

Synthesis and Metal Ion Adsorption Studies of Chelating Resins Derived from Macroporous Glycidyl Methacrylate-Divinylbenzene Copolymer Beads Anchored Schiff Bases

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ABSTRACT: Two novel chelating resins are prepared by anchoring diethylenetriamine bis- and mono-furaldehyde Schiff bases onto the macroporous GMA-DVB copolymer beads and utilized for the adsorption towards Cu(II), Co(II), Ni(II), and Zn(II). FTIR spectra show that Schiff base groups have been successfully introduced into the polymer matrix and the chelating resins can form complexes with the metal ions. The chelating resins show a higher adsorption capacity toward Cu(II). The conductivity method can be used for

determining the adsorption kinetics of the resins towards metal ions. The results show that the adsorption rates towards Cu(II) are much higher than those towards other ions and pseudo second-order and intraparticle diffusion models can be applied to treat the adsorption amount-time data. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 953–959, 2010

Key words: macroporous polymer; adsorption; metal-polymer complexes; resins; modification

INTRODUCTION

Chelating resins are designed for selective adsorption, separation, and preconcentration of metal ions and are usually employed in waste water treatment, in the recovery and removal of metal ions, and in accurate analysis of trace metal ions.^{1–3} They are generally a group of insoluble materials which have ligands usually containing oxygen, nitrogen, sulfur, and phosphorus donor atoms on the material surface and are obtained by incorporation of ligands into the polymer matrix. Among chelating resins, the most popular ones are those containing nitrogen donor atoms which have high adsorption capacity and adsorption selectivity towards transition metal ions. Schiff bases such as the ones formed by condensation of polyethylene polyamines with salicylaldehyde and furaldehyde have the azomethine groups ($>C=N-$) in their structures and are known to form complexes with transition metal ions readily.^{4–7} At present in a chelating resin, they are expected to show high affinity and selectivity towards these metal ions at an appropriate pH. Hence some chelating resins containing Schiff base ligands are successfully prepared by incorporation of Schiff base groups into the polymer matrix and polymerization of monomers containing Schiff base groups and utilized for adsorption and removal of metal ions.^{8–20}

Poly(glycidyl methacrylate) is a type of reactive polymer owing to having high activity epoxy groups. Its crosslinked resins modified by organic compounds containing amino groups such as diethylamine,^{21,22} polyethylene polyamine,^{23–25} iminodiacetic acid,^{26–28} imidazole,²⁹ piperazine,³⁰ and 8-aminoquinoline³¹ were widely used for the adsorption and separation of metal ions. In this article, two types of Schiff base chelating resins derived from macroporous glycidyl methacrylate-divinylbenzene copolymer beads are synthesized and their adsorptions towards metal ions are investigated.

EXPERIMENTAL

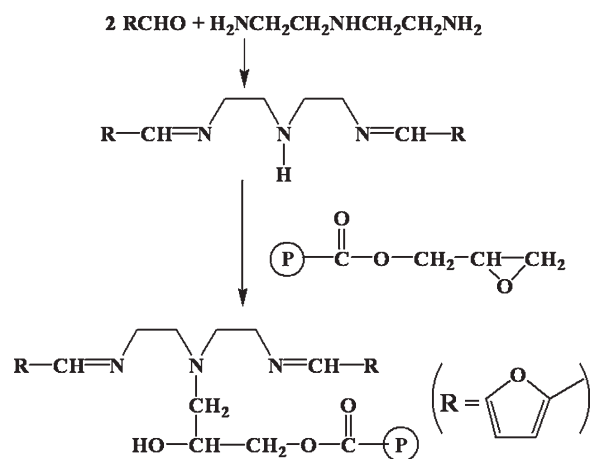
Materials and reagents

Furaldehyde, diethylenetriamine (DETA), toluene, *n*-heptane, 1,4-dioxane, ethanol, sodium ethylenediamine tetraacetic acid (EDTA), azobisisobutyronitrile (AIBN), and metal salts (CoSO₄·7H₂O, NiSO₄·6H₂O, CuSO₄·5H₂O, and ZnSO₄·5H₂O) were of analytical reagent grade and were used without further purification. Divinyl benzene (DVB) was obtained from Fluka Corp. (St. Louis, MO) (reagent grade) and used as received. Glycidyl methacrylate (GMA) and Poly(vinyl alcohol) (PVA) were industrial products and used as received.

