

REMOVAL OF NICKEL(II) FROM AQUEOUS SOLUTIONS BY CERALITE IR 120 CATIONIC EXCHANGE RESINS

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Abstract

The removal of nickel from aqueous solutions under different experimental conditions using a Ceralite IR 120 cationic exchange resin (CXR) as an adsorbent was investigated by batch adsorption techniques. Batch studies indicated that the percent adsorption decreased with increasing initial concentration of Ni²⁺. Maximum Ni²⁺ removal was observed near a pH of 5.0. The adsorption process obeys the Langmuir and Freundlich adsorption isotherms. The monolayer adsorption capacity was found to be 28.57 mg/g. The sorption of nickel on the resin was rapid during the first 25 minutes and the equilibrium was found to be attained within 35 minutes. The sorption of nickel onto the resins followed reversible first-order rate kinetics. Such ion exchange resins can be used for the efficient removal of nickel from water and wastewater.

Keywords: Nickel(II), CXR (Cationic exchange resin), Adsorption, Isotherms, Kinetics.

1. Introduction

Heavy metals contamination of water and wastewater is a common phenomenon. Industrial wastewaters are usually the cause of heavy metals pollution of the environment. Many plating and battery industries release heavy metals such as chromium, nickel, cadmium and lead in wastewaters. These heavy metals find many applications in our life are very harmful if they discharged into natural water resources and pose a serious health hazard [1–5]. The Nickel(II), Ni(II), concentration in wastewater from mine drainage, tableware plating, metal finishing and forging has been reported up to 130 mg/L [6]. The rinsewater from nickel plating industries having nickel concentrations of 2–900 mg/L is known to

Nomenclatures

C_e	Metal concentration at equilibrium, mg/L
C_f	Final metal concentration, mg/L
C_i	Initial metal concentration, mg/L
K_c	Equilibrium constant
K_f	Adsorption capacity by Freundlich isotherm model, $(\text{mg/g})(\text{L/mg})^{(1/n)}$
K_L	Empirical Constant by Langmuir isotherm model, L/mg
k_1	Forward reaction rate constant
k_2	Backward reaction rate constant
M	Molarity
n	Adsorption intensity by Freundlich isotherm model
q_e	Metal uptake at equilibrium, mg/g
q_m	Empirical Constant by Langmuir isotherm model, mg/g
U_i	Fractional attainment of nickel equilibrium

be one of the major toxic pollutants, which necessitates the development of effective and inexpensive methods to remove nickel from the effluent [7].

Conventional methods for the removal of Ni(II) from wastewaters include chemical precipitation, chemical reduction, flocculation, filtration, evaporation, solvent extraction, biosorption, activated carbon adsorption, ion-exchange, reverse osmosis, electrodialysis, membrane separation processes, etc. The chemical precipitation is the most cost-effective treatment technology. The possibility to precipitate metals in the form of insoluble compounds, mostly metal hydroxides, in solutions containing complexing agents depends on the complex stability constant and the hydroxide solubility product [8]. A broad range of biomass types including bacteria, algae, yeast, fungi, activated sludge, anaerobic sludge, digested sludge, peat have been used as biosorbents to remove Ni(II) metals from aqueous solution [9-20].

The nickel ion, compared with other heavy metal ions, was a more recalcitrant pollutant and many metal tolerant micro-algae had a relatively low Ni-binding capacity. The removal of nickel ions from electroplating effluent was far from satisfactory. The biosorption of nickel by different strains of microorganisms was less than that of other metal ions. This was probably due to the intrinsic chemical properties of nickel ions leading to steric hindrance of biosorption. Studies focusing specifically on nickel removal are rare. There is still no satisfactory precedent of employing biosorbent in the removal of nickel ions and the feasibility of employing micro-algae to remove Ni from electroplating wastewater is uncertain. Adsorption by activated carbon is widely used for the removal of toxic metal and has been studied extensively. In addition to conventional activated carbons, some low cost waste materials such as coir pith [21], hazelnut shell [22], almond husk [23], are also utilized for preparation of activated carbon and applied for nickel removal. The removal Ni(II) by clays [24, 25], was used in the fabrication of common products like wall or floor tiles, where nickel ions remain firmly attached and inertized. Higher cation-exchange capacity and development of surface negative charge on clay particles in contact with water also contribute to this promising performance, despite the lower available specific

surface area in comparison with granular activated carbon. These methods have several disadvantages of high operating cost, incomplete removal, low selectivity, high energy consumption, and they generate hazardous solid waste that are difficult to eliminate. Ion exchange has been widely applied for removal of heavy metal ions from electroplating effluent because it is effective and easy to operate. Recovery and removal of nickel ions from wastewater using ion-exchange method [26-31], was used.

