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Parametric experiments and kinetic studies on the removal of nickel using strong acid cation exchange resin 001 × 7

Natarajan Rajamohan

Faculty of Engineering, Department of Chemical Engineering, Sohar University, Sohar P.C.:311, Sultanate of Oman, email: natrajmohan@gmail.com (N. Rajamohan)

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ABSTRACT

In this research study, the feasibility of removal of nickel ions was evaluated by utilizing a strong acid cation exchange resin 001 × 7. Parametric experiments were performed in a shaker in order to determine the effect of process variables like pH, resin dose, initial metal concentration, agitation speed and temperature on the metal removal efficiency and uptake. It was observed that 88% of metal removal was achieved at optimal pH 5.0 at an initial metal concentration of 100 mg/L. With higher resin dose, the removal efficiency increased and higher concentrations of metal required more equilibrium time for maximum removal. The experimental data were fitted to two kinetic models and pseudo-first-order model was found to fit well based on the values of correlation coefficient. The pseudo-first-order rate constant was found to be 2.1×10^{-4} g/mg min for an initial nickel concentration of 100 mg/L. An inverse relation was found to exist between pseudo-first-order rate constant and initial metal concentration. The initial exchange rate and rate constant of the pseudo-second-order model were also evaluated. Fourier transform infrared spectroscopy studies were performed to verify the ion exchange mechanism.

Keywords: Cation resin; Nickel; Kinetics

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1. Introduction

Development and growth of mining, metallurgy, aircraft, electroplating and storage battery industries have led to the release of huge volumes of industrial effluents which are contaminated with toxic non-biodegradable heavy metals. Based on the strict regulations on discharge standards imposed by legislative bodies, environmental engineers and researchers have started working on developing a new technology for the effective treatment of heavy metal-polluted waters. Due to their high solubility, heavy metals enter the food chain through aquatic dissolution and tend to accumulate in the human body [1].Toxic heavy metals of high priority include zinc, copper, nickel and lead. Nickel enters the environment through the industrial activities like mining and metallurgy of nickel, electroplating, stainless steel, pigment and ceramic industries [2,3]. Nickel exceeding its permissible level is reported to cause serious lung and kidney diseases, gastrointestinal disorders, pulmonary fibrosis and skin dermatitis [4,5]. In addition, nickel is present as an enzyme component and participates in the biochemical reactions such as methane biogenesis, acidogenesis and urolysis [6]. Conventional methods like chemical precipitation, adsorption, reverse osmosis, solvent extraction and coagulation suffer from demerits like low removal

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efficiency, high capital and running cost and production of toxic sludge [7]. Ion exchange is proposed as a suitable alternative for the conventional methods already used for the removal of heavy metals. Ion exchange is categorized as a unique unit operation involving electrostatic forces, and shares some common features with adsorption. Ion exchange resin can be of natural or synthetic in its origin and possesses specific and selective ability to exchange its cations with the metal ions present in the industrial wastewater [4]. Ion exchange method using different resins have been successfully applied for the removal of metals [8–11]. Ion exchange using strong acid cationic resins is an attractive option for the removal of cations from industrial wastewaters. To elucidate the mechanism of metal transport in this process, it is very important to know the exchange phenomenon at the solid–liquid interface [12]. Kinetic data on sorption is required for the design and efficient operation of ion exchange process [13]. Cationic resin, Dowex HCR-S resin, has been utilized and the kinetic and thermodynamic studies were performed for the removal of nickel [14], cadmium [15] and zinc [16]. The maximum adsorption capacities of Pb(II), Cu(II) and Zn(II) using red loess were estimated to be 113.6, 34.2 and 17.5 mg/g, respectively, at 25˚C and pH 6 [17]. In this context, the present study is aimed to investigate the removal of Ni(II) cations using a strong acid cationic exchange resin 001 × 7. During the study, effect of various process conditions like initial pH, amount of resin, speed of agitation, initial metal concentration and operating temperature on the metal removal was evaluated. In addition, the kinetic experiments were conducted to evaluate the mechanism of metal removal.

2. Materials and methods

2.1. Resin preparation and metal solution

The strong acid cationic resin—001 × 7 contains sulphonic acid (–SO_3H) as the functional group. There are—SO_3H groups on styrene-based polymer and the acidity of this resin is similar to HCl and H_2SO_4. This cation exchange resin has moisture content in the range of 45–55% and was used for water softening applications. The particle size of the supplied resin was in the range of 0.42–1.2 mm in diameter. The resin was washed with deionized water (Millipore Milli-Q) repeatedly for several times and dried at 50˚C in a vacuum oven for 12 h. The sample metal solutions containing Ni(II) ions was prepared by diluting 1,000 mg/L of Ni $(NO_3)_2{\cdot}6H_2O$ standard solution (Merck, Germany) with deionized water. The pH of the working solution was maintained using analytical reagent grade HCl, NaOH and buffer solutions (Merck, Germany). The properties of the resin are presented in Table 1.

