Korean J. Chem. Eng., **21**(1), 187-194 (2004)

Batch Adsorptive Removal of Copper Ions in Aqueous Solutions by Ion Exchange Resins: 1200H and IRN97H

Selvaraj Rengaraj, Younghun Kim, Cheol Kyun Joo, Kyunghee Choi* and Jongheop Yi†

School of Chemical Engineering, Seoul National University, Kwanak-gu, Seoul 151-742, Korea
*National Institute of Environmental Research, Ministry of Environment, Seo-gu, Incheon 404-170, Korea

(*Received 7 October 2003 • accepted 17 December 2003*)

Abstract−The removal of copper from aqueous solution by ion exchange resins, such as 1200H and IRN97H, is described. Effect of initial metal ion concentration, agitation time and pH on adsorption capacities of ion exchange resins was investigated in a batch mode. The adsorption process, which is pH dependent, shows maximum removal of copper in the pH range 2-7 for an initial copper concentration of 10 mg/L. The experimental data have been analyzed by using the Freundlich, Langmuir, Redlich-Peterson, Temkin and Dubinin-Radushkevich isotherm models. The batch sorption kinetics have been tested for a first-order, pseudo-first order and pseudo-second order kinetic reaction models. The rate constants of adsorption for all these kinetic models have been calculated. Results showed that the intraparticle diffusion and initial sorption into resins of Cu(II) in the ion exchange resins was the main rate limiting step. The uptake of copper by the ion exchange resins was reversible and thus has good potential for the removal/recovery of copper from aqueous solutions. We conclude that such ion exchange resins can be used for the efficient removal of copper from water and wastewater.

Key words: Adsorption Isotherms, Adsorption Kinetics, Copper(II), Ion Exchange Resins

INTRODUCTION

The problem of removing pollutants from water is an important process and is becoming more important with the increasing of industrial activity. In order to solve heavy metal pollution in the ecosystem, it is important to bring applicable solutions to the subject. It is possible to clean the polluted environment only with long study requiring expensive and complex plants. Therefore, it is important to make effective precautions to prevent water, soil and air pollution.

Copper and its compounds are ubiquitous in the environment and are thus found frequently in surface water. Copper bearing mining wastes and acid mine drainage discharge significant quantities of dissolved copper bearing waste include plating baths, fertilizer industry, paints and pigments, municipal and storm water run off [Dean et al., 1972]. Human intake of excessively large doses of copper leads to severe mucosal irritation and corrosion, widespread capillary damage, hepatic and renal damage, and central nervous system irritation followed by depression [Camp, 1964]. Severe gastrointestinal irritation and possible necrotic changes in the liver and kidney could occur. Although the maximum permissible concentration by WHO and USPHS is 1.5 and 1.0 mg/dm^3 respectively, the maximum recommended concentration of Cu^{2+} for drinking water by these agencies is 1.0 mg/dm^3.

Several techniques such as chemical precipitation, oxidation, reduction, coagulation, solvent extraction, and adsorption have been commonly employed for the removal of metal ions. Among these, adsorption has been thought to be efficient and economically feasible as a wastewater treatment operation. Several adsorbents can be used to remove metal ions, including activated carbons, alumina, silica, bentonite and peat. The Yi group [Kim et al., 2000, 2003; Lee et al., 2001] has also studied the removal of inorganic metal ions namely cadmium, cobalt, zinc, silver, copper, mercury, chromium and lead from aqueous solution by using different adsorbents. Ion exchange resins with improved sorption capacity as well as adsorbents may have advantages over such non-specific adsorbents [Kim et al., 2002]. In this regard, ion exchange resins hold great potential for the removal of heavy metals from water and industrial wastewater [Rengaraj et al., 2002, 2003].

In the present study, 1200H and IRN97H cation exchange resins were used for the removal of copper from aqueous solution. Copper compounds are present in electronic process wastewater. The main objective of this study was to investigate the equilibrium and kinetic parameters of these ion exchange resins. In addition, parameters that influence adsorption, such as initial copper concentration, agitation time, pH, isotherm and kinetic studies were investigated.

EXPERIMENTAL

The cation exchange resins 1200H and IRN97H (Rohm and Hass, France) used in this study are generally used for the removal of heavy metals from water and wastewater. Their physical properties and specifications are presented in Table 1. All the chemicals used were of analytical grade.

A stock solution of Cu^{2+} (500 ppm) was prepared by dissolving 1.83 g of $Cu(NO_3)_2 \cdot 2.5H_2O$ (Aldrich, USA) in distilled water. The stock solution was diluted as required to obtain standard solutions containing 5 to 30 mg/*l* of Cu(II). One hundred ml of Cu(II) solution of a desired concentration, adjusted to a desired pH, was taken

---

†To whom correspondence should be addressed.
E-mail: jyi@snu.ac.kr
‡This paper is dedicated to Professor Hyun-Ku Rhee on the occasion of his retirement from Seoul National University.

Table 1. Characteristics properties of the ion exchange resins used[a]

Amberjet 1200 H	
Matrix	Styrene divinylbenzene copolymer
Functional groups	-SO$_3$-
Physical form	Insoluble, amber beads
Ionic form as shipped	H$^+$
Total exchange capacity	≥1.8 eq/*l* (H$^+$ form)–≥2.0 eq/*l* (Na$^+$ form)
Moisture holding capacity	49 to 55 % (H$^+$ form)
Shipping weight	800 g/*l*
Specific gravity	1.18 to 1.22 (H$^+$ form)
Uniformity coefficient	≤1.2
Harmonic mean size	630±50 μm
Fine content	<0.300 mm: 0.1% max
Coarse beads	>0.850 mm: 10% max
Maximum reversible swelling	Na$^+$→H$^+$: 10%
Amberlite IRN97H	
Matrix	Polystyrene DVB gel
Functional groups	-SO$_3$-
Physical form	Uniform particle size spherical beads
Ionic form as shipped	H$^+$
Total exchange capacity	≥2.15 eq/*l* (H$^+$ form)
Moisture holding capacity	45 to 51% (H$^+$ form)
Shipping weight	800 g/ dm^3
Uniformity coefficient	≤1.2
Harmonic mean size	525±50 μm

