Asian Journal of Chemistry Vol. 17, No. 3 (2005), 1877–1888

Removal of Ni(II) from Water by Oil Removed Coconut Residues

K. SRINIVASAN* and S. SARAVANAN†
Department of Chemistry, College of Engineering, Salem-636 011, India
E-mail: srini_vasank@hotmail.com

Activated carbon prepared from coconut residues, an agricultural waste byproduct obtained after oil extraction, has been used for the adsorption of Ni(II) from aqueous solution. The process of uptake obeys both Freundlich and Langmuir adsorption iso- therms. Kinetic studies indicate that it obeys Lagergran kinetic model. Quantitative removal of Ni(II) from 100 mL aqueous solution containing 10 mg/L of Ni(II) was observed over a pH range of 4.0 to 10.0. The suitability of this material for treating nickel-plating industry wastewater was also examined. A comparative study with a commercial granular activated carbon showed that coconut residues is 6 times more efficient compared to commercial activated carbon based on Langmuir adsorption capacity (Q_O).

Key Words: Activated carbon, Ni(II) removal, Coconut residues. 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 level of nickel in drinking water[2] is 0.01 mg/L. 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 jewelry. Acute Ni(II) poisoning causes dizziness, headache, nausea and vomiting, chest pain, dry cough and shortness of breath, rapid respiration, cyanosis and extreme weakness[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 from wastewaters, which include precipitation[5, 6], coagulation and flocculation[7], ion exchange[8], complexation/sequestration[9], electrochemical operations[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 from rice husk[14], coconut shell[15] and peanut hulls have been used for the removal of heavy metals from aqueous solutions. Activated carbons

---

†Department of Chemistry, Anna University, Chennai-600 025, India.

prepared from rice husk, tamarind nut and peanut hulls have been successfully employed for the removal of Cr(VI), Hg(II), Cd(II) and Ni(II) from aqueous solutions[16–19]. Coconut residue, which is obtained after the extraction of oil, an agricultural waste product, is generally utilized in India as a fuel or cattle feed. The investigation reported here deals with a comparative study of coconut residues and commercial activated carbon for the removal of Ni(II) from aqueous solutions and from a nickel-plating industry wastewater.

EXPERIMENTAL

All the chemicals used were of analytical reagent grade and were obtained from BDH, E.Merck, SDS and Ranbaxy. Coconut oil coke residue carbon (CORC) were prepared as reported earlier[19]. The particle size of 0.575 mm (20–50 mesh ASTM) was used. The granular activated carbon (CAC) obtained from M/s SD Fine Chemicals, India, was ground and sieved to the same size. The characteristics of CORC and CAC have been reported in Table-1.

TABLE-1
CARBON CHARACTERISTICS

Parameters	CAC	CORC
Bulk density (g/mL)	0.66	0.79
Moisture (%)	0.61	5.24
Ash (%)	0.91	22.60
Solubility in water (%)	0.32	10.54
Solubility in acid (%)	1.05	11.95
pH	7.66	4.25
Decolorizing power (mg/g)	0.6	4.50
Phenol number	37.47	50.84
Ion exchange capacity (meq/g)	—	0.29
Surface area (m^2/g)	210	312
Iron (%)	1.18	2.26

Batch mode studies: A stock solution of 1000 mg/L of Ni(II) was prepared by dissolving 0.4479 g of nickel sulphate ($NiSO_4 \cdot 6H_2O$) in distilled water containing 1.0 mL of concentrated nitric acid to prevent hydrolysis and diluted to 1000 mL. The stock solution was diluted as required to obtain standard solution of 10 mg/L Ni(II). 100 mL of Ni(II) solutions of a desired concentration, adjusted to a desired pH, were taken in reagent bottles of 350 mL capacity and known amounts of CORC and CAC were added. The pH was adjusted using dilute HNO_3 or NaOH solutions. The solutions were agitated for a predetermined period at 30°C in a rotary mechanical shaker. The bottles were removed and the carbons were separated by centrifugation and Ni(II) in the centrifugate was analyzed spectrophotometrically using dimethyl glyoxime[20]. Adsorption isotherms were drawn with different initial concentrations of Ni(II) while maintaining the carbon dosage at constant level. For pH effects, 10 mg/L Ni(II) and CORC and CAC dose of 100 mg/100 mL 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 negligible adsorption by the container walls.

