Studies on adsorptive removal of Co(II), Cr(III) and Ni(II) by IRN77 cation-exchange resin

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Abstract

The adsorption of cobalt, chromium and nickel from aqueous solutions on IRN77 cation-exchange resin has been studied comparatively. The percentage removal of cobalt, chromium and nickel was examined by varying experimental conditions, viz. dosage of adsorbent, pH of the solution and contact time. It was found that more than 95% removal was achieved under optimal conditions. The adsorption capacity (k) for cobalt, chromium and nickel were calculated from the Freundlich adsorption isotherm. The adsorption of cobalt, chromium and nickel on this cation-exchange resin followed the Lagergren kinetic model. Also the competitive adsorption of multi-metals onto the IRN77 resin was studied. The studies showed that this cation-exchange resin can be used as an efficient adsorbent material for the removal of cobalt, chromium and nickel from water and nuclear power plant coolant water. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Adsorption; Ion-exchange resin; Cobalt; Chromium; Nickel; Isotherm; Kinetics; Wastewater

1. Introduction

The tremendous increase in the use of heavy metals over the past few decades has inevitably resulted in an increased flux of metallic substances in the environment. The metals are of special concern because they are non-degradable and, therefore, persistent. In recent years, there has been a growing concern with environmental protection. This can be achieved either by decreasing the influx of pollutants to the environment or by their removal from contaminated media. The former is a feasible choice only for pollutants of anthropogenic origin, whereas the latter is unavailable for those of natural origin. Since cobalt, chromium

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and nickel are among the most toxic of elements, it is necessary to develop methods to lower their presence in contaminated media to innocuous quantities. Major anthropogenic sources of heavy metals in the environment include metal extraction, metal fabrication and surface finishing, paints and pigments, as well as the manufacture of batteries [1]. The most common methods for the removal of heavy metals are ion-exchange and chemical precipitation. The main advantages of ion-exchange over chemical precipitation are recovery of metal value, selectivity, less sludge volume produced and the meeting of strict discharge specifications. In ion-exchange systems, polymeric resins are usually employed [2–4].

Adsorption process has been and actually are the most frequently applied method in the industries, and consequently the most extensively studied. Yamamoto et al. [5] studied the recovery of chromate from cooling tower blowdown by ion-exchange resins. Kinetics of ion-exchange in soil organic matter that is adsorption and desorption of Pb^{2+}, Cu^{2+}, Cd^{2+}, Zn^{2+} and Ca^{2+} was studied by Bunzl et al. [6]. Baes et al. [7] studied ion-exchange and adsorption of some heavy metals in a modified coconut coir cation-exchanger. Jorgensen [8] examined the applicability of cellulose ion-exchangers for water and wastewater treatment. Pretreatment of tannery wastewaters by ion-exchange process for the removal of Cr(III) was studied by Tiravanti et al. [9]. Rengaraj et al. [10] studied the removal of chromium from water and wastewater by ion-exchange resins.

Zouboulis et al. [11] studied removal of toxic metal ions from solutions using industrial solid byproducts. Deshkar et al. [12] used bark as the adsorbing material, observing good adsorption capacity with respect to mercury, also considering its low cost. Sharma and Forster [13] studied the removal of hexavalent chromium using sphagnum moss peat. Netzer and Hughes [14] studied the adsorption of copper, lead and cobalt by activated carbon.

All the above-mentioned materials present good adsorption capacity, but in general they are not able to reduce the heavy metal concentration below the discharge limits established in environment legislation. Such discharge requirements can be matched using specific ion-exchange resins, characterized by a very high selectivity with respect to heavy metal. In particular, Ritter and Bibler [15] studied the performance of Duolite GT-73 ion-exchange resin in a large-scale process, discussing some operational problems encountered.

In the present study, IRN77 cation-exchange resin was used for the adsorption of Co(II), Cr(III) and Ni(II) from aqueous solution. These three metals are known as corrosion products in cooling water systems in nuclear power plants. The primary coolant is an essential cooling medium used to control heat in nuclear power plants. The most commonly used primary coolant is high-purity water. During the operation of a nuclear power plant, the surfaces of the primary circuits are released as corrosion products in the coolant system. These corrosion products may enter into the core, become activated, leading to activity build-up on the surface of the primary system. This will lead to contamination of the system and components and the occupational radiation exposure during the outage period in a nuclear power plant. Therefore, system decontamination is an important factor in reducing the radiation levels in a nuclear power plant. In order to achieve this, various physico-chemical treatment methods have been employed [16].

Ion-exchange is the most widely used process for purifying the primary coolant in pressurized water reactor (PWR)-type nuclear power plants due to its high decontamination

efficiency, simplicity, and easy operation. Since the method is non-selective in removing radionuclides and non-radionuclides, there is a large volume of waste, and volume-reduction technology has not been developed for the management of this radioactive waste. The waste is usually stored for lengthy time periods in the nuclear power plant itself, or it has been solidified into a radioactive resin waste by cementation [17]. In order to minimize the generation of solid wastes, a ion-exchange adsorptive process must be optimized in purifying the primary coolant. The main objectives of this work were to investigate equilibrium and kinetic parameters of this ion-exchange resin as an adsorbent for the removal of Co(II), Cr(III) and Ni(II) from water and nuclear power plant coolant water. The parameters which influence adsorption such as initial metal concentration, contact time and pH were investigated. Also competitive adsorption of coexisting multi-metals onto the resin was studied.