Table 1
Properties of the resin

Property	Units	Value
Moisture	%	45–52
Granularity	%	≥95
Effective grain size	mm	0.40–0.70
Uniformity coefficient		≤1.6
pH range		1–14
Maximum operating temperature	˚C	≤100

2.2. Experimental procedure

Optimization of process conditions was done by conducting a series of planned experiments. Batch ion exchange experiments were conducted by placing a sample of 100 mL of the metal solution and agitated in an orbital shaker at different experimental conditions based on the experimental design for an equilibrium time of 150 min, which was fixed using preliminary experiments. The effect of pH was studied in the range of 2.0–9.0 at fixed operating conditions. The adjustment of pH of the samples was done by adding either 0.1 N HCl or NaOH as the buffering agent. Different resin quantities ranging from 0.25 to 2.0 g/L was tested at optimal pH and an initial metal concentration of 100 mg/L. The effect of different initial nickel concentrations on the percentage metal removal was studied in the range of 0–100 mg/L at a predetermined optimal pH and resin quantity. In succession, the effect of speed of rotation was studied in the range of 0–300 rpm and the effect of temperature at 303, 308 and 313 K, respectively. At fixed time intervals, a sample of solution was withdrawn and filtered. The filtered sample was analyzed for residual metal concentrations using UV spectrophotometer (Biochrom, UK) at an analytical wavelength, $\lambda_{\max}$ of 420 nm. The kinetic experiments were performed to elucidate the exchange mechanism and to find the effect of concentration on the rate of ion exchange process. Pseudo-second order and intra particle diffusion models were fitted to the experimental data and linearity of fit is verified. The metal uptake was calculated by using the following Eq. (1):

$$q = (C_0 - C_e)V/R \tag{1}$$

where q is the amount of metal adsorbed by the resin at any time, t (mg/g); C_0 and C_e are the initial and final nickel concentrations (mg/L), respectively; V is the volume of sample solution (L) and R is the resin quantity (g).

The percentage nickel removal is defined by

$$\%\,\text{nickel removal} = \frac{(C_0 - C_e)}{C_0} \times 100 \tag{2}$$

2.3. Kinetic models

2.3.1. Pseudo-first-order model

The pseudo-first-order kinetic model is represented as (Eq. (3)):

$$\ln(q_e - q) = \ln q_e - k_1 t \tag{3}$$

where q_e is the amount of metal adsorbed by the resin at equilibrium (mg/g) and k_1 is the first order rate constant (g/mg min). The slope and intercept of the linear plot ln $(q_e - q)$ vs. time will give the values of the model constants.

2.3.2. Pseudo-second-order model

The pseudo-second-order model [18] can be represented in the following form:

$$\frac{t}{q} = \frac{1}{(h_2)} + \frac{t}{q_e} \tag{4}$$

where q_e is the amount of dye adsorbed at equilibrium (mg/g), $h_2 (= k_2 q_e^2)$ is the initial exchange rate (mg/g min) and the pseudo-second-order constant k_2 (g/mg min) can be determined experimentally from the slope and intercept of plot $\frac{t}{q}$ vs, t.

2.4. Characterization of the resin

Fourier transform infrared spectroscopy (FTIR) was used to identify the different chemical functional groups present in the ion exchange resin. FTIR analyses also helps in identifying the functional groups which are responsible for the nickel binding with the strong acid cation resin. The analysis was carried out in the spectral range varying from 4,000 to 400 cm^{-1}.

All spectra were obtained using a PerkinElmer Spectrum BX-FTIR.

3. Results and discussion

3.1. Effect of pH

pH is reported as a vital operating variable for all processes which involves surface sites for transfer of components [19]. Fig. 1 depicts the effect of pH on the metal removal efficiency studied over the range of 2.0–9.0 at fixed initial metal concentration of 100 mg/L. Maximum removal percentage (88%) was observed at pH 5.0 and was used for all other parametric experiments conducted. Low removal efficiencies in the highly acidic pH conditions of 2.0–4.0 was attributed to the excessive presence of protons which can compete with the Ni^{2+} cations in the ion exchange process. But, the removal percentages were observed to decrease after pH 5.0, which could be due to the precipitation of nickel ions. In addition, the electrostatic effects and creation of strong fields are reported to change with the pH of the solution. Similar observations on the pH experiments were reported on zinc, copper and lead removal using Dowex 50 W resin [20]. It is generally reported that uptake of heavy metal ions onto a cation exchanger resin like D-001 is non-specific in an ion exchange process and high acidity is undesired for better metal removal [21]. Higher removal efficiency of 99% was reported to be achieved using strong acid cation exchange resin for lead removal at pH 5.0 [22]. Blank experiments were also conducted without resin in order to verify the possibility of precipitation as the mechanism of metal removal and no precipitation was observed during the studies.