After adsorption experiments with 10 mg/L of Ni(II) and 100 mg of CORC or CAC, the nickel loaded carbons were separated, gently washed with distilled water. The carbons were then agitated with 100 mL of HCl of various strengths for 3 h in the case of CORC and 5 h in the case of CAC and the amount of desorbed nickel was estimated.

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

RESULTS AND DISCUSSION

Effect of agitation time: The effect of agitation time on the removal of Ni(II) by CORC and CAC were shown in Figs. 1 and 2. The percentage of removal increases with time and attains equilibrium at 3 h for CORC and 5 h for CAC for all the concentrations 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.

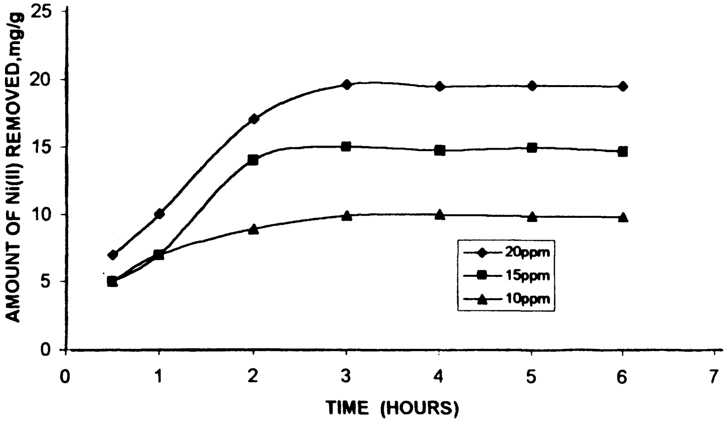

Fig. 1. Effect of agitation time on the removal of Ni(II) by CORC pH 5.0; carbon dosage, 100 mg/100 mL

Effect of carbon dosage: Fig. 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) from 100 mL solution containing 10 mg/L Ni(II), a minimum carbon dosage of 50 mg of CORC is required. However, for the same solution a maximum

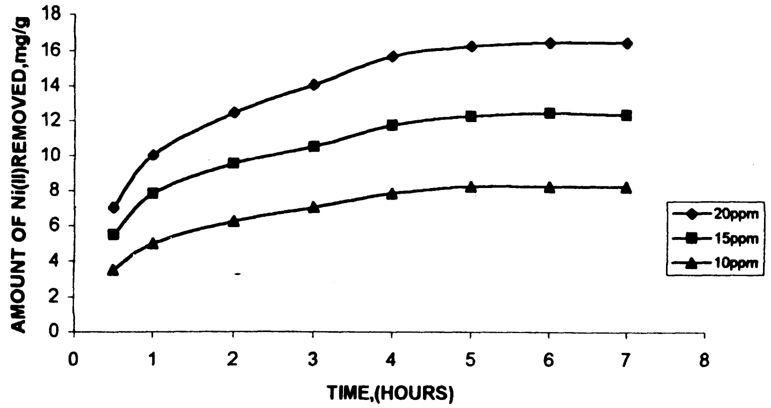

Fig. 2. Effect of agitation time on the removal of Ni(II) by CAC; carbon dosage 200 mg/100 mL