2. Materials and methods

The cation-exchange resin IRN77 (M/s Rohm and Haas, SA, France) was used in this study. This cation-exchange resin is generally used for the removal of radionuclides from water and wastewater. Their physical properties and specifications of the resin as reported by the suppliers are shown in Table 1. All the chemicals used were of analytical grade and obtained from Aldrich, USA.

A stock solution of 500 mg/l of cobalt, chromium and nickel were separately prepared by dissolving 2.4705 g of $Co(NO_3)_2$, 3.8475 g of $Cr(NO_3)_3$ and 2.4770 g of $Ni(NO_3)_2 \cdot 6H_2O$ in 1000 ml distilled water, respectively. These solutions were diluted as required to obtain standard solutions containing 10–150 mg/l of cobalt, chromium and nickel. One hundred milliliter of each solution of a desired concentration adjusted to a desired pH were transferred to reagent bottles of 300 ml capacity. Known amounts of IRN77 were added to each

Table 1
Characteristics of IRN77 cation-exchange resin[a]

Number	Characteristics	Values
Physical characteristics		
1	Physical form	Uniform particle size spherical beads
2	Shipping weight	800 g/l
3	Harmonic mean size	$650 \pm 50\,\mu m$
4	Uniformity coefficient	<1.2
5	Particle size	<0.300 mm, 0.2% maximum; >1.180 mm, 2.0% maximum
6	Whole beads	95% minimum
7	Breaking weight (average)	>350 g per bead
Chemical characteristics		
8	Matrix	Polystyrene DVB gel
9	Functional groups	Sulphonic acid
10	Ionic form as shipped	H^+
11	Total exchange capacity	>1.9 equiv. l^{-1} (H^+ form)
12	Moisture holding capacity	49–55% (H^+ form)
13	Ionic conversion	99% minimum H^+

[a] Information provided by the manufacturer.

Table 2
Composition of Co(II), Cr(III) and Ni(II) containing synthetic nuclear power plant coolant water

Number	Compound	Concentration (mg/l)
1	Sb_2O_5	5
2	$Co(NO_3)_2 \cdot 6H_2O$	1
3	$Fe(NO_3)_3 \cdot 9H_2O$	30
4	$Ni(NO_3)_2 \cdot 6H_2O$	15
5	$AgNO_3$	5
6	H_3BO_3	20
7	$Cr(NO_3)_3 \cdot 9H2O$	4
8	$LiOH \cdot H_2O$	0.5
9	$CsNO_3$	0.5

bottle and the pH was adjusted using 0.1N hydrochloric acid or dilute sodium hydroxide solutions. The solutions were agitated for a predetermined period at $25 \pm 1\,^{\circ}C$ in a shaking incubator (Model: Jeio Tech SI 900R). The resins were separated by filtration and the filtrate was analyzed by inductively coupled plasma atomic emission spectrophotometry (Model: Thermo Jarrel ash IRIS/AP) for cobalt, chromium and nickel content. Adsorption isotherm and kinetic studies were carried out with different initial concentrations of cobalt, chromium and nickel while maintaining the resin dosage at constant level. For pH effects, 100 mg/l of cobalt, chromium and nickel and a IRN77 dose of 500 mg/100 ml were used. In order to correct for any adsorption of metals on the container surface, control experiments were carried out without resins. It was found that there was no adsorption by the container walls. In addition, all mixing vessels were kept sealed throughout the duration of each isotherm test to minimize dissolution of gaseous species in the atmosphere. The effects of competitive adsorption of each metal ion on IRN77 resin solution was also investigated. The solution which contains Co(II), Ni(II) and Cr(III) coexisted at the concentrations of 100, 100 and 50 mg/l, respectively was agitated with 600 mg of IRN77 ion-exchange resins. A known amount of the solution was withdrawn at the predetermined time interval and the metal ion concentration determined.

The cobalt, chromium and nickel containing synthetic primary coolant water was prepared on the basis of the analysis of chemical composition from the primary coolant in a nuclear power plant, and its concentrations are presented in Table 2. This synthetic solution was used for the adsorption study with IRN77. For the study of adsorbent dosage, the sample was agitated with different dosages of IRN77 for 24 h at pH 2.7.