[a] Manufacturer supplied.

in reagent bottles of 300 ml capacity and known amounts of ion exchange resins were added. The solution pH was adjusted by using dilute hydrochloric acid or sodium hydroxide solutions. The solutions were agitated for a predetermined period at 25±1 °C in a shaking incubator (Vision Scientific Co., Ltd., KMC 8480S). The resins were separated and the filtrate was analyzed by an atomic absorption spectrometer (Perkin Elmer, AAS-3110) for copper content. Adsorption isotherm studies were carried out with different initial concentrations of Cu(II) while maintaining the resin dosage at constant level. For pH effects, 10 mg/*l* copper and ion exchange resins 1200H and IRN97H each of dose of 500 mg/100 ml were used. In order to correct for any adsorption of copper on the container surface, control experiments were conducted without resins. It was found that no adsorption occurred 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.

Kinetic experiments were conducted by using a known weight of resin dosage and employing Cu(II) concentration in the range of 10-20 mg/dm^3. After regular intervals of time, suitable aliquots were analyzed for copper concentration and recorded. The rate constants were calculated by using the conventional rate expression.

The copper containing synthetic electronic process wastewater was prepared on the basis of the analysis of chemical composition from the electronic process wastewater (http://www.cleantechindia.com/eicnew/guidelines/electronics1.htm). This synthetic solution was used for the adsorption study with ion exchange resins. For the study of adsorbent dosage, the sample was used at solution pH and agitated with different dosage of ion exchange resins for 24 hrs.

RESULTS AND DISCUSSION

1. Effect of pH

The effects of initial pH on the removal of Cu(II) by 1200H and IRN97H ion exchange resins were investigated. The percentage of adsorption decreases rapidly when the pH is increased above 7 due to the formation of a copper precipitate at higher pH values. For comparison, Cu(II) removal by precipitation as Cu(OH)$_2$ in the absence of any adsorbent was also investigated. Clearly, Cu(II) removal by adsorption by both the resins is much more efficient compared to Cu(OH)$_2$ precipitation in the absence of any adsorbent. Both the resins are effective for the maximum removal of Cu(II) over the pH range 2 to 7, for a solution containing 10 mg/*l* of copper. Therefore in the subsequent studies the solution pH of 5.8 was used.

2. Effect of Resin Dosage

Fig. 1 represents the removal of Cu(II) as a function of resin dosage by 1200H and IRN97H at the solution pH 5.8. Resin dosage was varied from 0.025 to 0.600 g and equilibrated for 24 hrs. Increasing resin dosage increased the percent removal of Cu(II). It shows that for the quantitative removal of Cu(II) from 100 ml solution containing 10 mg/dm^3 of Cu(II), a minimum resin dosage of 100 mg/100 ml each of 1200H and IRN97H is required for the maximum removal of Cu(II). The results also clearly indicate the removal efficiency increases up to the optimum dosage beyond which the removal efficiency has no change with the resin dosage [Rengaraj et al., 2002, 2003]. It may be concluded that by increasing the adsorbent dose the removal efficiency increases but adsorption density decreases. The decrease in adsorption density can be attributed to the fact that some of the adsorption sites remain unsaturated during the adsorption process; whereas the number of available adsorption sites increases by an increase in adsorbent and this results in an increase in removal efficiency. As expected, the equilibrium concentration decreases with increasing adsorbent doses for a given initial chromium concentration, because for a fixed ini-

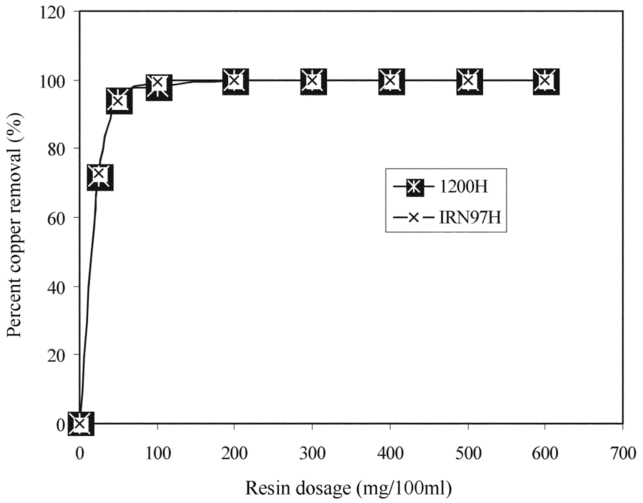

Fig. 1. Effect of resin dosage on the removal of copper by ion exchange resin 1200H and IRN97H.

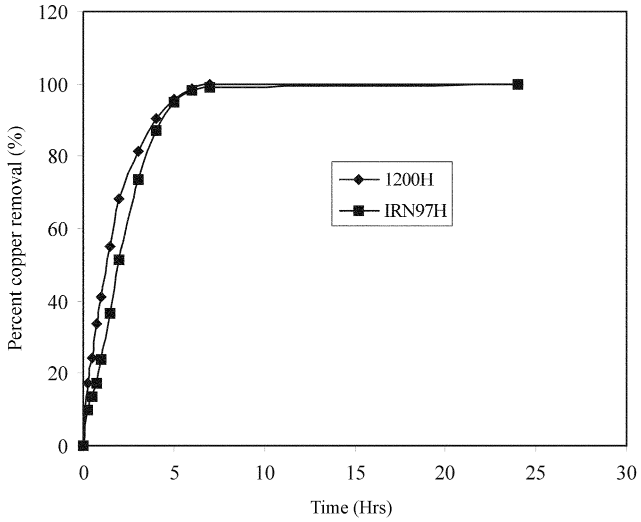

Fig. 2. Effect of contact time on the removal of copper by ion exchange resins 1200H and IRN97H.