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

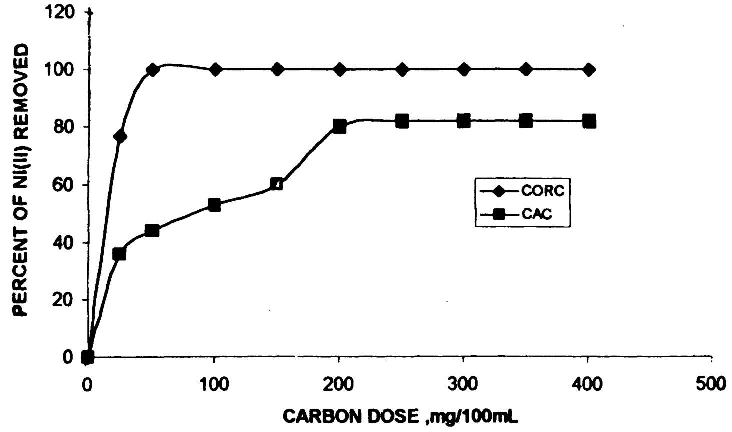

Fig. 3. Effect of carbon dosage on the adsorption of Ni(II); Ni(II) concentration 10 m/L; pH 6.0; CORC: Agitation time 3 h, CAC: Agitation time 5 h

Effect of pH: The effects of initial pH on the removal of Ni(II) by CORC and CAC were shown in Fig. 4. For comparison, Ni(II) removal by precipitation as $Ni(OH)_2$ in the absence of any adsorbent is also shown (Fig. 4). Significantly, Ni(II) removal by adsorption by both CORC and CAC are much more efficient compared to $Ni(OH)_2$ precipitation in the absence of any sorbent. The Ni(II) removal, in both cases, increases with increase in pH and attains 99.9 and 80% for CORC and CAC, respectively at pH 4.0. However, CORC is effective for the maximum removal of Ni(II) over the pH range 4.0–10.0 which CAC is effective for the maximum removal in the pH range 4.0–8.0. Also note that 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 non-porous but in actual practice some

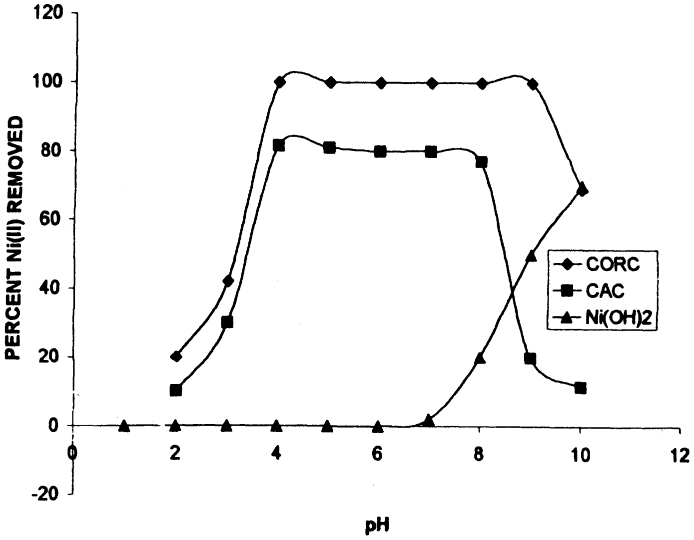

Fig. 4. Effect of pH on the removal of Ni(II); concentration 10 mg/L; CORC dose 100 mg/100 mL; agitation time 3 h; CAC dose 200 mg/L. Agitation time 5 h; $Ni(OH)_2$: Precipitation of Ni(II) as its hydroxide in the absence of adsorbent

carbon-oxygen complexes are usually present, which render the surface slightly polar[21]. As the pH decreases, the surface of the carbon exhibits an increasing positive tendency. Since the species to be adsorbed, $Ni(OH)^+$, is also positive, the adsorption of Ni(II) is not favoured. Moreover, a higher concentration of H^+ ions present in the reaction mixture competes with Ni(II) ions for the adsorption sites, resulting 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 favourable. Similar results were reported for the adsorption of Ni(II) on iron hydrous oxide gels[22] and goethite[23].