3. Results and discussion

3.1. Effects of agitation time and initial concentration

Fig. 1a–c show the effect of reaction time on the removal of Co(II), Cr(III) and Ni(II) by IRN77 cation-exchange resin. The Co(II), Cr(III) and Ni(II) removal increased with time and attained equilibrium at 200 min for Co(II), 150 min for Cr(III) and 175 min for Ni(II) for all the initial metal ion concentrations used. The metal removal versus time curves were
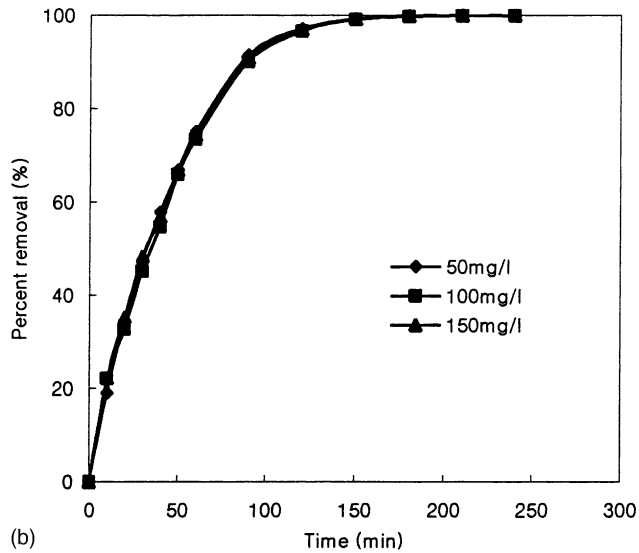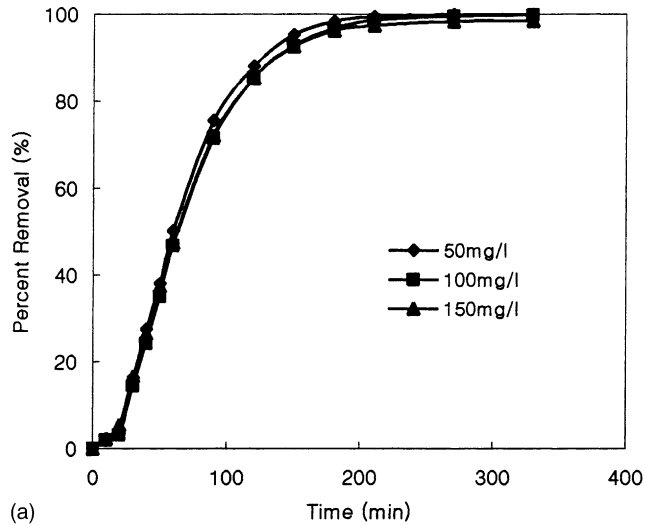
Fig. 1. (a) Effects of reaction time and initial concentration of Co(II) on the adsorption of Co(II) on IRN77 (initial concentration of metals = 50, 100, 150 mg/l; pH = 5.3; resin dosage = 200 mg/100 ml). (b) Effects of reaction time and initial concentration of Cr(III) on the adsorption of Cr(III) on IRN77 (initial concentration of metals = 50, 100, 150 mg/l; pH = 3.5; resin dosage = 200 mg/100 ml). (c) Effects of reaction time and initial concentration of Ni(II) on the adsorption of Ni(II) on IRN77 (initial concentration of metals = 50, 100, 150 mg/l; pH = 4.8; resin dosage = 300 mg/100 ml.
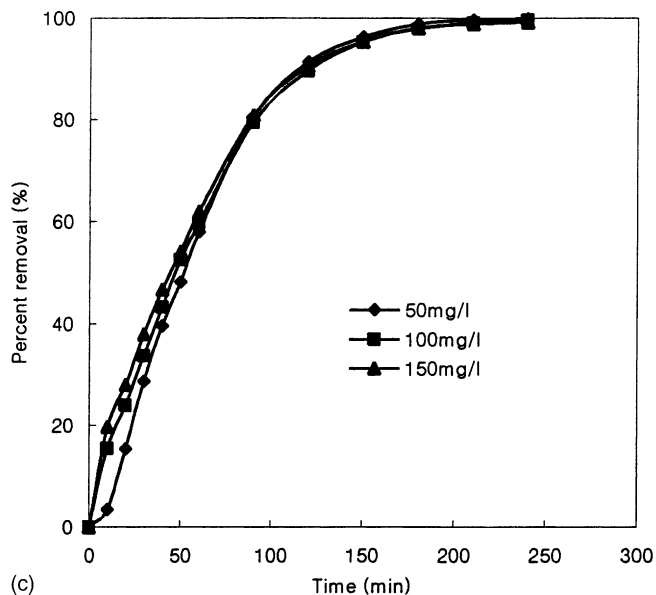
Fig. 1. (*Continued*).

single, smooth and continuous indicating monolayer adsorption of metals on the surfaces of the IRN77 resins [10,18].

3.2. Adsorption kinetics

The kinetics of Co(II), Cr(III) and Ni(II) adsorption on IRN77 followed the first order rate expression given by Lagergren [18–21]:

$$\log(q_e - q) = \log q_e - k_{ad}\left(\frac{t}{2.303}\right)$$

where q and q_e are the amounts of Co(II), Cr(III) and Ni(II) adsorbed (mg/g) at time t (min) and at equilibrium time, respectively and k_{ad} is the rate constant of adsorption. Linear plots of $\log(q_e - q)$ versus t showed the applicability of the above equation for IRN77 (Fig. 2a–c). The k_{ad} values were calculated from the slopes of the linear plots and are presented in Table 3 for different concentrations. From the results it was observed that there is no significant change in the k_{ad} values at various concentration of metal ions.