3.2. Effect of resin quantity

Effect of the cation resin dose on the metal removal efficiency and uptake was studied by varying the amount of resin added in the range of 0.25–2.0 g/L at optimal pH of 5.0. Fig. 2 explains the effect of resin quantity on the performance factors and the metal removal efficiency was found to increase with increase in resin dose. From the plot, it was noticed that the

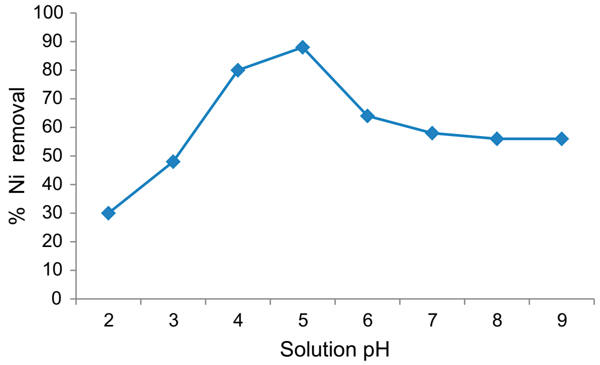


Fig. 1. Effect of pH on nickel removal using resin 001 × 7 (t = 150 min, C_0 = 100 mg/L, speed = 150 rpm).

removal efficiency increases exponentially with the resin dose in the range of 0.25–1.0 g/L, followed by a flat trend in the range of 1.0–2.0 g/L. This effect was related to the availability of more surface sites for ion exchange and increased surface area for metal–resin contact at higher resin doses. The rate of ion exchange depends on the availability of free surface sites. During the initial stages of contact, the exchange rate was observed to be high followed by a decrease, due to the saturation of ion exchange sites. But the metal uptake was found to decrease with increase in resin dose, which is attributed to insufficiency of metal ions for corresponding higher resin doses and binding sites interferences [7].

3.3. Effect of initial metal concentration

Fig. 3 presents the effect of initial nickel concentration on the percentage removal under fixed conditions of pH 5.0 and resin dose = 1.0 g/L with an equilibrium time of 150 min. The concentration of nickel was varied from 50 to 200 mg/L and the removal efficiency was observed to decrease with increase in metal concentration. This phenomenon was related to the availability of same number of ion exchange sites for different concentration and limited availability of free surface with the cation exchange resin [19]. The experimental observations revealed that the removal efficiency increased with increase in time of equilibration and reached a steady state after 150 min. Studies on chromium removal with identical metal concentrations was reported to have same behaviour with respect to the effect of initial concentration [23].

3.4. Effect of agitation speed

A set of experiments was conducted to investigate the effect of agitation speed on metal uptake; the initial concentration of nickel and pH were 100 mg/L and 5.0, respectively. The agitation speed was varied in the range 0–200 rpm. The metal uptake increased with speed up to 150 rpm and this effect was related to the stirring velocity in the system. The ion exchange process should be controlled by either chemical rate or intraparticle diffusion or both. The stirring velocity always influences the external diffusion in the liquid film. The optimal agitation speed was found to be 150 rpm and is shown in Fig. 4. The independence of metal uptake at speeds greater than 150 rpm confirms the presence of more than one rate-controlling mechanisms. Similar observations were reported in the ion exchange removal of copper (II) ions using Purolite C 100: MB resin [12].

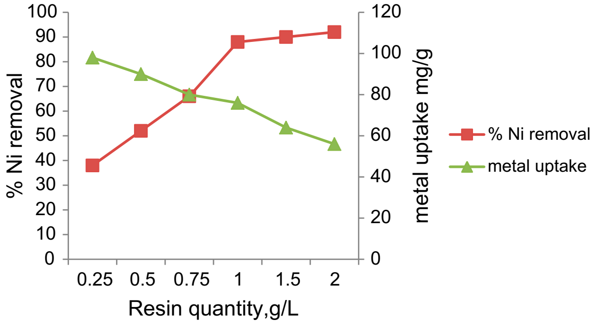


Fig. 2. Effect of resin quantity on % nickel removal using resin 001 × 7 ($t = 150$ min, $C_0 = 100$ mg/L, pH 5.0, speed = 150 rpm).