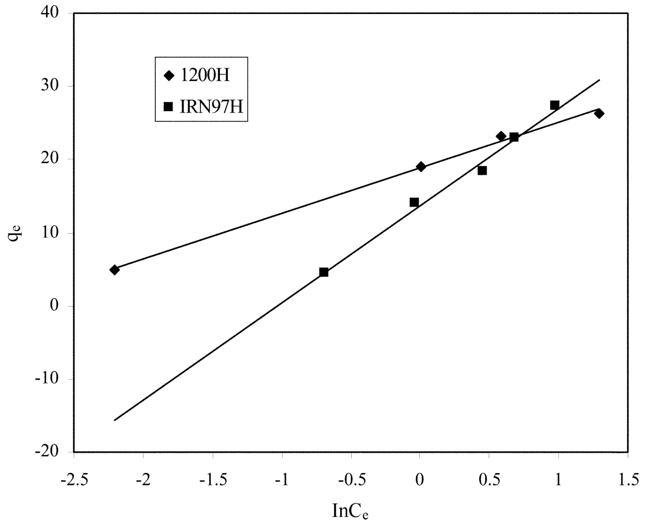

Fig. 4. Temkin isotherm plot for copper and 1200H and IRN97H ion exchange resins.

tial solute concentration, increasing the adsorbent doses provides a greater surface area or adsorption sites.

3. Effect of Agitation Time

Fig. 2 shows the effect of agitation time on the removal of Cu(II) by ion exchange resins. The Cu(II) removal increases with time and attains equilibrium at 7 hrs for 10 mg/dm^3 of Cu(II) used. This indicates that the residence time required for maximum Cu(II) removal by both the ion exchange resins 1200H and IRN97H would be 7 hrs. The equilibrium time was independent of initial concentration of Cu(II). The Cu(II) removal versus time curves are single, smooth and continuous, indicating a monolayer adsorption of Cu(II) on the surface of resins [Namasivayam and Kadirvelu, 1999].

4. Equilibrium Studies

In order to optimize the design of a sorption system for the removal of metals from effluents, it is important to establish the most appropriate correlation for the equilibrium curves. Five isotherm equations have been tested in the present study: Freundlich, Langmuir, Redlich-Peterson (Fig. 3), Temkin (Fig. 4) and Dubinin-Radushkevich (Fig. 5). These plots were used to calculate the isotherm parameters given in Table 2 for copper.

Freundlich proposed that if the concentration of solute in the solution at equilibrium, C_e, is raised to the power n, the amount of solute adsorbed being q_e, then C_e^n/q_e is a constant at a given temperature. The Freundlich isotherm is derived by assuming a heterogeneous surface with a nonuniform distribution of heat of adsorption over the surface. Hence the empirical equation can be written:

$$q_e = K_F \cdot C_e^n \tag{1}$$

where K_F is the Freundlich constant and n the Freundlich exponent. Therefore a plot of $\log q_e$ vs. $\log C_e$ enables the constant K_F and exponent n to be determined.

Langmuir proposed a theory to describe the adsorption of gas molecules onto metal surfaces. The Langmuir adsorption isotherm

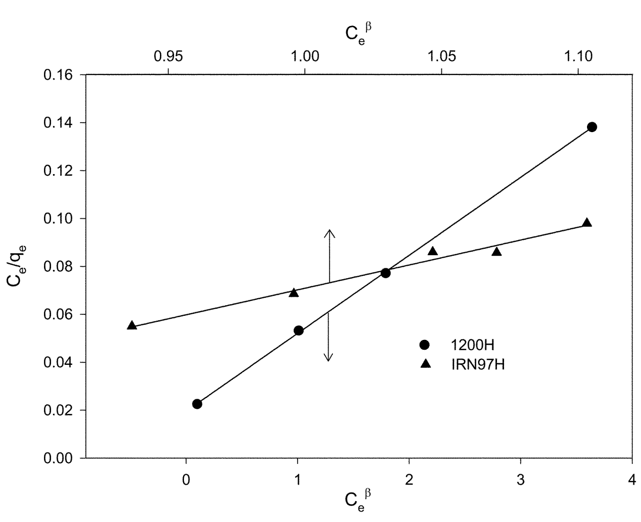

Fig. 3. Redlich-Peterson isotherm plot for copper and 1200H and IRN97H ion exchange resins.

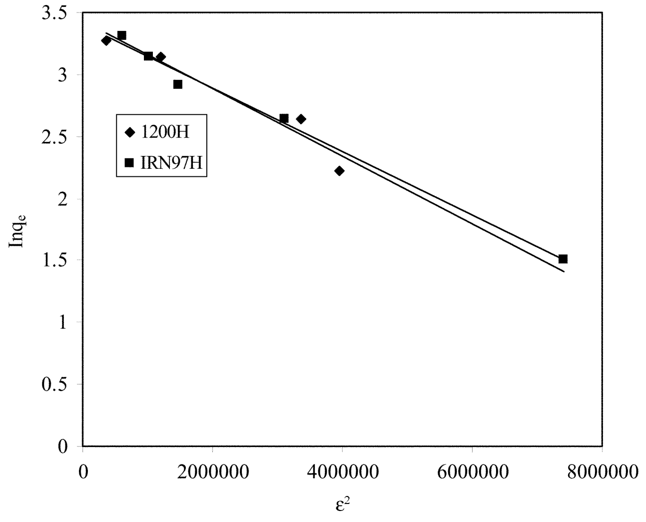

Fig. 5. The D-R isotherm plot for copper and 1200H and IRN97H ion exchange resins.