3.3. Effect of resin dosage

Fig. 3 presents the removal of Co(II), Cr(III) and Ni(II) as a function of IRN77 resin dosage. The resin dosage was varied from 0.5 to 10 g/l and equilibrated for 24 h. Increasing resin dosage increased the percent removal of Co(II), Cr(III) and Ni(II). Results showed that for the quantitative removal of Co(II), Cr(III) and Ni(II) from 100 ml solution containing 100 mg/l of Co(II), Cr(III) and Ni(II), a minimum resin dosage of 200 mg was required for
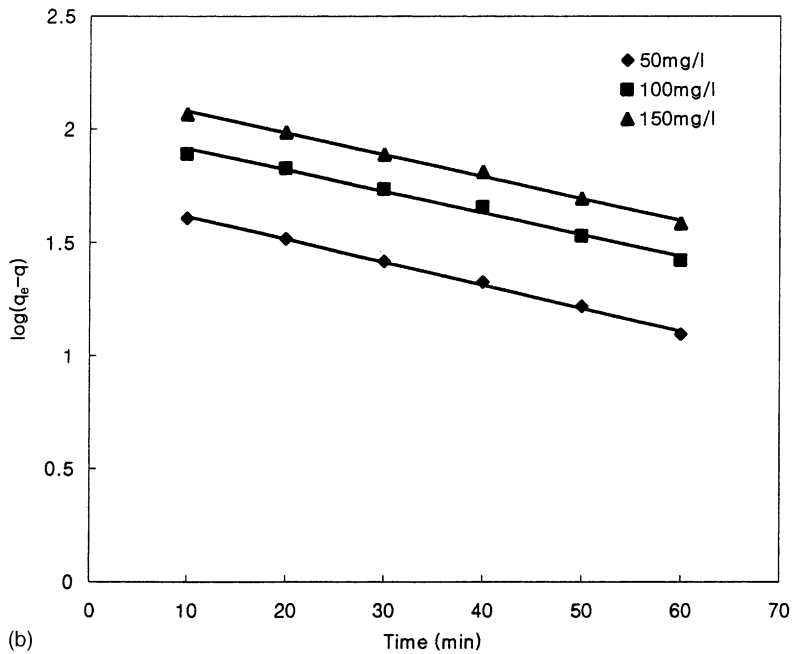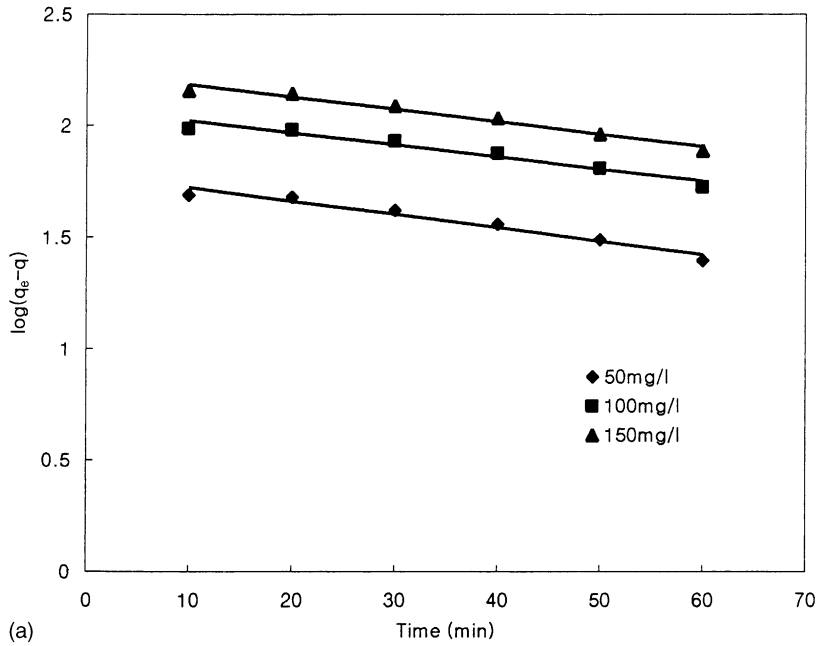
Fig. 2. (a) Lagergren plot for the adsorption of Co(II) on IRN77. (b) Lagergren plot for the adsorption of Cr(III) on IRN77. (c) Lagergren plot for the adsorption of Ni(II) on IRN77.
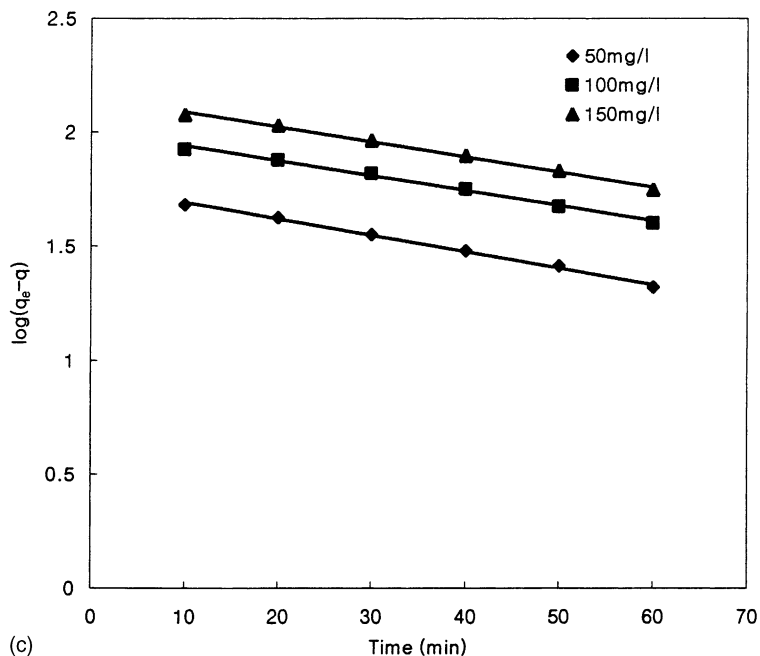
Fig. 2. (*Continued*).