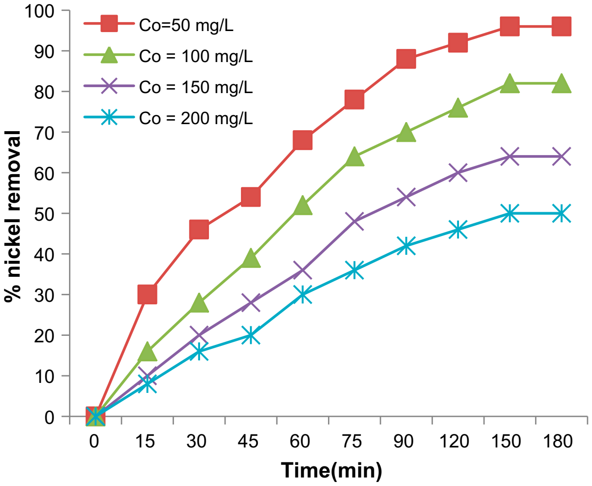


Fig. 3. Effect of initial nickel concentration on % metal removal using resin 001 × 7 ($t = 180$ min, pH 5.0, speed = 150 rpm).

3.5. Effect of temperature

Fig. 5 shows the effect of operating temperature on the nickel uptake at constant experimental conditions of initial metal concentration 100 mg/L, pH 5.0 and

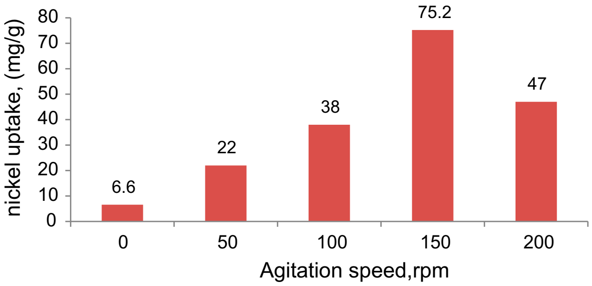


Fig. 4. Effect of speed of rotation on metal uptake using resin 001 × 7 ($t = 120$ min, $C_0 = 100$ mg/L, pH 5.0).

speed of agitation 150 rpm. The metal uptake capacities increased with increase in temperature and thus confirmed the endothermic nature of the ion exchange process. The ion exchange resins working capacity was reported to be strongly influenced by temperatures and metal concentration. In addition, the surface energy of the resin increases with temperature. Studies on the removal of divalent metal cations using Dowex 50W resin have reported similar results [24].

3.6. Ion exchange kinetics

Kinetic experiments are required to elucidate the mechanism of the transfer process and thus play a significant role in the design of the ion exchange systems. Determination of rate of the metal uptake is required for the selection of optimal operating conditions for the batch ion exchange systems. Kinetic studies help to determine the metal uptake rates. In this study, the kinetics of the ion exchange process was studied at different metal concentrations namely 50, 100, 150 and 200 mg/L. All other parameters were fixed at optimal conditions based on the parametric experiments.

The ion exchange process mechanism [14] can be expressed as given below in Eq. (5):

$$\mathrm{Ni}_s^{2+} + 2R - \mathrm{Na} \rightarrow R_2\mathrm{Ni} + 2\mathrm{Na}^+ \qquad (5)$$

The experimental data were fitted to linearized forms of equations of the pseudo-first-order and pseudo-second-order models, and plotted as Figs. 6 and 7. The linearity of the data was verified using correlation coefficient and the pseudo-first-order model was found to fit the results with the values of $R^2 >$ 0.950. The kinetic constants, namely the rate constants (k_1, k_2) and uptakes (q_e), were estimated from the slopes and intercepts of the kinetic plots. Table 2 presents the values of the kinetic constants for the two models selected at different initial metal concentrations. The change in rate constant with respect to the metal concentration was discussed with the best fit model, pseudo-first-order model, rate constant (k_1) and it was observed that the rate constant decreased with increase in metal concentration. This behaviour was due to the increased rate of mass transfer with increase in concentration gradient [25].

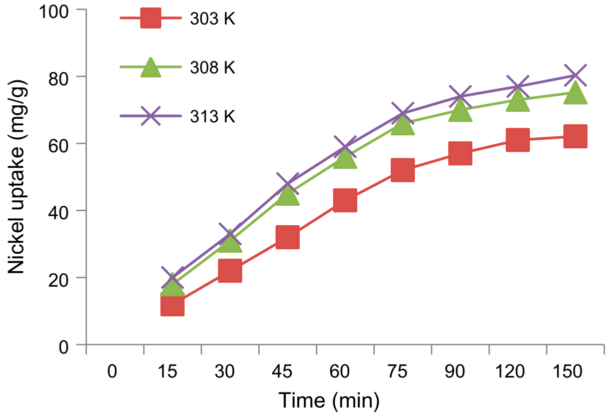


Fig. 5. Effect of temperature on metal uptake using 001 × 7 ($t = 150$ min, $C_0 = 100$ mg/L, pH 5.0, speed = 150 rpm).