In the present paper, cationic exchange resins were examined for their sorption properties towards Nickel ion. The influence of experimental parameters such as pH, contact time, adsorbent dosage and initial nickel concentrations were studied at 25°C. The kinetic data and equilibrium data of adsorption studies were processed to understand the adsorption mechanism of the nickel ions onto the cationic exchange resin.

2. Experimental

2.1. Materials

All the chemicals used were of analytical reagent (AR) grade. Ceralite IR 120 is an H⁺ form strongly CXR. The properties of ion exchange resin Ceralite IR 120 is shown in the Table 1. Stock solution of nickel (500 mg/L) was prepared by dissolving NiSO₄.6H₂O (procured from Merck, India) in double distilled water. The concentration range of nickel prepared from stock solution varied between 100 to 500 mg/L.

Table 1. Properties of Ion Exchange Resin Ceralite IR 120.

Parameter	Ceralite IR 120
Manufacturer/supplier	CDH, New Delhi
Ionic group	H ⁺ form strongly CXR
Particle size	0.45–0.6 mm (effective size)
Physical form beads	Yellow brown spherical beads
Density	0.77 g/ml
Exchange capacity (fresh)	4.5 mm equiv./g
Moisture content	45–50 wt%
Maximum Temperature	120 °C
pH range	0–14
Cross-linking	8% DVB
Porosity	0.42
Nominal diameter	0.5mm

2.2. Analysis

The concentrations of nickel in the solutions before and after equilibrium were determined by Atomic absorption spectrometer. The pH of solution was measured with a Hanna pH meter using a combined glass electrode.

2.3. Adsorption Experiment

Batch studies were carried out at the room temperature of 25°C. In the adsorption experiment, weighed quantity of CXR was taken in an Erlenmeyer flasks

(250 mL) containing 100 mL wastewater sample. The pH of the wastewater - CXR system was adjusted to the desired value by using 0.1 M NaOH or HCl and the mixture was shaken for a predetermined period using a wrist action shaker operated at 120 rpm. Kinetics of adsorption was determined by analyzing adsorptive uptake of the nickel ion at different time intervals. Independent bottles containing 100 mL wastewater sample and 2 g CXR were used during the kinetic studies to get accurate results for each point on the graph. Isothermal studies were conducted with different initial concentrations (100–500 mg/L) and 100 mL sample by shaking the reaction mixture for equilibrium time. The residual nickel concentration in the reaction mixture was analyzed by filtered through Whatman filter paper No. 40 and the filtrate samples were analyzed by Atomic absorption spectrometer. All the experiments were performed in duplicates. The percentage removal of nickel from the aqueous solution was calculated according to the following equation:

$$\%Removal = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

where C_i and C_f are the initial and final nickel concentration (mg/L), respectively.

3. Results and Discussion

3.1. Effect of pH

The adsorption of Ni^{2+} was found to be strongly dependent on the pH of the solution. Figure 1 demonstrates that the optimum pH for the adsorption of Ni^{2+} was about 5 which was rather acidic. At low pH (below 3), there was excessive protonation of the active sites at adsorbent surface and this often refuses the formation of links between Ni^{2+} ion and the active site. At moderate pH values (3-6), linked H^+ is released from the active sites and adsorbed amount of Ni^{2+} ions is generally found to increase.

At higher pH values (above 6), the precipitation is dominant or both ion exchange and aqueous metal hydroxide formation may become significant mechanisms in the metal removal process. This condition is often not desirable as the metal precipitation could lead to a misunderstanding for the adsorption capacity.

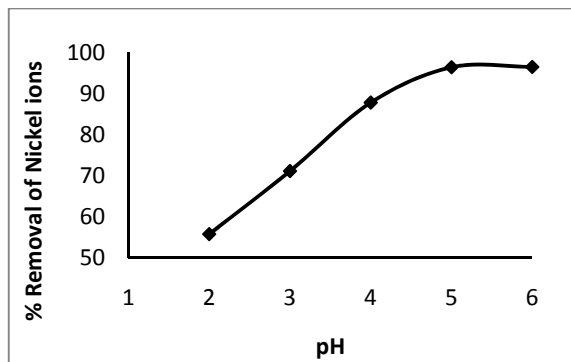


Fig. 1. Effect of pH.