Table 2. The summary of isotherm parameters for copper on 1200H and IRN97H ion exchange resin system

Isotherms	Resins					
	1200H			IRN97H		
Freundlich isotherm	K_F/mg g^{-1}	n	R^2	K_F/mg g^{-1}	n	R^2
$q_e = K_F \cdot C_e^n$	15.81	0.51	0.995	14.37	0.65	0.993
Langmuir isotherm	Q^o/mg g^{-1}	b/l mg^{-1}	R^2	Q^o/mg g^{-1}	b/l mg^{-1}	R^2
$q_e = \frac{Q^o bC_e}{1+bC_e}$	26.73	2.03	0.988	43.29	0.53	0.989
Redlich-Peterson isotherm	K_R/l g^{-1}	a_R/l mg^{-1}	R^2	K_R/l g^{-1}	a_R/l mg^{-1}	R^2
$q_e = \frac{K_R C_e}{1+a_R C_e^{\beta}}$	51.81	1.69	0.999	5.43	1.38	0.981
Temkin isotherm	B	A/l g^{-1}	R^2	B	A/l g^{-1}	R^2
$q_e = \frac{RT}{b}\ln(AC_e)$	6.26	20.38	0.997	12.29	2.82	0.990
Dubinin-Radushkevich isotherm	q_s/mg g^{-1}	E	R^2	q_s/mg g^{-1}	E	R^2
$q_e = q_s \exp(-B\varepsilon^2)$	30.84	1.29 k	0.942	29.94	1.29 k	0.991

has been successfully applied to many other real sorption processes and it has been used to explain the sorption of metal onto ion exchange resin. A basic assumption of the Langmuir theory is that sorption takes place at specific homogeneous sites within the adsorbent. It is then assumed that once a metal ion occupies a site, no further adsorption can take place at that site. Theoretically, therefore, a saturation value is reached beyond which no further sorption can take place. The saturated monolayer curve can be represented by the expression:

$$q_e = \frac{Q^o bC_e}{1+bC_e} \tag{2}$$

where b and Q^o are the Langmuir constants. Therefore, a plot of 1/q_e vs. 1/C_e yields a linear plot of Langmuir isotherm. As shown in Table 2, maximum uptake of IRN97H is about two times larger than that of 1200H. This may be due to the intrinsic characteristics such as exchange capacity of resins in Table 1.

Redlich and Peterson [1959] incorporated the features of the Langmuir and Freundlich isotherms into a single equation and presented a general isotherm equation as followed:

$$q_e = \frac{K_R C_e}{1+a_R C_e^{\beta}} \tag{3}$$

where the exponent, β, lies between 0 and 1. There are two limiting behaviors: Langmuir form for β=1, and Henry's law form for β=0. Plotting the C_e/q_e of the above equation against C_e^{β} to obtain the isotherm constants is not applicable because of the three unknowns, a_R, K_R and β. Therefore, a minimization procedure is adopted to solve the above equation by maximizing the correlation coefficient between the theoretical data for q_e predicted from the above equation and experimental data. The fitted values of β for 1200H and IRN97H are 1.0 and 0.1, respectively. It means that 1200H resin is well fitted with the Langmuir isotherm, while IRN97H follows Henry's law.

Temkin and Pyzhev considered the effects of indirect adsorbate/adsorbate interactions on adsorption isotherms. The heat of adsorption of all the molecules in the layer would decrease linearly with coverage due to adsorbate/adsorbate interactions [Hosseini et al., 2003]. The Temkin isotherm has been used in the form as follows:

$$q_e = \frac{RT}{b}\ln(AC_e) \tag{4}$$

where RT/b=B. Therefore a plot of q_e vs. logC_e enables one to determine the constants A and b. As shown in Table 2, an A value of 1200H is larger than that of IRN97H. This means that the adsorbate/adsorbate interaction of 1200H resin is larger than that of IRN97H.

Another popular equation for the analysis of isotherms of a high degree of rectangularity is that proposed by Dubinin and Radushkevich [1947].

$$q_e = q_s \exp(-B\varepsilon^2) \tag{5}$$

where ε can be correlated:

$$\varepsilon = RT\ln\left[1+\frac{1}{C_e}\right] \tag{6}$$

The constant B gives the mean free energy E of sorption per molecule of the sorbate when it is transferred to the surface of the solid from infinity in the solution and can be computed by using the relationship:

$$E = \frac{1}{\sqrt{2B}} \tag{7}$$

where R is the gas constant (8.31 Jmol^{-1}K^{-1}) and T is the absolute temperature. Therefore a plot of lnq_e vs ε^2 enables one to determine the constants q_s and E. Both resins have the same sorption energy per sorbate.

Five isotherm models have been tested and the equilibrium data fits very well to all sorption isotherms. Uptake capacity of IRN97H is larger than that of 1200H due to the intrinsic exchange capacity, while the adsorbate/adsorbate interaction of IRN97H is smaller than that of 1200H.

5. First Order Adsorption Kinetic Model

Kinetics of sorption describing the solute uptake rate, which in turn governs the residence time of the sorption reaction, is one of the important characteristics defining the efficiency of sorption. Hence in the present study, the kinetics of copper removal has been car-

Table 3. The first order reversible reaction rate constant for the removal of copper by 1200H and IRN97H ion exchange resins

Sorbents	Copper (mg/dm^3)	Overall rate constant $k=k_1+k_2$ (h^{-1}) (R^2)	Equilibrium constant k_c	Forward rate constant k_1 (h^{-1})	Backward rate constant k_2 (h^{-1})
1200H	10	0.7054 (0.9758)	1006	0.7047	0.0007
	15	0.6706 (0.9774)	744	0.6697	0.0009
	20	0.5884 (0.9864)	201	0.5855	0.0029
IRN97H	10	0.5808 (0.9857)	967	0.5802	0.0006
	15	0.5866 (0.9852)	1465	0.5862	0.0004
	20	0.4994 (0.9884)	2496	0.4992	0.0002

ried out to understand the behavior of these ion exchange resins.