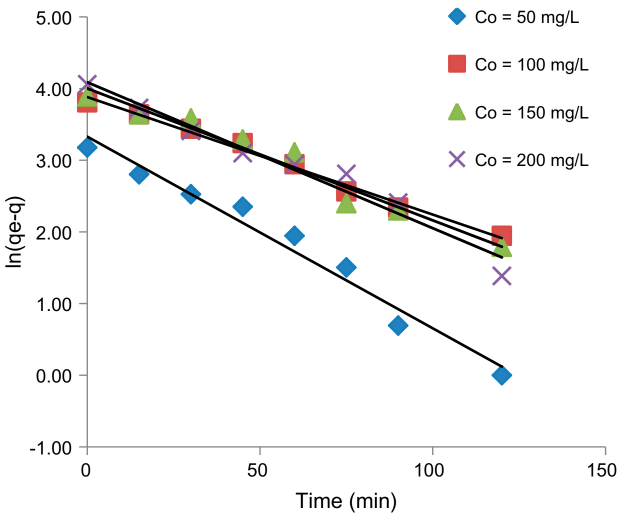


Fig. 6. Pseudo-first-order kinetic model plot for the removal of nickel.

3.7. FTIR analysis of the resin

To investigate the role functional groups of the resin on nickel removal, a FTIR study was carried out

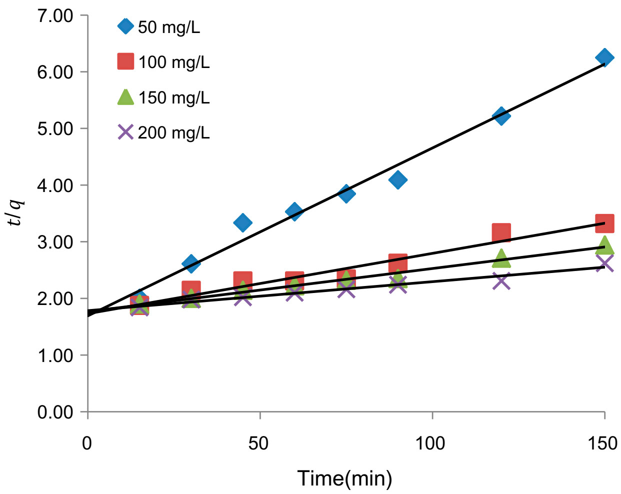


Fig. 7. Pseudo-second-order kinetic model plot for the removal of nickel.

Table 2
Kinetic model constants

Kinetic model	Initial nickel concentration (mg/L)			
	50	100	150	200
Pseudo-first order				
q_e (mg/g)	27.95	48.07	56.5	61.04
$k_1 \times 10^4$ (g mg^{-1} min^{-1})	2.67	2.1	1.89	1.86
R^2	0.98	0.98	0.97	0.952
Pseudo-second order				
q_e (mg/g)	33.78	94.34	131.58	196.08
h_2 (mg g^{-1} min^{-1})	1.693	1.731	1.767	1.784
$k_2 \times 10^4$ (g mg^{-1} min^{-1})	5.1	0.65	0.33	0.145
R^2	0.984	0.95	0.94	0.91