Desorption studies: Desorption studies indicate the nature of adsorption and recover valuable metals from wastewaters and the sorbent. Experiments were conducted to desorb Ni(II) from the spent carbons using HCl of various strengths ranging from 0.05 to 0.25 M. The per cent recoveries of Ni(II) for CORC were found 7.5, 85.0, 95.0, 95.0 and 97.0 by 0.05, 0.10, 0.15, 0.20 and 0.25 M HCl 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 ion exchange mechanism is important in connection with adsorption process for both carbons.

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 (1020 mg/L), it was diluted 10 times for study with CORC and CAC respectively and then subjected to treatment.

TABLE 2
CHARACTERISTICS OF NICKEL PLATING INDUSTRY WASTEWATER

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

Fig. 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.

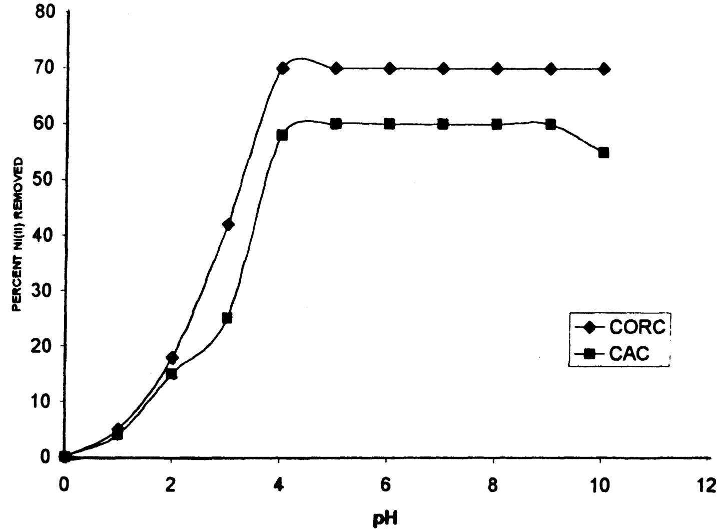

Fig. 5. Effect of pH on the removal of Ni(II) from nickel plating industry waste water; CORC: Ni(II) concentration 102 mg/L; carbon dosage 500 mg/100 mL; agitation time 3 h. CAC: Ni(II) concentration 102 mg/L; carbon dosage 1000 mg/100 mL; agitation time 5 h.

Fig. 6 presents the effect of adsorbent dosage on the removal of Ni(II) from wastewater. To get a quantitative removal of Ni(II) from 100 mL wastewater containing 102 mg/L Ni(II), minimum dosage of 820 mg is required. However, in the case of CAC, for the maximum removal (68%) of Ni(II) from 100 mL wastewater containing 102 mg/L Ni(II) a minimum dosage of 2200 mg is required. This indicates that the CORC is more effective when compared to CAC, in connection with the treatment of nickel-plating wastewater.

Adsorption kinetics: The kinetics of nickel adsorption on both CORC and CAC follows the first order rate expression[24]

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

where $U(t) = \dfrac{(C_o - C_t)}{(C_o - C_e)}$

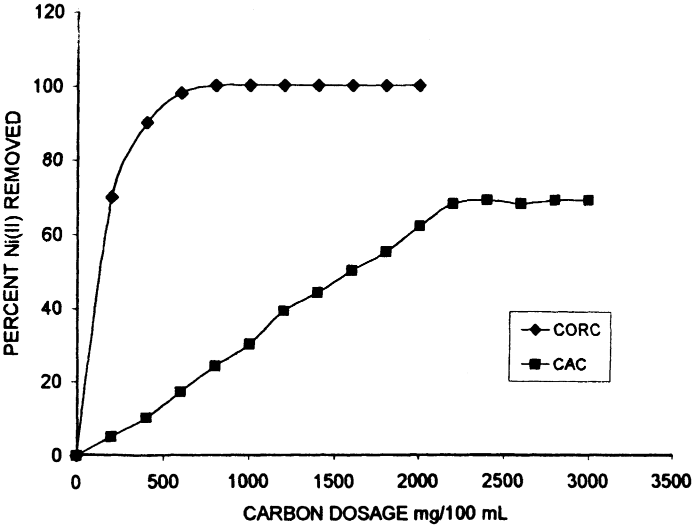

Fig. 6. Effect of carbon dose on the removal of nickel(II) from plating wastewater pH 5.0; Nickel concentration 102 mg/L; CORC: agitation time 3 h; CAC: agitation time 5 h