Co(II) and Cr(III) and 300 mg required for Ni(II). The results also clearly indicated that the removal efficiency increases up to the optimum dosage beyond which the increase in removal efficiency is negligible [22]. It is apparent that the equilibrium metal ion concentration decreases with increasing resin dosage for a given initial metal concentration. This is to be expected because, for a fixed initial solute concentration, increasing adsorbent doses provides greater surface area or adsorption sites [23].

3.4. Adsorption isotherm

The experimental results obtained for the adsorption of cobalt, chromium and nickel on IRN77 ion-exchange resins at room temperature ($25 \pm 1\,^\circ$C) under optimum conditions of contact time and dose of adsorbent were found to obey Freundlich adsorption isotherm [24] (Fig. 4).

Table 3
Adsorption rate constants of Lagergren plots for Co(II), Cr(III) and Ni(II) with IRN77 system

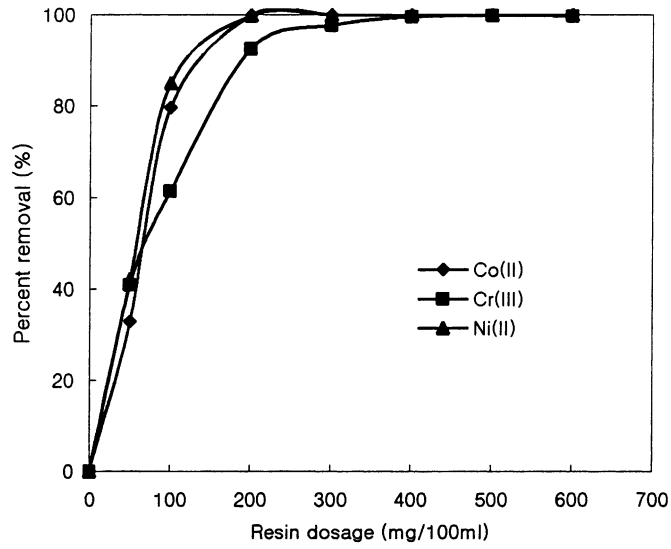| Initial concentration of metals (mg/l)	k_{ad} (l/min)		
	Co(II)	Cr(III)	Ni(II)
50	0.9862	0.9770	0.9835
100	0.9876	0.9783	0.9849
150	0.9871	0.9781	0.9849

Fig. 3. Effect of resin dosage on the removal of Co(II), Cr(III) and Ni(II) on IRN77 (initial concentration of metals = 100 mg/l; equilibration time = 24 h).
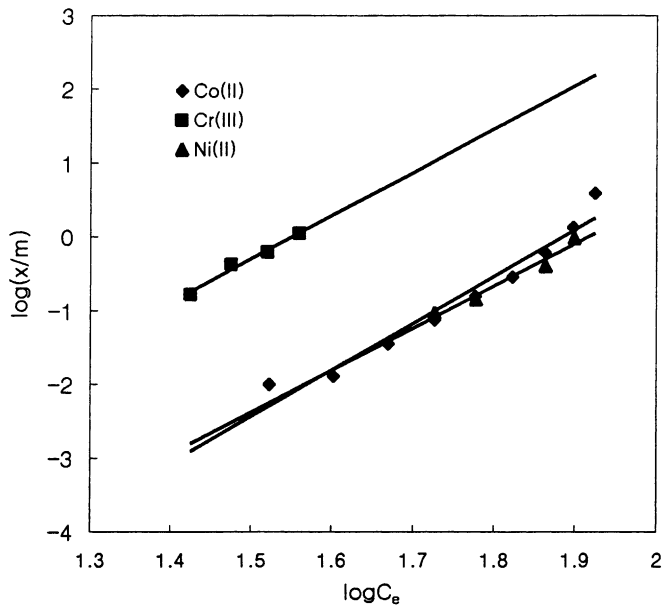

Fig. 4. Freundlich adsorption isotherm for Co(II), Cr(III) and Ni(II) on IRN77.