Preparation of macroporous GMA-DVB(80-20) copolymer bead

Macroporous GMA-DVB copolymer bead was prepared by radical suspension polymerization in a 1 L

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Scheme 1 Synthetic routes to F-1 resin.

three-neck flask. The monomer phase containing 64 g of GMA, 16 g of DVB, 0.8 g of initiators (AIBN), and 60 mL of diluents (48 mL toluene and 12 mL *n*-heptane) was suspended in the aqueous phase consisting of 450 g of water, 22.5 g of NaCl, and 0.45 g of PVA. The polymerization was performed at 348 K for 3 h and at 358 K for 1 h under constant stirring. After completion of the reaction, the copolymer beads were filtered and washed well with water (3 × 300 mL) and ethanol (5 × 100 mL), kept in ethanol for 24 h and dried under vacuum at 333 K. The product in perfect spherical bead was sieved and the fraction with the sizes of 0.2–0.9 mm was used for further reactions.

Preparation of the chelating resin anchored diethylenetriamine bis-furaldehyde Schiff base

Diethylenetriamine bis-furaldehyde Schiff base was prepared by following the literature procedure with slight modification.^{32,33} DETA (0.6 mol) was dissolved in 200 mL of dioxane and toluene (volume ratio = 4 : 1), to this solution, furaldehyde (1.2 mol) in 200 mL of dioxane and toluene (volume ratio = 4 : 1) was added dropwise under stirring. The reaction was continued for 2 h at 353 K. The Schiff base solution was heated to 363 K and 63 g of GMA-DVB copolymer beads with the size of 0.2–0.6 mm were added to this solution. The mixture was kept for 10 h at this temperature under stirring. The resin beads were filtered and washed with ethanol (5 × 100 mL) and dried under vacuum at 333 K. Chelating resins (77.2 g) labeled as F-1 were obtained, which contain 1.43 mmol/g of the azomethine groups estimated by the increase in mass. The proposed reactions are given as Scheme 1.

Preparation of the chelating resin anchored diethylenetriamine mono-furaldehyde Schiff base

The diethylenetriamination of the GMA-DVB copolymer was performed according to the literature procedure with slight modification.²⁴ 50 g of GMA-DVB

copolymer beads with the size of 0.6–0.9 mm were mixed with 80 g of DETA, 120 mL of dioxane, and 30 mL of toluene. The reaction was performed under constant stirring at 363 K for 10 h to produce the diethylenetriaminated resin (DETA-resin) beads. The beads were filtered and washed well with ethanol (8 × 100 mL), kept in ethanol for 24 h and dried under vacuum at 333 K. 63.5 g of the DETA-resin beads were obtained, which contain 2.06 mmol/g of DETA groups estimated by the increase in mass. The beads were swelled in 240 mL of dioxane and 60 mL of toluene for 10 h and 96 g of furaldehyde were added to this mixture. The reaction was performed under constant stirring at 363 K for 10 h to produce the chelating resin beads. The beads were filtered and washed well with ethanol (5 × 100 mL), kept in ethanol for 24 h and dried under vacuum at 333 K. Chelating resins (71.4 g) labeled as F-2 were obtained, which contain 1.38 mmol/g of the azomethine groups estimated by the increase in mass. The proposed reactions are given as Scheme 2.

Measurement and characterization

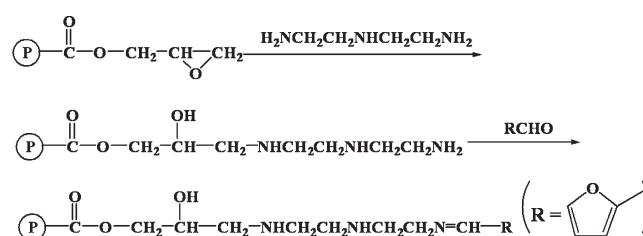
FTIR spectra were recorded using KBr discs on a Spectrum BX II spectrometer (Perkin-Elmer Instruments LLC), pH was determined on a pHs-3 acidometer (Shanghai Leici Instrument Factory, Shanghai, China), and conductivity was measured on a Con 510 Bench Conductivity/TDS meter (Oakton Instruments, Vernon Hill, IL).