The sorption of copper from liquid phase to solid may be considered as a reversible reaction with an equilibrium state being established between two phases. A simple first-order reaction model was, therefore, used to correlate the rates of reaction, which can be expressed as:

$$A \underset{k_2}{\overset{k_1}{\rightleftarrows}} B \tag{8}$$

where k_1 is the forward reaction rate constant and k_2 is the backward reaction rate constant. If a is the initial concentration of copper and x is the amount transferred from liquid phase to solid phase at any time t, then rate

$$\frac{dx}{dt}=\frac{-d(a-x)}{dt}=k(a-x) \tag{9}$$

where k is the overall reaction rate constant. Since k_1 and k_2 are the rate constants for the forward and reverse process, the rate can be expressed as:

$$\frac{dx}{dt}=k_1(a-x)-k_2x \tag{10}$$

If X_e represents the concentration of copper adsorbed at equilibrium, then at equilibrium, $k_1(a-X_e)-k_2X_e=0$, because under these conditions:

$$\frac{dx}{dt}=0 \text{ or } k_C=\frac{X_e}{a-X_e}=\frac{k_1}{k_2} \tag{11}$$

where k_C is the equilibrium constant. Now under equilibrium conditions, the rate becomes:

$$\frac{dx}{dt}=[k_1(a-x)-k_2x]-[k_1(a-X_e)-k_2X_e] \tag{12}$$

The above equation is in the form $dx/dt=k(a-x)$. Therefore,

$$k_1+k_2=\frac{1}{t}\ln\frac{X_e}{X_e-x} \tag{13}$$

$$\ln(1-U_t)=-(k_1+k_2)t=-kt=-k_1\left(1+\frac{1}{k_C}\right) \tag{14}$$

where $U_t=x/X_e$ and k is the overall rate constant. U_t is called the fractional attainment of equilibrium of copper and this was calculated by considering copper adsorption over the resins in a given time range 1-24 hrs. In the present study a concentration of copper over the range 12 to 20 mg/dm^3 was examined. Using the kinetic equations, the overall rate constant, the forward and backward rate constants were calculated. For instance, by plotting $\ln(1-U_t)$ vs. t the overall rate constant k for a given concentration of copper was calculated by considering the slope of the straight line, and by using Eq. (14) the equilibrium constant k_C, forward and backward rate constants k_1 and k_2 were calculated and shown in Table 3. From Table 3, it can be seen that the forward rate constants for the removal of copper are much higher than the backward rate constants, namely the desorption process. The uptake of copper by the ion exchange resins was reversible and thus has good potential for the removal/recovery of copper from aqueous solutions.

As increasing of initial concentration of copper (a), overall rate constant and forward rate constant were decreased as shown in Table 3. The equilibrium constant, $k_c=k_1/k_2$, of 1200H was decreased with increase of a, while that of IRN97H was increased. It is noted that the adsorption reaction of IRN97H resin is dominant to desorption reaction as with the increase with initial concentration and then has an effect on the adsorption capacity.

6. Pseudo-first Order and Pseudo-second Kinetic Models

The sorption kinetics may be described by a pseudo-first order [Quek et al., 1998].

The differential equation is as follows:

$$\frac{dq_t}{dt}=k_1(q_e-q_t) \tag{15}$$

Integrating Eq. (15) for the boundary conditions t=0 to t=t and $q_t=q_t$, gives:

$$\log\left(\frac{q_e}{q_e-q_t}\right)=\frac{k_1}{2.303}t \tag{16}$$

which is the integrated rate law for a pseudo-first order reaction, where q_e is the amount of copper sorbed at equilibrium (mg/g), q_t the amount of copper sorbed at time t (mg/g), k_1 is the equilibrium rate constant of pseudo-first sorption (min^{-1}). In order to obtain the rate constants, the straight line plots of $\log(q_e-q_t)$ against t for different metal and different experimental conditions have been analyzed. The rate constants, k_1, values of the metals under different conditions were calculated from these plots. Fig. 6a and 6b show examples for these plots. Approximately, linear fits were observed for all concentrations, indicating that sorption reaction can be approximated to pseudo-first order kinetics. Constants k_1 for all situations tested have been calculated and summarized in Table 4.

A pseudo-second order model [Quek et al., 1998; Namasivayam and Ranganathan, 1995] may also describe the kinetics of sorption of copper on ion exchange resins. The IX (Ion Exchange resins)-Cu reaction may be represented in two ways:

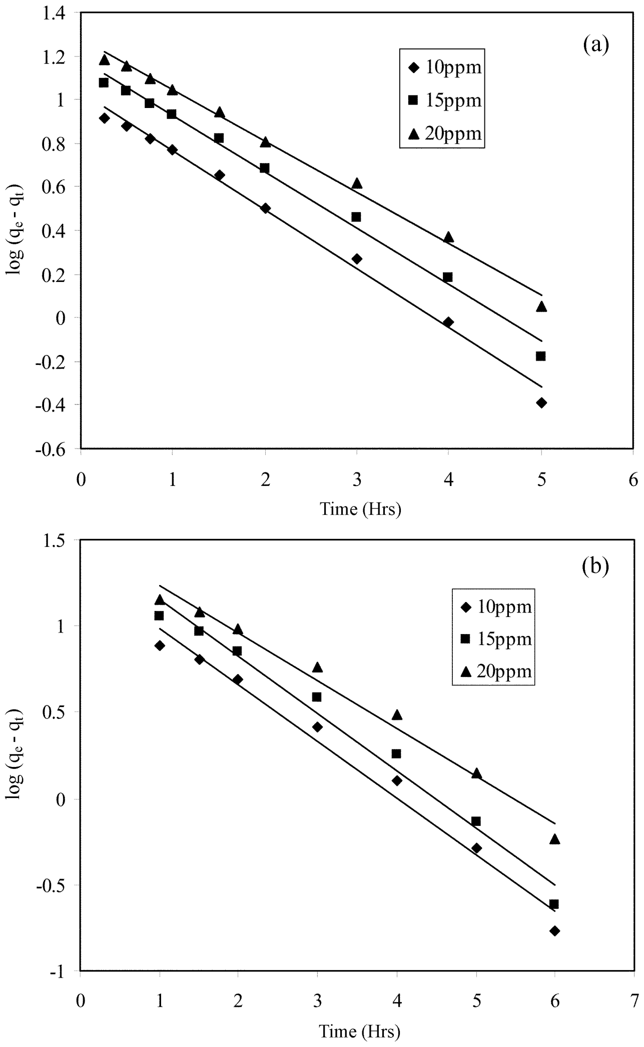

Fig. 6. (a) Pseudo-first order kinetic fit for adsorption of copper by ion exchange resin 1200H. (b) Pseudo-first order kinetic fit for adsorption of copper by ion exchange resin IRN97H.

$$2IX^{-}+Cu^{2+}\Leftrightarrow Cu(IX)_2 \tag{17}$$

or

$$2HIX+Cu^{2+}\Leftrightarrow Cu(IX)_2+2H^{+} \tag{18}$$

where IX^{-} and HIX are polar sites on the resin surface. A pseudo-second order rate expression based on sorption equilibrium capacity may be derived from Eqs. (17) and (18).

$$\frac{d(IX)_t}{dt}=k[(IX)_o-(IX)_t]^2 \tag{19}$$

or

$$\frac{d(HIX)_t}{dt}=k[(HIX)_o-(HIX)_t]^2 \tag{20}$$

where $(IX)_t$ and $(HIX)_t$ are the number of active sites occupied on the ion exchange resins at time t, $(IX)_o$ and $(HIX)_o$ are the number of equilibrium sites available on the sorbent. It is assumed that the sorption capacity is proportional to the number of active sites occupied on the adsorbent, and then the kinetic rate law can be rewritten as follows:

$$\frac{dq_t}{dt}=k(q_e-q_t)^2 \tag{21}$$

where k is the rate constant of sorption (g/mg min), q_e the amount of copper sorbed at equilibrium (mg/g), q_t amount of copper sorbed on the surface of the sorbent at any time t (mg/g). Integrating this for the boundary conditions t=0 to t=t and q_t=0 to q_t=q_t gives

$$\frac{t}{q_t}=\frac{1}{kq_e^2}+\frac{1}{q_e}t \tag{21}$$

which is the integrated rate law for a pseudo-second order equation. The constants can be determined by plotting t/q_t vs. t. The initial sorption rate, h, as $t\rightarrow 0$ can be defined as $h=kq_e^2$. The initial sorption rate, h, the equilibrium sorption capacity, q_e, and the pseudo-second order rate constant, k can be determined experimentally from slope and intercept of plotting of t/q_t vs. t. Fig. 7a and 7b show an example of these plots. Good fits were observed for all concentrations, indicating that the sorption reaction can be approximated with the pseudo second order kinetics model. The constant k is calculated from the figures and represented in Table 4. It can be observed that h (the initial sorption rate, mg/g min) is generally higher for higher concentrations.

For the 1200H resin, a pseudo-second order kinetic model is more matched than a pseudo-first order kinetic one; while for the IRN97H, a pseudo-first order kinetic model is well fitted the experiment data (considered data numbers in Fig. 6 and Fig. 7). As shown in Table 4, the rate constant (k_1, k), except initial sorption rate, was decreased with increase of initial concentration. This means that the initial sorption into the resins becomes fast with input concentration, but over-

Table 4. The pseudo-first and second order rate constant and intraparticle diffusion value at different initial concentrations of copper on 1200H and IRN97H ion exchange resin

Sorbent	Copper (mg/dm^3)	Pseudofirst order rate constant, k_1 (l/hr) (R^2)	Pseudo-second order		Intraparticle rate constant, k_{id} ($mg/g/hrs^{1/2}$) (R^2)
			Rate constant, k (g/mg·min) (R^2)	Initial copper sorption rate, h (mg/g)	
1200H	10	0.6220 (0.9931)	0.0373 (0.9932)	6.5488	5.5292 (0.9921)
	15	0.5958 (0.9919)	0.0311 (0.9936)	11.0132	7.7141 (0.9937)
	20	0.5389 (0.9944)	0.0256 (0.9935)	15.3139	9.7053 (0.9912)
IRN97H	10	0.7526 (0.9807)	0.0239 (0.9888)	5.1440	5.5698 (0.9708)
	15	0.7607 (0.9807)	0.0169 (0.9889)	7.9745	8.1494 (0.9679)
	20	0.6368 (0.9833)	0.0100 (0.9905)	9.2507	9.8367 (0.9736)