Table 4
Freundlich constants for adsorption of Co(II), Cr(III) and Ni(II) on IRN77

Name of the heavy metals	Freundlich constants	
	k	n
Co(II)	75.63	6.61
Cr(III)	35.38	5.98
Ni(II)	81.82	5.91

$$\frac{x}{m} = kC_{e}^{1/n}$$

where x is the amount of metal removed (mg); m the amount of resin (g); C_e the equilibrium concentration (mg/l); and k and n are the Freundlich constants, where k and n are the constants representing the adsorption capacity and intensity of adsorption, respectively. The logarithmic form of the equation becomes

$$\log\left(\frac{x}{m}\right) = \log k + \frac{1}{n}\log C_{e}$$

Freundlich adsorption isotherm represents the relationship between the amount of metal adsorbed per unit mass of the adsorbent (x/m) and the concentration of the metal in solution at equilibrium (C_e).

The plot of $\log(x/m)$ versus $\log C_e$ for various initial concentrations was found to be linear, indicating the applicability of the classical adsorption isotherm to this adsorbate–adsorbent system. The adsorption capacities (k) and adsorption intensities (n) are presented in Table 4. Values of $1 < n < 10$ show favorable adsorption of metals on IRN77 cation-exchange resin. Higher value for k indicates higher affinity for cobalt, chromium and nickel [25].

3.5. Effect of pH

In order to optimize the pH for maximum removal efficiency, experiments were conducted with 100 ml of 100 mg/l of metal solution containing 500 mg of IRN77 cation-exchange resin in the pH range 2–8 and the results are depicted in Fig. 5. The result represent the effect of initial pH on the removal of Co(II), Cr(III) and Ni(II) by IRN77. Metal removal by adsorption onto IRN77 is much more efficient compared to metal hydroxide precipitation in the absence of any adsorbent [26,27]. IRN77 resin is more effective for the removal of Co(II), Cr(III) and Ni(II) at their solution pH.

3.6. Competitive adsorption of coexisting multi-metals onto IRN77

Adsorption of coexisting multi-metal ions onto the resin was examined, and the results are presented in Fig. 6. Initially, Co(II), Cr(III) and Ni(II) were observed to be adsorbed onto IRN77. After a few minutes, however, Cr(III) started to be dominantly adsorbed on the resin attaining equilibrium after 2 h. Cobalt(II) and nickel(II) were desorbed from the resin with time. After 2 h, negligible amounts of these metal ions had been removed by
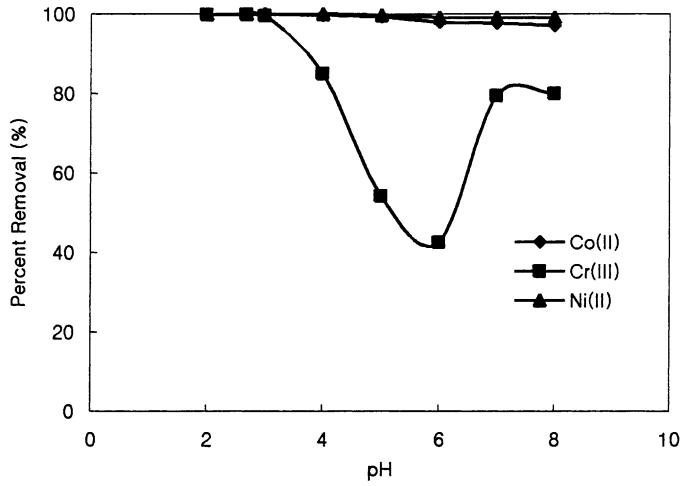
Fig. 5. Effect of pH on the removal of Co(II), Cr(III) and Ni(II) on IRN77 (initial concentration of metals = 100 mg/l; resin dosage = 500 mg/100 ml; equilibration time = 24 h).
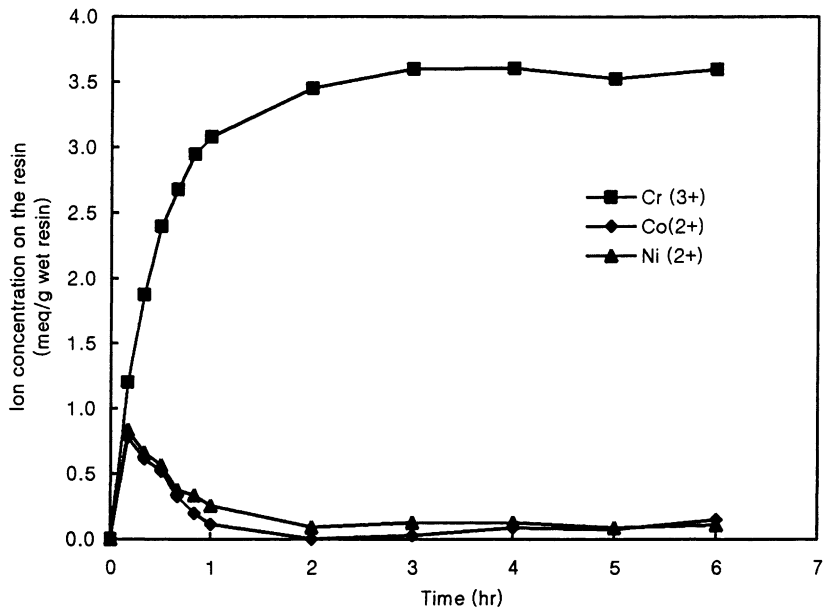