3.2. Effect of adsorbent dose

The effect of the adsorbent dose was studied by varying the sorbent amounts from 5.0 to 30 g/L. For all these runs, initial concentration of nickel was fixed as 100 mg/L. Figure 2 shows the adsorption of Ni^{2+} ions increases rapidly with increase in the amount of CXR due to greater availability of the surface area at higher concentration of the adsorbent. The significant increase in uptake was observed when the dose was increased from 5.0 to 20 g/L. Any further addition of the adsorbent beyond this did not cause any significant change in the adsorption. From the results, it is revealed that within a certain range of initial metal concentration, the percentage of metal adsorption on CXR is determined by the sorption capacity of the resin. The maximum removal of nickel was obtained in the adsorbent dose of 20 g/L. Considering this fact for the subsequent studies, the amount of adsorbent was taken as 20 g/L.

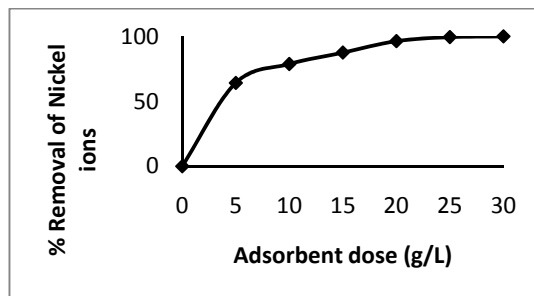


Fig. 2. Effect of Adsorbent Dose.

3.3. Effect of contact time

Adsorption of nickel was measured at given contact times for five different initial Ni^{2+} concentrations of 100, 200, 300, 400 and 500 mg/L. CXR was used as an adsorbent in bench-scale studies. From Fig. 3, the plot reveals that the rate of percent nickel removal is higher at the beginning. This is probably due to larger surface area of the CXR being available at beginning for the adsorption of Ni^{2+} ions. As the surface adsorption sites become exhausted, the uptake rate is controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the adsorbent particles.

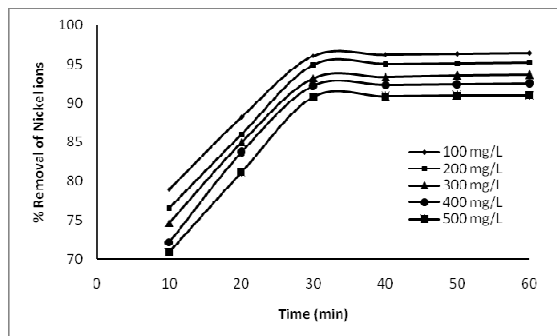


Fig. 3. Effect of Contact Time.

Most of the maximum percent nickel removal was attained after about 60 min of shaking time at different concentrations. The increasing contact time increased the nickel adsorption and it remains constant after equilibrium reached in 35 min for different initial concentrations.

3.4. Effect of initial concentration

The effect of initial Ni^{2+} concentration in the range of 100 to 500 mg/L on adsorption was investigated and the results are shown in Fig. 4. It was found that the percentage nickel removal decreased with increase in initial nickel concentration, in other words the adsorption capacity increasing from 4.28 to 22.76 mg/g as the metal concentration increase from 100 to 500 mg/L (not shown). While the percentage nickel removal was found to be 96.42% for 100 mg/L of initial concentration, this value was 91.02% for that of 500 mg/L. This trend is that of the result of the progressive increase in the electrostatic interaction between the nickel ions and the adsorbent active sites. Moreover, this can be explained by the fact that more adsorption sites were being covered as the nickel ions concentration increases.

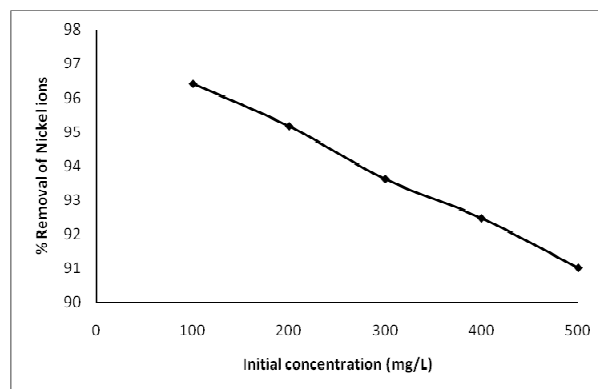


Fig. 4. Effect of Initial Nickel Concentration.