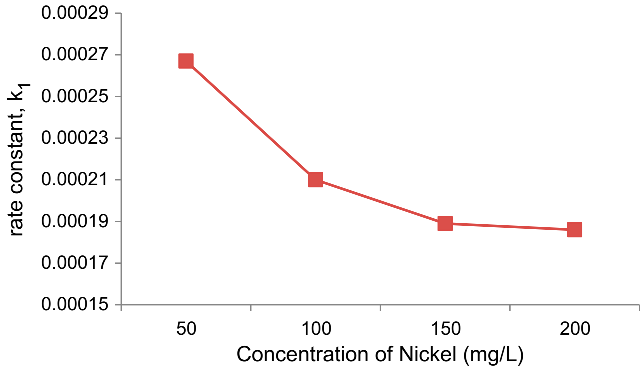
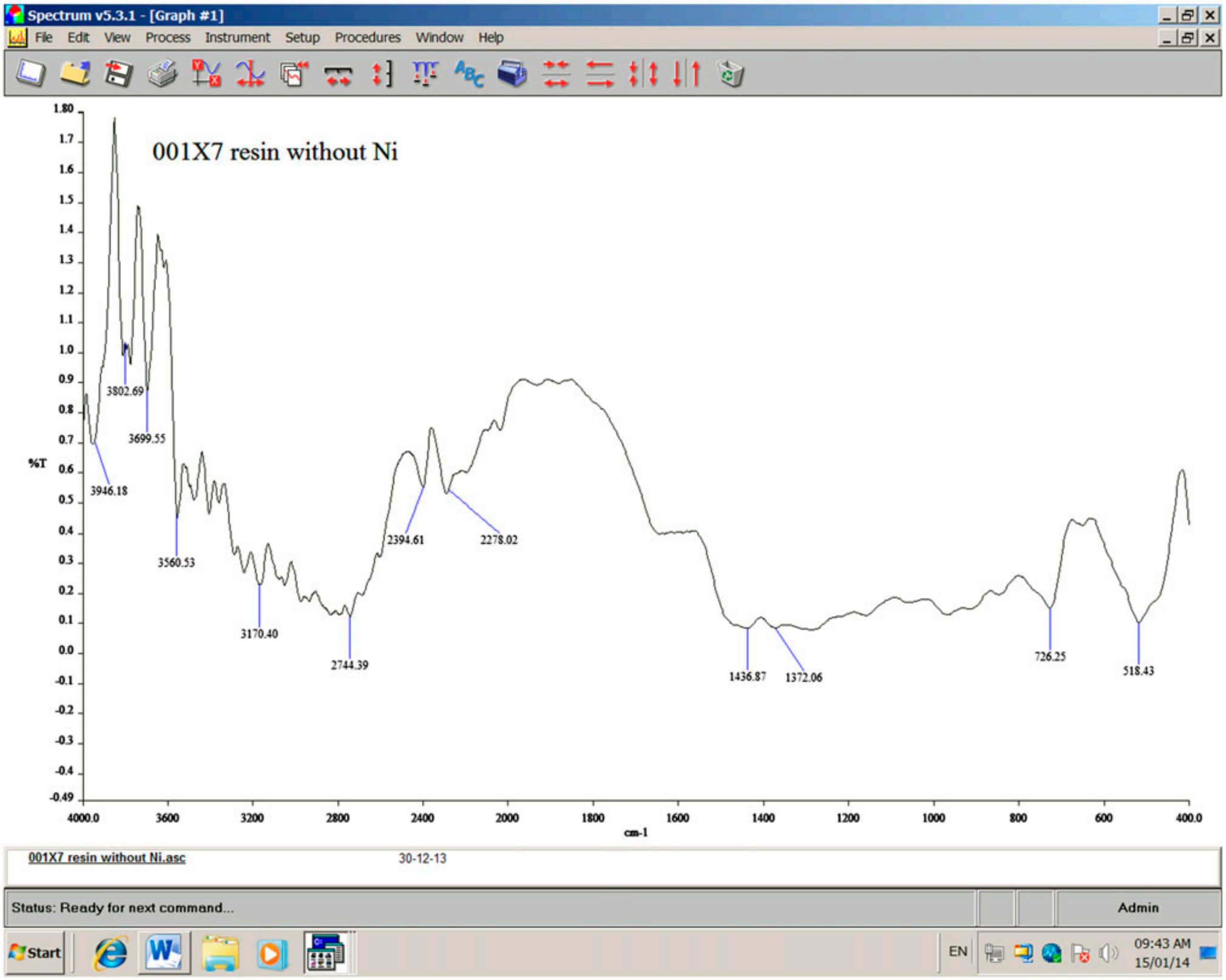


Fig. 8. Variation of best fit model rate constant with metal concentration.



001X7 resin without Ni.asc 30-12-13

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Fig. 9. FTIR spectrum of resin.