Fig. 6. Competitive adsorption curves for the removal of Co(II), Cr(III) and Ni(II) on IRN77 resin with time (initial concentration of metals: Co(II) = 100 mg/l, Ni(II) = 100 mg/l, Cr(III) = 50 mg/l; pH = 3.34; resin dosage = 600 mg/100 ml).
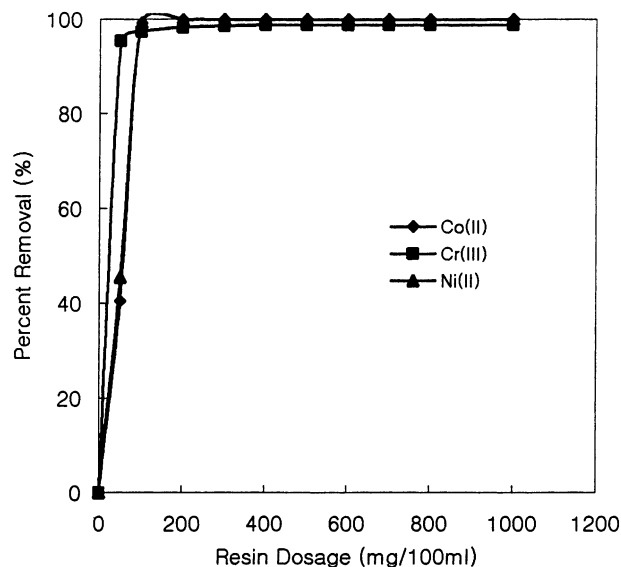
Fig. 7. Effect of resin dosage on the removal of Co(II), Cr(III) and Ni(II) from synthetic nuclear power plant coolant water by IRN77 (pH = 2.75; contact time = 24 h).

adsorption. The results were likely due to high adsorption affinity of Cr(III) onto IRN77 which led to Cr(III) substitution for Co(II) and Ni(II) already adsorbed in the adsorption sites [28]. These results are of significance in practical ion-exchange treatment of aqueous environments concomitantly contaminated with high amounts of heavy metals such as Co, Cr and Ni. Favored adsorption of a metal onto the resin can lead to desorption of other metals into the solution if the adsorption capacity is not sufficient for the less-favored species.

3.7. Application to nuclear power plant coolant water

The composition of synthetic nuclear power plant coolant water is presented in Table 2. Effect of resin dosage on Co(II), Cr(III) and Ni(II) removal from this synthetic coolant water is shown in Fig. 7. Maximum adsorptive removal of Co(II), Cr(III) and Ni(II) from 100 ml of wastewater containing 1 mg/l of Co(II), 4 mg/l of Cr(III) and 15 mg/l of Ni(II) agitated with 100 mg of IRN77 resin or greater dosage at a solution pH of 2.75. Effect of contact time on the removal of Co(II), Cr(III) and Ni(II) removal is shown in Fig. 8. The removal increases with time and attains equilibrium within 100 min for the removal of Co(II), Cr(III) and Ni(II) by IRN77 resin. Considering the different resin dosage for the individual metal experiments, the efficiency of the resin towards the removal of these metal ions from synthetic coolant water is the nearly same as those of individual metals without trace metals. The results implies that interference of trace metals on the adsorption capacity may not be significant unless the resin is saturated.
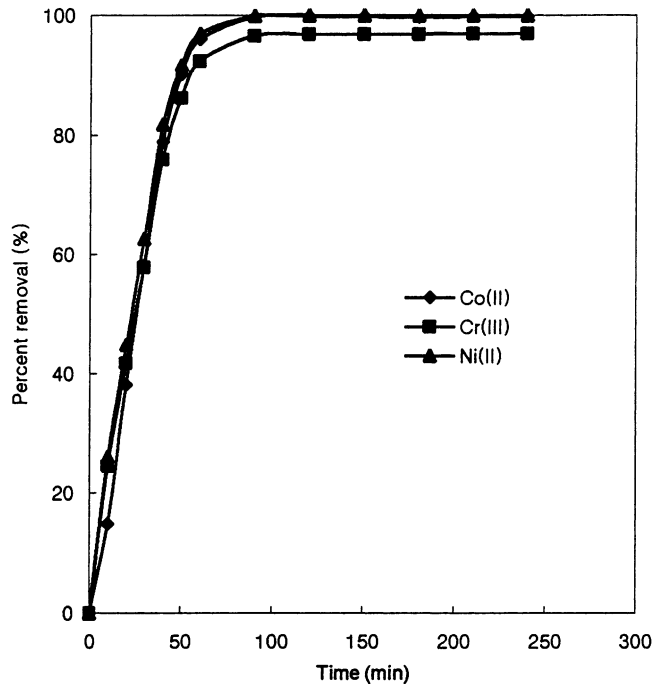
Fig. 8. Effect of contact of reaction time on the removal of Co(II), Cr(III) and Ni(II) on IRN77 from nuclear power plant coolant water (pH = 2.75; resin dosage = 100 mg/100 ml)