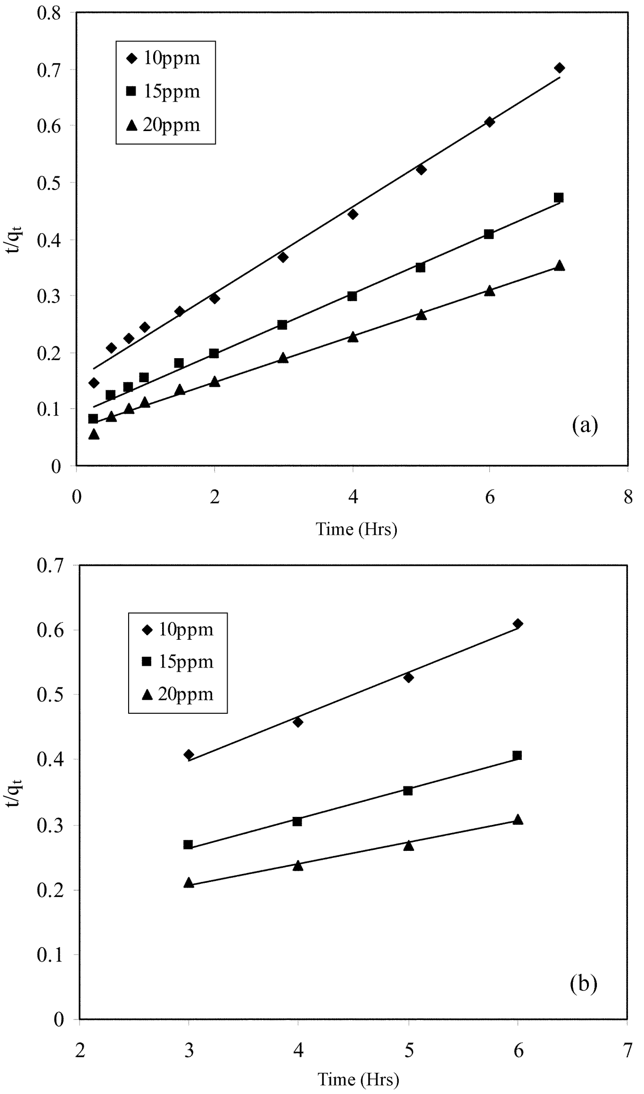

Fig. 7. (a) Pseudo-second order kinetic fit for adsorption of copper by ion exchange resin 1200H. (b) Pseudo-second order kinetic fit for adsorption of copper by ion exchange resin IRN97H.

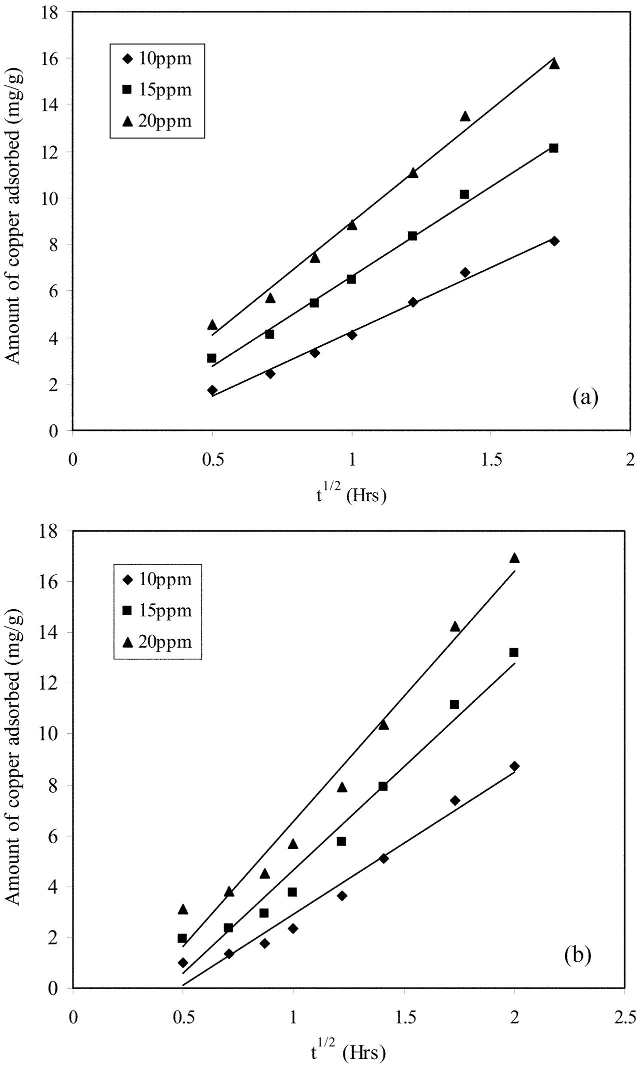

Fig. 8. (a) Intraparticle diffusion plot for adsorption of copper on 1200H ion exchange resins. (b) Intraparticle diffusion plot for adsorption of copper on IRN97H ion exchange resins.

all sorption rate becomes slow.

7. Intraparticle Diffusion Model

The rate constant for intraparticle diffusion (k_{id}) is given by Weber and Morris [Sun and Yang, 2003]:

$$q = k_{id} t^{1/2} \tag{22}$$

where q is the amount adsorbed (mg/g) at time, t (hrs). Plots of q vs. $t^{1/2}$ are shown in Fig. 8a and 8b for different initial concentrations. k_{id} values were obtained from the slope of the linear portion of the curves for each concentration of metal ion (Table 4). The copper was initially adsorbed by the exterior surface of resins. When the adsorption of the exterior surface reached the saturation level, the copper ions entered into resins via the networks within the resins and were adsorbed by the interior surfaces. When the copper ion diffused into the pores of the resins, the diffusion resistance increased, which in turn caused the diffusion rate to decrease. With the decrease in copper concentration in the solution, the diffusion rate became constantly lower, and consequently the diffusion processes reached equilibrium. k_{id} value was higher at higher concentration. The intraparticle diffusion rate as well as initial sorption rate was increased with the increase of initial concentration of copper. In addition, this diffusion rate of IRN97H is slightly larger than that of 1200H, indicating that copper ion into IRN97H is more easily diffused and transported than 1200H. Consequently, the intraparticle diffusion and initial sorption into resins of Cu(II) in the ion exchange resins was the main rate limiting step.