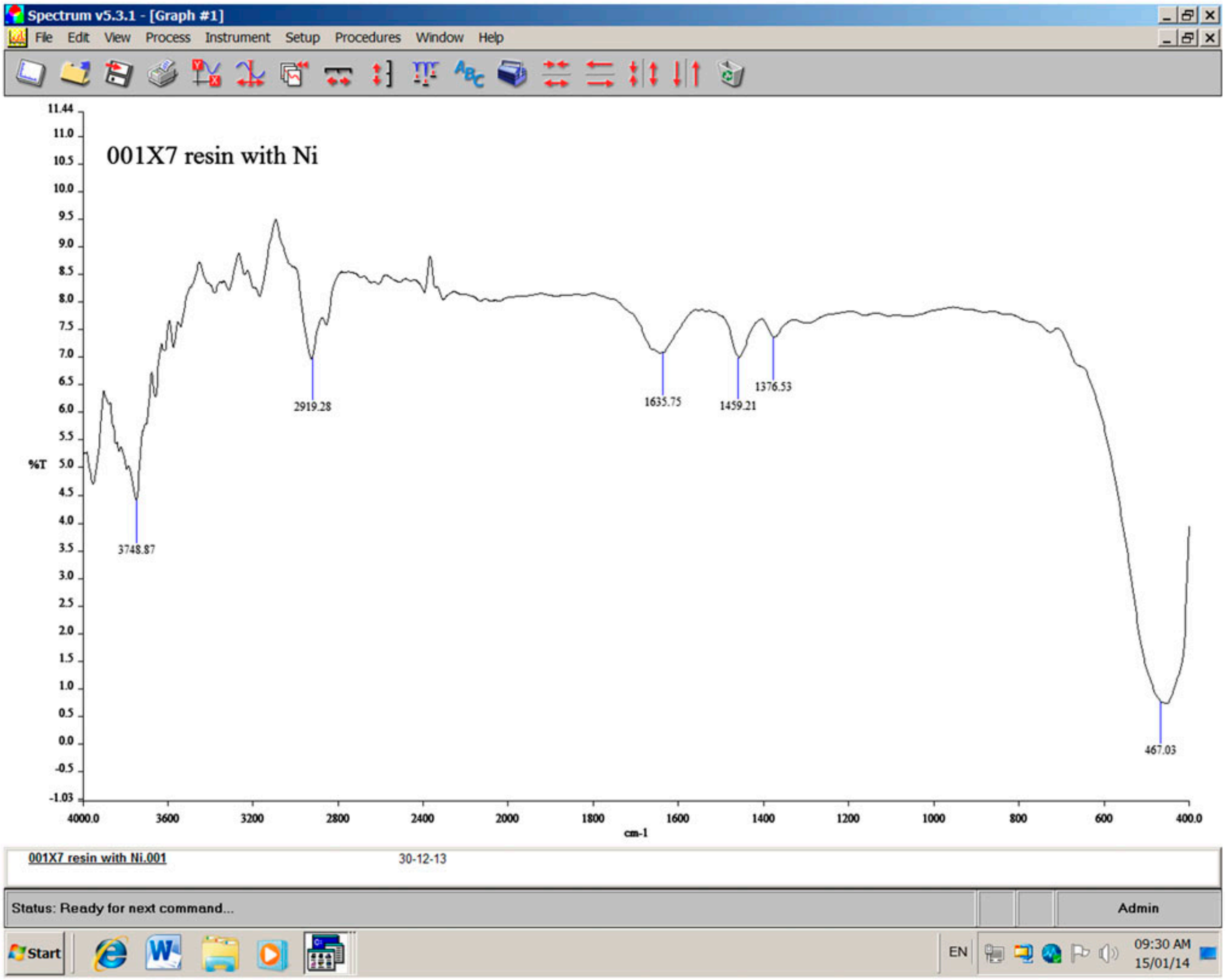

Fig. 10. FTIR spectrum of Ni loaded resin.

and the spectra before and after contact with the metal were shown in Figs. 8 and 9. The ion exchange resin displayed a number of absorption peaks, reflecting their complex nature. The absence of the peaks at 1,007 and 1,038 cm^{-1} corresponding to S–OH and S=O functional groups was observed in the FTIR spectrum and thus, confirmed the involvement of these functional groups in binding of Ni(II). The shifts in the absorption peaks generally observed indicate the existence of a metal binding process on the ion exchange resin (Fig. 10).

4. Conclusions

Experimental data on the ion exchange studies were obtained for the removal of nickel using 001 × 7 resin. Optimal removal conditions were estimated with batch experiments. Ion exchange process was found to be strongly driven by the pH, and the optimal pH was found to be 5.0 which yielded a maximum nickel removal of 88%. The resin dose was found to have a positive effect on metal removal efficiency, whereas the uptake decreased with increase in resin dose. The removal efficiency decreased with increase in metal concentration due to the reduction on exchange sites/metal ions ratio. The optimal speed of agitation was found as 150 rpm. This ion exchange process was observed to be endothermic in nature which favoured higher temperatures for better performance. Pseudo-first-order model fitted well to the ion exchange kinetic data and the model constants were valuated at different nickel concentrations. The experimental observations and theoretical validations confirm the applicability of the strong acid cation exchanger resin 001 × 7 for the successful removal of nickel ions from aqueous solutions.

References

[1] M.A. Barakat, New trends in removing heavy metals from industrial wastewater, Arab. J. Chem. 4 (2011) 361–377.

[2] W.S. Wan Ngah, M.A.K.M. Hanafiah, Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: A review, Bioresour. Technol. 99 (2008) 3935–3948.

[3] I. Alomá, M.A. Martín-Lara, I.L. Rodríguez, G. Blázquez, M. Calero, Removal of nickel (II) ions from aqueous solutions by biosorption on sugarcane bagasse, J. Taiwan. Inst. Chem. Eng. 43 (2012) 275–281.

[4] F. Fu, Q. Wang, Removal of heavy metal ions from wastewaters: A review, J. Environ. Manage. 92 (2011) 407–418.

[5] C.E. Borba, R. Guirardello, E.A. Silva, M.T. Veit, C.R.G. Tavares, Removal of nickel(II) ions from aqueous solution by biosorption in a fixed bed column: Experimental and theoretical breakthrough curves, Biochem. Eng. J. 30 (2006) 184–191.

[6] N. Akhtar, J. Iqbal, M. Iqbal, Removal and recovery of nickel(II) from aqueous solution by loofa sponge-immobilized biomass of *Chlorella sorokiniana*: Characterization studies, J. Hazard. Mater. 108 (2004) 85–94.

