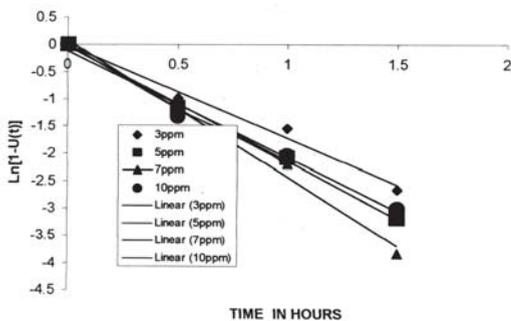

Fig. -7: Lagergren plots for the adsorption of Ni(II) on CORC Ni(II) concentration 3-10 mg/L, pH 5.0
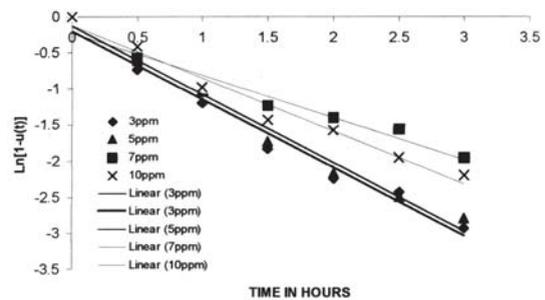

Fig. -8: Lagergren plots for the adsorption of Ni(II) on CAC Ni(II) concentration 3-10 mg/L, pH 6.0

wastewater containing 102mg/L Ni(II), minimum dosage of 820 mg is required. However, in the case of CAC, for the maximum removal (68%) of Ni(II) form 100mL wastewater containing 102mg/L Ni(II) a minimum dosage of 220mg is required. This indicate that the CORC is more effective when compared to CAC, in the connection with the treatment of nickel-plating wastewater.

Adsorption kinetics

The kinetic of nickel adsorption on both CORC and CAC follows the first order rate exprssion[24].

$$Ln(I-U_t) = -kt.$$
Where $U(t) = (C_0-C_1)/(C_0-C_e)$

C_o, C_t and C_e are the concentration in mg/L of nickel intitally, at any time t, and at equilibrium, respectively. A straight line plot of ln (1-Ut) vs t indicates the adsorption process follows first order kinetics (fig 7&8). The straight line portions of the curves were used for calculating he slope values which give the overall rate constant k of the process. The forward (k_1) and backward (k_2) rate constant were calculated using the following equation

$k = k_1+k_2$
$k= k_1/k_e$
$k= k_1 (1+1/k_e)$
ke= k_1/k_2 where k_e is the quilbrium constant.

The data are furnished in Table 3.1. It is evident that the forward rate constant is much higher than the backward rate constant suggesting that the rate of adsorption is clearly dominant.

In order to assess the nature of the diffusion process responsible for the adsorption of nickel on CORC and CAC, attempts were made to calculate the coefficients of the process. If film diffusion to be the rate determining step in the adsorption of nickel on CORC and CAC surface, the value of film diffusion coefficient (D_f) should be in the range 10^{-6} to 10^{-8} cm^{2}s^{-1}. If pore diffusion is to be the rate limiting the pore diffusion coefficient (D_p) should be in the range 10^{-11} to 10^{-13} cm^{2}s^{-1}. Assuming spherical geometry for the sorbent the overall rate constant of the process can be correlated to the pore diffusion coefficient and film diffusion coefficient in accordance with the expressions given by Michelson *et al.*[24]. Employing the appropriate data and the respective overall rate constant, pore and film diffusion coefficients for various concentration of nickel were caluclated for CORC and CAC. The results are presented in Table 4. It is evident that the removal of nickel by CORC and CAC follows the film diffusion process since the coefficient values are in the range of 10^{-6} to 10^{-8} cm^{2}s^{-1} for these carbons.
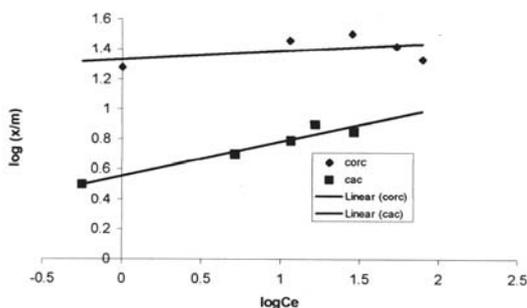