8. Removal of Copper from Synthetic Electronic Process Wastewater

The use of ion exchange resins 1200H and IRN97H in the removal of copper from synthetic electronic process wastewater was attempted by batch studies in order to asses the suitability and applicability of these ion exchange resins for treatment purposes. Since electronic process wastewater has a copper concentration of 0.5 mg/dm^3, it was used for the study with 1200H and IRN97H, and then subjected to treatment. At optimum pH (5.8) the maximum removal of copper from 100 ml of wastewater containing 0.5 mg/*l* copper was adsorbed by 300 mg/100 ml of 1200H and 75 mg/100 ml of IRN97H ion exchange resins. The efficiency of these resins with respect to the removal of copper from the synthetic copper solution alone is higher than that for the synthetic electronic process wastewater. This can be attributed to the presence of other impurities (metal ions) present in the electronic process wastewater which may interfere in the ion exchange process.

CONCLUSIONS

In this paper, it has been shown that adsorbent materials of ion exchange resins can be used for the removal of copper from water and wastewater. Quantitative removal of copper from synthetic wastewater confirms the validity of results obtained in batch mode studies. The kinetic data would be useful for developing an appropriate technology for designing a waste water treatment plant. For all the systems studied, chemical reaction seems significant in the rate-controlling step and the pseudo-second order chemical reaction kinetics provide the best correlation of the experimental data for 1200H, whereas the pseudo-first order model proposed fits the experimental data well for IRN97H. We conclude that ion exchange resins could be exploited for applications in the tertiary level treatment of potable water as well as industrial effluents. The adsorption of copper was hindered by the presence of other metals. In the case of electronic process wastewater, copper adsorption was particularly damped by the presence of other metal ions. Detailed studies will be needed to further evaluate ion exchange resins in terms of their competitive adsorption and their reaction chemistry.

ACKNOWLEDGMENT

This work was supported by National Research Laboratory (NRL) of the Korean Science and Engineering Foundation (KOSEF).

REFERENCES

Bae, E., Chah, S. and Yi, J., “Preparation and Characterization of Ceramic Hollow Microspheres for Heavy Metal Ion Removal in Wastewater,” *J. Colloid Interf. Sci.*, **230**, 367 (2000).

Camp, R. T., “Water and its Impurities,” 2nd Ed. Reinhold, New York (1964).

Chah, S., Kim, J. S. and Yi, J., “Separation of Zinc Ions from Aqueous Solutions using Modified Silica Impregnated with CYANEX 272,” *Separ. Sci. Technol.*, **37**, 701 (2002).

Dean, J. G., Borqui, F. L. and Labouette, K. H., “Removing Heavy Metals from Waste Water,” *Environ. Sci. Tech.*, **6**, 518 (1972).

Hosseini, M., Mertens, S. F. L., Ghorbani, M. and Arshadi, M. R., “Asymmetrical Schiff Bases as Inhibitors of Mild Steel Corrosion in Sulphuric Acid Media,” *Mater. Chem. Phys.*, **78**, 800 (2003).

Kang, T., Park, T., Park, J. C., Cho, Y. S. and Yi, J., “Preparation of Chemically Active Mesoporous Adsorbent for Pt(II) and Pd(II) Adsorption from Aqueous Solutions,” *Korean J. Chem. Eng.*, **19**, 685 (2002).

Kim, J. S., Chah, S. and Yi, J., “Preparation of Modified Silica for Heavy Metal Removal,” *Korean J. Chem. Eng.*, **17**, 118 (2000).

Kim, S. J., Lim, K. H., Joo, K. H., Lee, M. J., Kil, S. G. and Cho, S. Y., “Removal of Heavy Metal Cyanide Complexes by Ion Exchange,” *Korean J. Chem. Eng.*, **19**, 1078 (2002).

Kim, Y., Lee, B. and Yi, J., “Preparation of Functionalized Mesoporous Silica Containing Magnetite (MSM) for the Removal of Copper Ions in Aqueous Solutions and its Magnetic Separation,” *Separ. Sci. Technol.*, **38**, 2533 (2003).

Lee, B., Kim, Y., Lee, H. and Yi, J., “Synthesis of Functionalized Porous Silicas via Templating Method as Heavy Metal Ion Adsorbents: The Introduction of Surface Hydrophilicity onto the Surface of Adsorbents,” *Micropor. Mesopor. Mat.*, **50**, 77 (2001).

Namasivayam, C. and Kadirvelu, K., “Uptake of Mercury(II) from Wastewater by Activated Carbon from an Unwanted Agricultural Solid By-product,” *Carbon*, **37**, 79 (1999).

Namasivayam, C. and Ranganathan, K., “Removal of Cd(II) from Wastewater by Adsorption on Waste Fe(III)/Cr(III) Hydroxide,” *Water Res.*, **29**, 1737 (1995).

Quek, S. Y., Wase, D. A. J. and Forster, C. F., “The Use of Sago Waste for the Sorption of Lead and Copper,” *Water SA*, **24**, 251 (1998).

Redlich, O. and Peterson, D. L., “A Useful Adsorption Isotherm,” *J. Phys. Chem.*, **63**, 1024 (1959).

Rengaraj, S. and Moon, S. H., “Kinetics of Adsorption of Co(II) Removal from Water and Wastewater by Ion Exchange Resins,” *Water Res.*, **36**, 1783 (2002).

Rengaraj, S., Joo, C., Kim, Y. and Yi, J., “Kinetics of Removal of Chromium from Water and Electronic Process Wastewater by Ion Exchange Resins: 1200H, 1500H and IRN97H,” *J. Hazard. Mater.*, **B102**, 257 (2003).

Sun, Q. and Yang, L., “The Adsorption of Basic Dyes from Aqueous Solution on Modified Peat-resin Particle,” *Water Res.*, **37**, 1535 (2003).