3.5. Adsorption isotherms

Adsorption isotherms are mathematical models that describe the distribution of the adsorbate species among liquid and adsorbent, based on a set of assumptions that are mainly related to the heterogeneity/homogeneity of adsorbents, the type of coverage and possibility of interaction between the adsorbate species. Adsorption data usually described by adsorption isotherms, such as Langmuir and Freundlich isotherms. These isotherms relate metal uptake per unit weight of adsorbent (q_e) to the equilibrium adsorbate concentration in the bulk fluid phase C_e . The results of the adsorption experiment conducted in this study were fitted with the well known adsorption models namely Langmuir and Freundlich.

The Langmuir model is based on the assumption that maximum adsorption occurs when a saturated monolayer of solute molecules is present on the adsorbent surface, and the energy of adsorption is constant and there is no

migration of adsorbate molecules in the surface plane. The Langmuir isotherm [32] is given by:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (2)$$

The constants in the Langmuir isotherm can be determined by plotting $(1/q_e)$ versus $(1/C_e)$ and making use of above equation rewritten as:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_L} \frac{1}{C_e} \quad (3)$$

From Fig. 5 the empirical constants q_m and K_L were found to be 28.57 mg/g and 0.056 respectively.

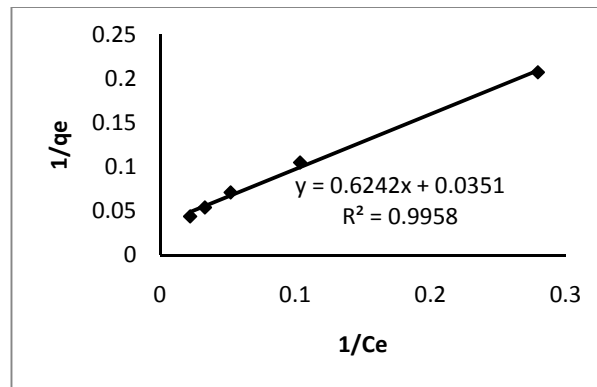


Fig. 5. Langmuir Adsorption Isotherm.

The Freundlich isotherm model is an empirical relationship describing the adsorption of solutes from a liquid to a solid surface and assumes that different sites with several adsorption energies are involved. Freundlich adsorption isotherm is the relationship between the amounts of nickel adsorbed per unit mass of adsorbent, q_e , and the concentration of the nickel at equilibrium, C_e .

$$q_e = K_f C_e^{1/n} \quad (4)$$

The logarithmic form of the equation becomes,

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (5)$$

where K_f and n are the Freundlich constants which represent the adsorption capacity and adsorption intensity, respectively [33].

The ability of Freundlich model to fit the experimental data was examined. For this case, the plot of $\log C_e$ vs. $\log q_e$ was employed to generate the intercept value of K_f and the slope of n . From Fig. 6 the Freundlich constants K_f and n were found to be 2.270 mg/g and 1.631 respectively.

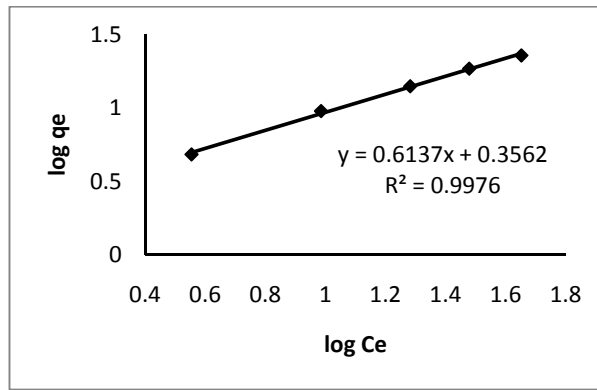


Fig. 6. Freundlich Adsorption Isotherm.