C_o, C_t and C_e are the concentrations in mg/L of nickel initially, at any time t, and at equilibrium, respectively. A straight line plot of ln (1 – U(t)) *vs.* t indicating the adsorption process follows first order kinetics (Figs. 7 and 8). The straight line portions of the curves were used for calculating the slope values which give the overall rate constant k of the process. The forward (k_1) and backward (k_2) rate constants were calculated using the following equation:

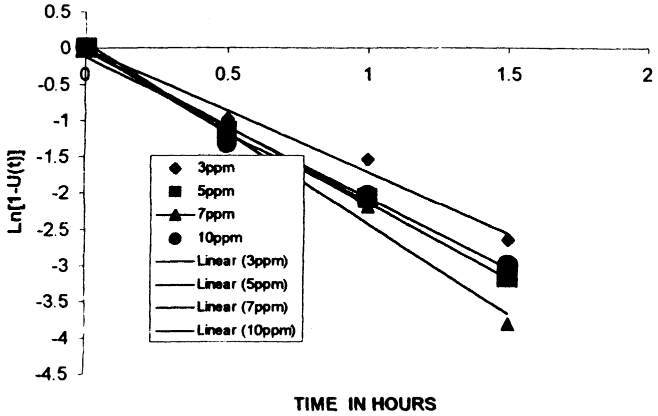

Fig. 7. Lagergren plots for the adsorption of Ni(II) on CORC; Ni(II) concentration 3–10 mg/L, pH 5.0

$$k = k_1 + k_2$$

$$k_2 = \frac{k_1}{k_c}$$

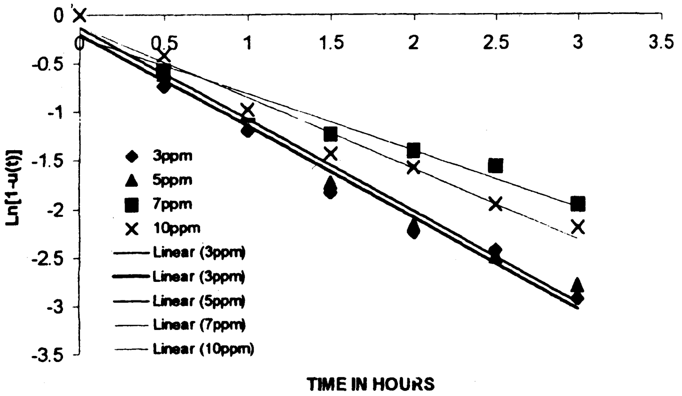

Fig. 8. Lagergren plots for adsorption of Ni(II) on CAC, Ni(II) concentration 3–10 mg/L, pH 6.0

$$k = k_1\left(1 + \frac{1}{k_c}\right)$$

$$k_c = \frac{k_1}{k_2}$$

where k_c is the equilibrium constant.

The data are furnished in Table-3. 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.

TABLE-3
RATE CONSTANTS PER HOUR

Ni(II) mg/L	CORC			CAC		
	k	k_1	k_2	k	k_1	k_2
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

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 processes. 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}–10^{-8} $cm^2 s^{-1}$. If pore diffusion is to be the rate limiting step, the pore diffusion coefficient (D_p) should be in the range 10^{-11}–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.*[4] Employing the appropriate data and the respective overall rate constants, pore and film diffusion coefficients for various concentrations of nickel were calculated for CORC and CAC (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}–10^{-8} cm^2 s^{-1} for these carbons.