[7] U. Shafique, A. Ijaz, M. Salman, W.U. Zaman, N. Jamil, R. Rehman, A. Javid, Removal of arsenic from water using pine leaves, J. Taiwan. Inst. Chem. Eng. 43 (2012) 56–263.

[8] F. Wang, L. Wang, J. Li, X. Sun, W. Han, Adsorption behavior and mechanism of cadmium on strong-acid cation exchange resin, Trans. Nonferrous Met. Soc. China 19 (2009) 740–744.

[9] A. Bilge, V. Sevil, Kinetics and equilibrium studies for the removal on nickel and zinc from aqueous solutions by ion exchange resins, J. Hazard. Mater. 167 (2009) 482–488.

[10] R.S. Juang, H.C. Kao, W. Chen, Column removal of Ni (II) from synthetic electroplating waste water using a strong-acid resin, Sep. Purif. Technol. 49 (2006) 36–42.

[11] S. Rengaraj, K.H. Yeon, S.Y. Kang, J.U. Lee, K.W. Kim, S.H. Moon, Studies on adsorptive removal of Co (II), Cr(III) and Ni (II) by IRN77 cation-exchange resin, J. Hazard. Mater. B 92 (2002) 185–198.

[12] O. Hamdaoui, Removal of copper(II) from aqueous phase by Purolite C100-MB cation exchange resin in fixed bed columns: Modeling, J. Hazard. Mater. 161 (2009) 737–746.

[13] P.E. Franco, M.T. Veit, C.E. Borba, G.D.C. Gonçalves, M.R.F. Kle, R. Bergamasco, E.A. da Silva, P.Y.R. Suzaki, Nickel(II) and zinc(II) removal using Amberlite IR-120 resin: Ion exchange equilibrium and kinetics, Chem. Eng. J. 221 (2013) 426–435.

[14] B.A. Fil, R. Boncukcuoğlu, A.E. Yilmaz, S. Bayar, Adsorption of Ni(II) on ion exchange resin: Kinetics, equilibrium and thermodynamic studies, Korean J. Chem. Eng. 29 (2012) 1232–1238.

[15] B.A. Fil, R. Boncukcuoglu, A.E. Yilmaz, S. Bayar, Removal of divalent heavy metal ions from aqueous solutions by Dowex HCR-S synthetic resin, Bulg. Chem. Commun. 44 (2012) 201–207.

[16] B.A. Fil, R. Boncukcuoglu, A.E. Yilmaz, S. Bayar, Adsorption kinetics and isotherms for the removal of zinc ions from aqueous solution by an ion-exchange resin, J. Chem. Soc. Pak. 34 (2012) 841–848.

[17] S. Xing, M. Zhao, Z. Ma, Removal of heavy metal ions from aqueous solution using red loess as an adsorbent, J. Environ. Sci. 23 (2011) 1497–1502.

[18] Y.S. Ho, G. McKay, Pseudo-second order model for sorption processes, Process Biochem. 34 (1999) 451–465.

[19] N. Rajamohan, M. Rajasimman, R. Rajeshkannan, B. Sivaprakash, Kinetic modelling and isotherm studies on a batch removal of acid red 114 by an activated plant biomass, J. Eng. Sci. Technol. 8 (2013) 778–792.

[20] E. Pehlivan, T. Altun, The study of various parameters affecting the ion exchange of Cu^{2+}, Zn^{2+}, Ni^{2+}, Cd^{2+} and Pb^{2+} from aqueous solution on Dowex 50 W synthetic resin, J. Hazard. Mater. 134 (2006) 149–156.

[21] B. Pan, H. Qiu, B. Pan, G. Nie, L. Xiao, L. Lv, W. Zhang, Q. Zhang, S. Zheng, Highly efficient removal of heavy metals by polymer-supported nanosized hydrated Fe(III) oxides: Behavior and XPS study, Water Res. 44 (2010) 815–824.

[22] D. Kavak, M. Demir, B. Başsayel, A.S. Anagün, Factorial experimental design for optimizing the removal of lead ions from aqueous solutions by cation exchange resin, Desalin. Water Treat. 51 (2013) 1712–1719.

[23] G. Moussavi, B. Barikbin, Biosorption of chromium (VI) from industrial wastewater onto pistachio hull waste biomass, Chem. Eng. J. 162 (2010) 893–900.

[24] B. Alyüz, S. Veli, Kinetics and equilibrium studies for the removal of nickel and zinc from aqueous solutions by ion exchange resins, J. Hazard. Mater. 167 (2009) 482–488.

[25] G. Moussavi, R. Khosravi, Removal of cyanide from wastewater by adsorption onto pistachio hull wastes: Parametric experiments, kinetics and equilibrium analysis, J. Hazard. Mater. 183 (2010) 724–730.