The true density of dried resins was estimated by pycnometer method. 0.5 g (W_0) of dried resins were placed into a 10 mL pycnometer given mass at 298 K. Into the pycnometer was added 8 mL of *n*-heptane and the mixture was kept at 298 K for 24 h. The pycnometer was then filled with *n*-heptane to the mark and was weighed (W_1). The true density (d) was calculated according to the following equation:

$$d = \frac{W_0}{10 - (W_1 - W_0)/d_s}$$

where W_1 (g) is the total mass of the resin and solvent, W_0 (g) the mass of the resin, d_s (g/cm³) the density of the solvent ($d_{n\text{-heptane}} = 0.6845$ g/cm³).

The pore volume and porosity were obtained by monitoring the mass gain of the resins in *n*-heptane.³⁴ The dried resins were placed into tubes with



Scheme 2 Synthetic routes to F-2 resin.

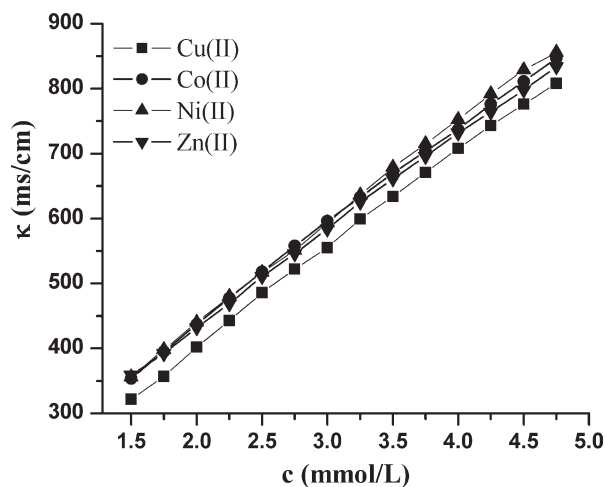


Figure 1 Dependence of conductivity on the concentration of the metal ion.

a porous glass bottom. The tubes were kept inside a beaker filled with *n*-heptane for 24 h at 298 K. The excess solvent was removed by centrifugation at 2000 rpm for 1 min. The pore volume (V_P) was obtained from the resin mass gain divided by the density of *n*-heptane and the porosity (ϕ) was calculated according to the following equation:

$$\phi = \frac{V_P}{V_P + W_0/d}$$

Optimum pH of metal ion adsorption

The optimum pH of metal ion adsorption was determined by batch experiments. 0.25 g of the resins were added to 50 mL of 5 mmol/L of metal ion solution at different pHs. The pH was adjusted before adding resin using H_2SO_4 solution or NH_3-NH_4Cl buffer solution. This mixture was mechanically shaken for 2 h at room temperature. Then the chelating resin was separated by filtration, washed with distilled water, and the amount of the remaining metal ions in the filtrate was determined by standard EDTA titration method. The adsorption amount for the metal ion was calculated according to the following equation:

$$Q = \frac{5 \times 0.05 - M}{0.25}$$

where Q (mmol/g) is the adsorption amount and M (mmol) the amount of the remaining metal ions in the filtrate.

Adsorption capacity of chelating resin

The adsorption capacities of F-1 and F-2 resins towards Cu(II), Co(II), Ni(II), and Zn(II) ions were

determined by batch experiments. 0.5 g of the resins were added to 50 mL of 100 mmol/L of metal ion solution at optimum adsorption pH. This mixture was mechanically shaken for 2 h and kept for 22 h at room temperature to attain adsorption equilibrium. Then the chelating resin was separated by filtration, washed with distilled water, and the amount of the remaining metal ions in the filtrate was determined by standard EDTA titration method. The adsorption capacity of the resin was calculated according to the following equation:

$$Q = \frac{100 \times 0.05 - M}{0.5}$$

where Q (mmol/g) is the adsorption capacity and M (mmol) the amount of the remaining metal ions in the filtrate.