TABLE-4
DIFFUSION COEFFICIENTS OF THE ADSORBENTS FOR THE REMOVAL OF Ni(II)

Sorbent	Ni(II) concentration (mg/L)	Film diffusion coefficient (cm^2/s)	Pore diffusion coefficient (cm^2/s)
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}

Adsorption isotherms: Langmuir equation[25] was applied for adsorption equilibrium for both CORC and CAC. The Langmuir treatment is based on the assumptions that maximum adsorption corresponds to mono-layer of adsorbate molecules on the adsorbent surface, that the energy of adsorption is constant, and that there is no transmigration of adsorbate in the plane of the surface.

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0}$$

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 constants related to adsorption capacity and energy 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. 9).

The essential characteristics of Langmuir isotherms were expressed in terms of a constant separation factor or equilibrium parameter R_L, which is defined by

$$R_L = \frac{1}{1 + bC_0}$$

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 favourable adsorption of nickel(II) on both CORC and CAC. (Table-6).

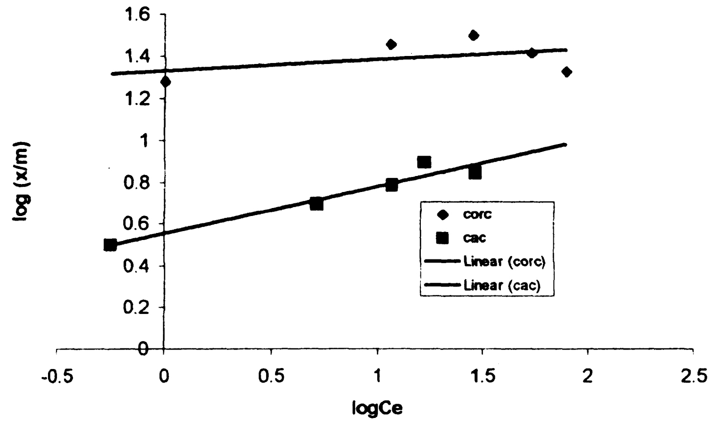

Fig. 9. Langmuir plots for the adsorption of Ni(II). Ni(II) concentration 20–60 mg/L; pH 6.0; agitation time 24 h. CORC dose 100 mg/100 mL; CAC dose 200 mg/100 mL

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) concentration	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

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

$$\log\left(\frac{x}{m}\right) = \log K_f \times \frac{1}{n} \log C_e$$

where C_e is the equilibrium concentration (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 $1 < n < 10$ show favourable 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.

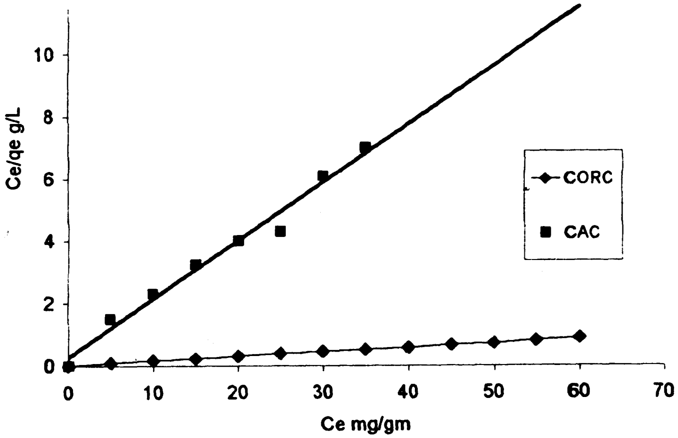

Fig. 10. Freundlich plots for the adsorption of Ni(II). Ni(II) concentration 20–100 mg/L; pH 6.5; agitation time 24 h. CORC dose 100 mg/L; CAC dose 200 mg/L

Conclusion

The study presented here shows that coconut oil cake residue carbon is an effective adsorbent for the removal and recovery of Ni(II) from aqueous solutions. Its adsorption capacity is moderately high as compared 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 extraction, CORC may be exploited for commercial applications in connection with the treatment of wastewater containing nickel.