4. Conclusions

The results showed that the IRN77 cation-exchange resin can be used as an adsorbent for the effective removal of Co(II), Cr(III) and Ni(II) from aqueous solution. Quantitative removal of these metals from synthetic nuclear power plant coolant water confirmed the validity of the results obtained in these batch mode studies. The kinetic data would be useful for the fabrication and designing of wastewater treatment plants. Application of this ion-exchange resin to wastewater treatment is expected to be economical and efficient. In a long term equilibrium test, trivalent metal (Cr) replaced the adsorbed divalent metals (Co and Ni). Therefore, it is essential to fully understand the mechanism of competitive adsorption of coexisting metals onto the resin for effective operation of ion-exchange process. Further studies on equilibrium and kinetics of multi-metal systems at low concentrations are under progress.

Acknowledgements

References

 [1] A.A. Ali, R.E. Bishtawi, J. Chem. Tech. Biotechnol. 69 (1997) 27.
 [2] G. Tiravanti, D. Petruzzelli, R. Passino, Water Sci. Tech. 36 (1997) 197.
 [3] S. Chiarle, M. Ratto, M. Rovatti, Water Res. 34 (2000) 2971.
 [4] G.P. Miller, D.I. Norman, P.L. Frisch, Water Res. 34 (2000) 1397.
 [5] D. Yamamoto, Y. Koichi, A. Osamu, in: Proceedings of the Cooling Tower Institute Annual Meeting on Recovery of Chromate from Cooling Tower Blowdown by Ion-Exchange Resins, Houston, TX, 1975.
 [6] K. Bunzl, W. Schmidt, B. Sansoni, J. Soil Sci. 27 (1976) 32.
 [7] A.U. Baes, S.J.P. Umali, R.L. Mercado, Water Sci. Tech. 34 (11) (1996) 193.
 [8] S.E. Jorgensen, Water Res. 13 (1979) 1239.
 [9] G. Tiravanti, D. Petruzzelli, R. Passino, Water Res. 36 (1997) 197.
[10] S. Rengaraj, K.-H. Yeon, S.-H. Moon, J. Hazard. Mater. B87 (2001) 273–287.
[11] A.I. Zouboulis, K.A. Kydros, K.A. Matis, Water Sci. Tech. 10 (1993) 83.
[12] A.M. Deshkar, S.S. Bokade, S.S. Dara, Water Res. 24 (1990) 1011.
[13] D.C. Sharma, C.F. Forster, Water Res. 27 (1993) 1201.
[14] A. Netzer, D.E. Hughes, Water Res. 18 (1984) 927.
[15] J.A. Ritter, J.P. Bibler, Water Sci. Tech. 25 (1992) 165.
[16] J. Severa, B. Jaromir, Handbook of Radioactive Contamination and Decontamination, Elseveir, Amsterdam, 1991.
[17] D.W. Kang, K.B. Sung, S.H. Lee, H.Y. Kim, J. Korea Solid Wastes Eng. Soc. 15 (1998) 24.
[18] K. Periyasamy, C. Namasivayam, Waste Manage. 15 (1995) 63.
[19] D.B. Singh, G. Prasad, D.C. Rupainwar, V.N. Singh, Water Air Soil Pollut. 42 (1989) 373.
[20] S. Lagergren, B.K. Svenska, Ventempskapaka Handl, Vol. 24, 1898.
[21] C. Namasivayam, K. Ranganathan, Bioresources Technol. 40 (1992) 201.
[22] C. Namasivayam, K. Ranganathan, Water Res. 29 (1995) 1737.
[23] Y.S. Ho, D.A. John Wase, C.F. Forster, Water Res. 29 (1995) 1327.
[24] F. Slejko, Adsorption Technology: A Step by Step Approach to Process Evaluation and Application, Marcel Dekker, New York, 1985.
[25] G. Mckay, M.S. Otterburn, A.G. Sweeney, Water Res. 14 (1980) 15.
[26] A. Netzer, D.E. Hughes, Water Res. 18 (1984) 927.
[27] K. Periyasamy, K. Srinivasan, P.K. Murugan, Indian J. Environ. Health 33 (1991) 433.
[28] C.A. Christophi, L. Axe, J. Environ. Eng. 126 (2000) 66.