The Langmuir and Freundlich adsorption constants calculated from the corresponding isotherms with the correlation coefficients are presented in Table 2. The correlation coefficient shows that the adsorption process could be described by the both Langmuir and Freundlich model equation. The Langmuir constants (q_m and K_L) values were fit the experimental data. On the other hand, the magnitudes of K_f and n show easy separation of Ni^{2+} ions from the wastewater and indicate favorable adsorption. As seen from the Table 2, n value was found high enough for separation.

Table 2. Isotherm Models Constants and Correlation Coefficients for Adsorption of Nickel from Aqueous Solutions.

Adsorbent	Langmuir isotherm			Freundlich isotherm		
	q_m (mg/g)	K_L (L/mg)	R^2	K_f (mg/g)(L/mg) ^(1/n)	n	R^2
CXR	28.57	0.056	0.995	2.270	1.631	0.997

3.6. Adsorption kinetics

Experiments were also performed in order to understand the kinetics of nickel removal by CXR. It is a well established fact that the adsorption of nickel ions in aqueous system follows reversible first-order kinetics, when a single species is considered on a heterogeneous surface. It must be remembered that the two important physicochemical aspects for parameter evaluation of the sorption process as a unit operation are the kinetics and the equilibrium.

Kinetics of sorption describing the solute uptake rate which in turn governs the residence time of sorption reaction is one of the important characteristics defining the efficiency of sorption. Hence, in the present study, the kinetics of nickel removal has been carried out to understand the behavior of this adsorbent.

The sorption of nickel from liquid to solid phase may be expressed as:



where k_1 is the forward reaction rate constant and k_2 is the backward reaction rate constant. The overall rate constant, the forward and backward rate constants were calculated using the kinetic equations, Eqs. 6-9 in reference [34], U_t is called fractional attainment of equilibrium of nickel and this was calculated by considering nickel adsorption over the CXR in 30 minutes. By plotting $\ln(1-U_t)$ versus t (Fig. 7), the overall rate constant k for given concentration of nickel was calculated by considering the slope of straight line in Fig. 7 and by using Eq. (8) in reference [34].

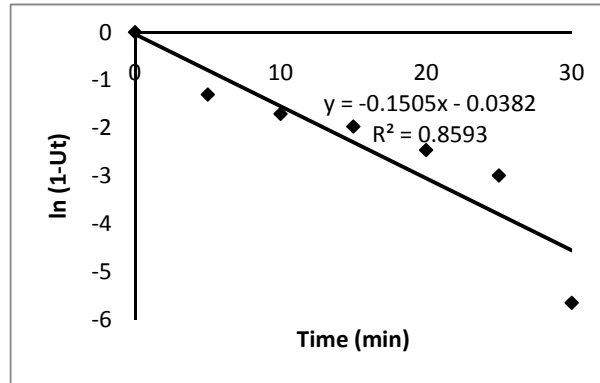


Fig. 7. First Order Reversible Reaction Kinetics Plot for the Adsorption of Ni(II) on Ceralite IR 120 resin.

The equilibrium constant, K_c , forward and backward rate constants, k_1 and k_2 , were calculated and are shown in Table 3. From Table 3, it is seen that the forward rate constants for the removal of nickel were much higher than the backward rate constants, namely the desorption process. The rate for the sorption of Ni^{2+} ions on the CXR was rapid during the first 25 minutes and equilibrium was found to be attained within 35 min. The sorption of Ni^{2+} onto the CXR followed reversible first-order rate kinetics. This suggests that the rate of adsorption is clearly dominant.

Table 3. Rate Constant for the Removal of Ni(II) with Ceralite IR 120.

Initial Ni(II) concentration (mg/L)	Overall rate constant, $k = k_1 + k_2$ (min^{-1})	Forward rate constant, k_1 (min^{-1})	Backward rate constant, k_2 (min^{-1})
100	0.150	0.1441	0.0059

4. Conclusions

Nickel ions are significantly adsorbed on Ceralite IR 120 CXR. The study indicates that removal of Ni(II) from aqueous solutions depends on the solution pH, adsorbent dose, contact time and initial nickel concentration. The adsorption process obeys both Langmuir and Freundlich adsorption isotherms. The sorption

of nickel onto the resins followed reversible first-order rate kinetics. The ion-exchangers can be used as an efficient sorbent for the removal of Ni(II) from aqueous solution. The sorption is relatively quick and the process is very efficient especially for water containing low concentrations of pollutants. These cation-exchangers are thus attractive sorbents for the treatment of wastewater containing Ni(II) ion at trace levels. Ceralite IR 120 CXR has provided new solutions for removing nickel from aqueous solution. The nickel ion exchange process is likely to become a very viable and alternative to other traditional treatment processes.