Fig. -9: Freundlich plots for the adsorption of Ni(II), Ni(II) concentration 20-100mg/L; pH 6.5; Agitation time 24 hr CORC dose 100 mg/L; CAC dose 200mg/L
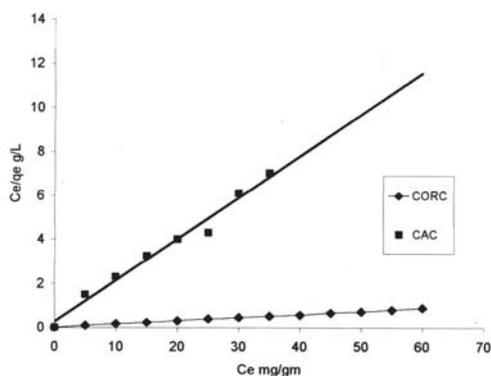

Fig. -10: Langmuir plots for the adsorption of Ni(II), Ni(II) concentration 20-60mg/L; pH 6.0; agitation time 24 hr CORC dose 100 mg/100mL; CAC dose 200mg/100mL

Adsorption isotherms

Langmuir equation[25] was applied for adsorption equilibrium for both CORC and CAC. The langmuir treatment is based on the assumption that maximum adsorption corresponds to monolayer of adsorbate molecules on the adsorbent surface, that the energy of adsorption is constant, and that there is no trasmigration of adsorbate in the plane of the surface.

$$C_e/q_e = 1/Q_0 b + C_e/Q_0$$

where C_e is the equilibrium concentration (mg/L), q_e is the amount adsorbed at equilibrium mg/g, Q_0 and b are Langmuir constant related to adsorption capacity and enery of adsorption, respectively. The linear plots of C_e/q_e vs C_e show that the adsorption obeys. Langmuir adsorption model for both CORC and CAC[4]. Q_0 and b, respectively were determined from the Langmuir plots and found to be 40.7 mg/g and 1.288 for CORC 6.02 mg/g and 0.237 for CAC. The ratio of Q_0 values of CORC and CAC works out to be 6.73. (Fig. 10).

The essential characteristics of Langmuir isotherms were expressed in terms of a constant separation factor or equilibrium parameters R_L, which is defined by $R_L = 1/1 + b\, C_0$ where b is the Langmuir constant and C_0 is the initial concentration of nickel (II)[22]. The parameter indicates the isotherm shapes as in Table 5. R_L values observed between 0 and 1 indicate favorable adsorption of nickel (II) on both CORC and CAC (Table 6)

The Freundlich equaiton was also applied for the the adsorption. It is genearlly emeprical and agrees quite well with Langmuir equation and experimental date over a moderate range of adsorbate concentrations. It is represented by the equation[26].

$$\log_{10}(x/m) = \log_{10} K_f + 1/n \log_{10} C_e$$

where C_e is the equilibrium concentraion (mg/L), and (x/m) is the amount adsorbed per unit mass of CORC and CAC (mg/g). Plots of log x/m vs log C_e are linear for both CORC and CAC (Fig. -9). The constants K_f and n respectively were found to be 20.19 and 6.66 for CORC and 3.55 and 4.55 for CAC. Values of 1<n< 10 shows favorable adsorption of Nickel (II) on both CORC and CAC. The ratio of K_f values of CORC and CAC works out to be 5.68.

Conclusions

The study presented here show that coconut oilcake residue is and effective adsorbent for the removal and recovery of Ni(II) from aqueous solution. Its adsorption capacity is moderately high to commercial activated carbon. The adsorption of nickel on to both the carbons follows first order reversible kinetics with film diffusion being the essential rate-controlling step. The kinetic data may be useful for designing of wastewater treatment plants. As the material is available as an agricultural waste product after oil extractio, CORC may be exploited for commercial applications in connection with the treatment of wastewater containng nickel.

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