REFERENCES

1. P.P. Vishwakarma, K.P. Yadava and V.N. Singh, *Pertanika*, **12**, 357 (1989),
2. Y.C. Sharma, G. Prasad and D.C. Rupainwar, *Intern. J. Environ. Studies*, **40**, 41 (1992).
3. R.P. Belliles, The lesser metals, in: F.W. Oeheme (Ed.), Toxicity of Heavy Metals in the Environment, Part 2, Marcel-Dekker, New York, p. 583 (1979).
4. S.P. Parker (Ed.), Encyclopedia of Environmental Sciences, 2nd Edn., McGraw-Hill, New York (1980).
5. J.V. Dean, F.L. Bosqui and K.H. Lanoutte, *Environ. Sci. Technol.*, **6**, 518 (1972)
6. S.L. McAnally, Benefield and R.V. Reed, *Sep. Sci. Tech.*, **19**, 191 (1984).
7. R. Nilsson, *Water Res.*, **5**, 51 (1971).
8. EPA Summary report: Control and treatment technology for metal finishing industry, Ion Exchange, EPA 625/8-81-007, EPA, Cincinnati, OH (1981).
9. K.V. Mayenkar and A.L. Lagvankar, *Proc. 38th Perdue Industrial Waste Conf.*, **38**, 457 (1983).

10. J.L. Ayres and P.S. Fedkiw, Report No. 207, Wat. Resources, Research Institute of the University of North Carolina, North Carolina State University, Raleigh, NC (1983).
11. G.W. Reid, R.Y. Nelson, C. Hall, U. Bonilla and B. Reid, *Water Sewage Works,* **115**, 320 (1968).
12. M. Jevtitch and D. Bhattacharyya, *Chem. Eng. Commun.,* **23,** 191 (1983).
13. J.W. Hassler, Purification with Activated Carbon, Chemical Publishing Co., New York (1974).
14. K. Srinivasan, K. Balasubramanian and T.V. Ramakrishna, *Indian J.Environ. Health,* **30,** 376 (1988).
15. A. Arulanantham, K. Balasubramanian and T.V. Ramakrishna, *Metal Finishing,* **87,** 51 (1989).
16. K. Periasamy, K. Srinivasan and P.K. Murugan, *Indian J. Environ. Health,* **33,** 433 (1991)
17. C. Namasivayam and K. Periyasamy, *Water Res.,* **27,** 1663 (1993).
18. ———, *Waste Manag.,* **15,** 63 (1995).
19. ———, *Ind. Eng. Chem. Res.,* **33,** 317 (1994).
20. H.E. Allen and R.A. Minear, Metallic ions, in: M.J. Sues (Ed.), Examination of Water for Pollution Control, Physical, Chemical and Radiological Examination, Vol. 2, Pergamon, Oxford, p.141 (1982).
21. M.K.N. Yenkie and G.S. Natarajan, *Sep. Sci. Tech.,* **26,** 661 (1994).
22. D.G. Kinniburgh, M.L. Jackson and J.K. Syers, *Soil Sci. Soc. Am. J.,* **40,** 796 (1978).
23. G.W. Bruemmer, J. Guerten and K.B. Tiller, *Soil Sci.,* **39,** 37 (1988).
24. L.D. Michelson, P.G. Gideon, E.G. Pace and L.H. Kutal, US Dept. Industry, Office of Water Research and Technology, Bull. No.74 (1975).
25. L.J. Langmuir, *Am. Chem. Soc.,* **40,** 1361 (1918).
26. G. McKay, H.S. Blair and J.R. Gardon, *J. Appl. Polymer Sci.,* **27,** 3043 (1982).

(*Received*: 21 October 2004; *Accepted:* 16 April 2005) AJC-4182