References

1. Denkhaus, E.; and Salnikow, K. (2002). Nickel essentially, toxicity, and carcinogenicity. *Critical Reviews in Oncology/Hematology*, 42(1), 35-56.
2. Pane, E.F.; Richards, J.G.; and Wood, C.M. (2003). Acute waterborne nickel toxicity in the rainbow trout (*Oncorhynchus mykiss*) occurs by a respiratory rather than ionoregulatory mechanism. *Aquatic Toxicology*, 63(1), 65-82.
3. Axtell, N.R.; Sternberg, S.P.K.; and Claussen, K. (2003). Lead and nickel removal using *Microspora* and *Lemna minor*. *Bioresource Technology*, 89(1), 41-48.
4. Akhtar, N.; Iqbal, J.; and Iqbal, M. (2004). Removal and recovery of nickel(II) from aqueous solution by loofa sponge-immobilized biomass of *Chlorella sorokiniana*: characterization studies. *Journal of Hazardous Materials*, 108(1-2), 85-94.
5. Pane, E.F.; Patel, M.; and Wood, C.M. (2006). Chronic, sublethal nickel acclimation alters the diffusive properties of renal brush border membrane vesicles (BBMVs) prepared from the freshwater rainbow trout. *Comparative Biochemistry and Physiology Part C: Toxicology & Pharmacology*, 143(1), 78-85.
6. Erdogan, S.; Onal, Y.; Alanil-Basar, C.; Bilmiz-Erdemoglu, S.; Sarici-ozdemir, C.; Koseoglu, E. and Icduygu, G. (2005). Optimization of nickel adsorption from aqueous solution by using activated carbon prepared from waste apricot by chemical activation. *Applied Surface Science*, 252(5), 1324-1331.
7. Patterson, J.W. (1985). *Industrial wastewater treatment technology*. 2nd Ed., Butterworth Publisher, Stoneham, MA.
8. Gyliene, O.; Aikaite, J.; and Nivinskiene, O. (2004). Recycling of Ni(II)-citrate complexes using precipitation in alkaline solutions. *Journal of Hazardous Materials*, 109(1-3), 105-111.
9. Malkoc, E.; and Nuhoglu, Y. (2006). Removal of Ni(II) ions from aqueous solutions using waste of tea factory: adsorption on a fixed-bed column. *Journal of Hazardous Materials*, 135(1-3), 328-336.
10. Ho, Y.S.; Wase, D.A.J.; and Forster, C.F. (1995). Batch nickel removal from aqueous solution by Sphagnum moss peat. *Water Research*, 29(5), 1327-1332.
11. Selatnia, A.; Madani, A.; Bakhti, M.Z.; Kertous, L.; Mansouri, Y.; and Yous, R. (2004). Biosorption of Ni²⁺ from aqueous solution by NaOH-treated bacterial dead *Streptomyces rimosus* biomass. *Minerals Engineering*, 17(7-8), 903-911.

12. Abu Al-Rub, F.A.; El-Nass, M.H.; Benyahia, F.; and Ashour, I. (2004). Biosorption of nickel on blank alginate beads, free and immobilized algal cells. *Process Biochemistry*, 39(11), 1767-1773.
13. Kalyani, S.; Srinivasa Rao, P.; and Krishnaiah, A. (2004). Removal of nickel(II) from aqueous solutions using marine macroalgae as the sorbing biomass. *Chemosphere*, 57(9), 1225-1229.
14. Borba, C.E.; Guirardello, R.; Silva, E.A.; Veit, M.T.; and Tavares, C.R.G. (2006). Removal of nickel(II) ions from aqueous solution by biosorption in a fixed bed column: experimental and theoretical breakthrough curves. *Biochemical Engineering Journal*, 30(2), 184-191.
15. Xu, H.; Liu, Y.; and Tay, J.H. (2006). Effect of pH on nickel biosorption by aerobic granular sludge. *Bioresource Technology*, 97(3), 359-363.
16. Wong, P.K.; and Fung, K.Y. (1997). Removal and recovery of nickel ion (Ni^{2+}) from aqueous solution by magnetite-immobilized cells of *Enterobacter* sp. 4-2. *Enzyme and Microbial Technology*, 20(2), 116-121.
17. Ho, Y.S.; and McKay, G. (1999). Pseudo-second order model for sorption processes. *Process Biochemistry*, 34(5), 451-465.
18. Wong, J.P.K.; Wong, Y.S.; and Tam, N.F.Y. (2000). Nickel biosorption by two chlorella species, *C. Vulgaris* (a commercial species) and *C. Miniata* (a local isolate). *Bioresource Technology*, 73(2), 133-137.
19. Yu, Q.; and Kaewsarn, P. (2000). Adsorption of Ni^{2+} from aqueous solutions by pretreated biomass of marine macroalga *Durvillaea potatorum*. *Separation Science and Technology*, 35(5), 689-701.
20. Patmavathy, V.; Vasudevan, P.; and Dhingra, S.C. (2003). Biosorption of nickel(II) ions on Baker's yeast. *Process Biochemistry*, 38(10), 1389-1395.
21. Kadirvelu, K.; Thamaraiselvi, K.; and Namasivayam, C. (2001). Adsorption of nickel(II) from aqueous solution onto activated carbon prepared from coirpith. *Separation and Purification Technology*, 24(3), 497-505.
22. Demirbas, E.; Kobya, M.; Oncel, S.; and Sencan, S. (2002). Removal of Ni(II) from aqueous solution by adsorption onto hazelnut shell activated carbon: equilibrium studies. *Bioresource Technology*, 84(3), 291-293.
23. Hasar, H. (2003). Adsorption of nickel(II) from aqueous solution onto activated carbon prepared from almond husk. *Journal of Hazardous Materials*, 97(1-3), 49-57.
24. Marquez, G.E.; Ribeiro, M.J.P.; Ventura, J.M.; and Labrincha, J.A. (2004). Removal of nickel from aqueous solutions by clay-based beds. *Ceramics International*, 30(1), 111-119.
25. Gupta, S.S.; and Bhattacharyya, K.G. (2006). Adsorption of Ni(II) on clays. *Journal of Colloid and Interface Science*, 295(1), 21-32.
26. Elshazly, A.H.; and Konsowa, A.H. (2003). Removal of nickel ions from wastewater using a cation-exchange resin in a batch-stirred tank reactor. *Desalination*, 158(1-3), 189-193.
27. Rodriguez-Iznaga, I.; Gomez, A.; Rodriguez-Fuentes, G.; Benitez-Aguilar, A.; and Serrano-Ballan, J. (2002). Natural clinoptilolite as an exchanger of Ni^{2+} and NH_4^+ ions under hydrothermal conditions and high ammonia concentration. *Microporous and Mesoporous Materials*, 53(1-3), 71-80.

28. Rodriguez-Iznaga, I.; Rodriguez-Fuentes, G.; and Benitez-Aguilar, A. (2000). The role of carbonate ions in the ion-exchange $\text{Ni}^{2+} = 2\text{NH}_4^+$ in natural clinoptilolite. *Microporous and Mesoporous Materials*, 41(1-3), 129-136.
29. Seggiani, M.; Vitolo, S.; and D'Antone, S. (2006). Recovery of nickel from Orimulsion fly ash by iminodiacetic acid chelating resin. *Hydrometallurgy*, 81(1), 9-14.
30. Tokuyama, H.; Maeda, S.; and Takahashi, K. (2004). Development of a novel moving bed with liquid-pulse and experimental analysis of nickel removal from acidic solution. *Separation and Purification Technology*, 38(2), 139-147.
31. Papadopoulos, A.; Fatta, D.; Parperis, K.; Mentzis, A.; Haralambous, K.J.H.; and Loizidou, M. (2004). Nickel uptake from a wastewater stream produced in a metal finishing industry by combination of ion-exchange and precipitation methods. *Separation and Purification Technology*, 39(3), 181-188.
32. Langmuir, I. (1918). The adsorption of gases on plane surfaces of glass, mica and platinum. *Journal of the American Chemical Society*, 40(9), 1361-1403.
33. Freundlich, H.M.F. (1906). Over the adsorption in solution. *Journal of Physical Chemistry*, 57, 385-471.
34. Kumar, S.P.; Kirthika, K.; and Kumar, S.K. (2008). Removal of Hexavalent chromium ions from aqueous solutions by an anion-exchange resin. *Adsorption Science and Technology*, 26(9), 693-703.