Adsorption kinetics studies

To determine the concentration of a metal ion in its solution by conductivity method, the conductivity of a series of standard metal ion solutions was measured. Figure 1 shows the dependence of conductivity on the standard ion concentration. The slope and intercept values and correlation coefficients obtained from Figure 1 by linear fitting are listed in Table I. High correlation coefficients indicate that conductivity method can be applied to measure the concentration of the metal ion in the range from 1.5 to 5 mmol/L.

The adsorption kinetics of F-1 and F-2 resins towards Cu(II), Co(II), Ni(II), and Zn(II) ions was determined by batch experiments and the conductivity method. 1.25 g of the resins were added to 125 mL of 5 mmol/L of metal ion solution at optimum adsorption pH. This mixture was mechanically shaken at 298 K and the conductivity of the solution at different time intervals was recorded. The adsorption amount was calculated according to the following equation:

$$Q_t = \frac{(c_0 - c_t)V}{W} = \frac{(c_0 - c_t)c_0V}{c_0W} = \frac{\kappa_0 - \kappa_t}{2(\kappa_0 - A)}$$

where Q_t (mmol/g) is the adsorption amount at contact time t , V (L) the solution volume, W (g) the

TABLE I
Scope, Intercept, and Correlation Coefficient (r^2)
Obtained from Figure 1 by Linear Fitting

Metal ion	Intercept (A)	Scope	Correlation coefficient
Cu(II)	104.6	149.8	0.9994
Co(II)	139.5	149.9	0.9994
Ni(II)	132.0	153.9	0.9996
Zn(II)	142.0	146.4	0.9997

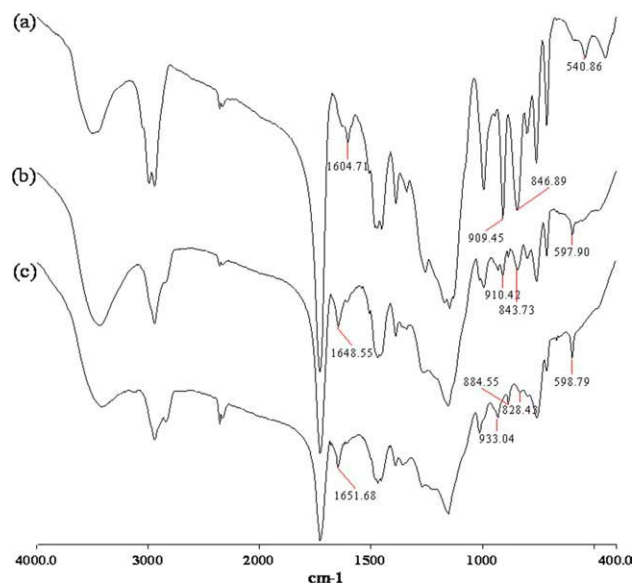


Figure 2 FTIR spectra of GMA-DVB copolymer (a), F-1 resin (b), and F-2 resin (c). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

resin mass, A ($\mu\text{S} \cdot \text{cm}$) the intercept of the standard straight line, c_0 and c_t (mmol/L) are the concentration of the solution at initial time and contact time t respectively, and κ_0 and κ_t ($\mu\text{S} \cdot \text{cm}$) the conductivity of the solution at initial time and contact time t respectively.

RESULTS AND DISCUSSION

Infrared spectra characterization

Figure 2 shows the FTIR spectra of GMA-DVB copolymer, F-1 and F-2 resins. By comparison with the curve of the copolymer, the relative intensity of epoxy characteristic peaks at 910 cm^{-1} and 844 cm^{-1} decreases in the curves of F-1 and F-2 resins, and a new peak appears at 1648 or 1652 cm^{-1} , which is the characteristic peak of C=N bond, indicating that Schiff base groups have been introduced into the polymer matrix successfully. Figure 3 shows the FTIR spectra of F-1 resin-metal ion complexes. By comparison with the curve of F-resin, the ν (C=N) band undergoes a less negative shift and a new peak appears at 620 cm^{-1} , which may be the characteristic peak of M—O bond.¹⁵

True density, pore volume, and porosity of the resins

The pore volume or porosity has an obvious influence on the adsorption rate for metal ions, high porosity is helpful for intraparticle diffusion of metal ions. The true density, pore volume, and porosity of the resins are listed in Table II. By comparison with

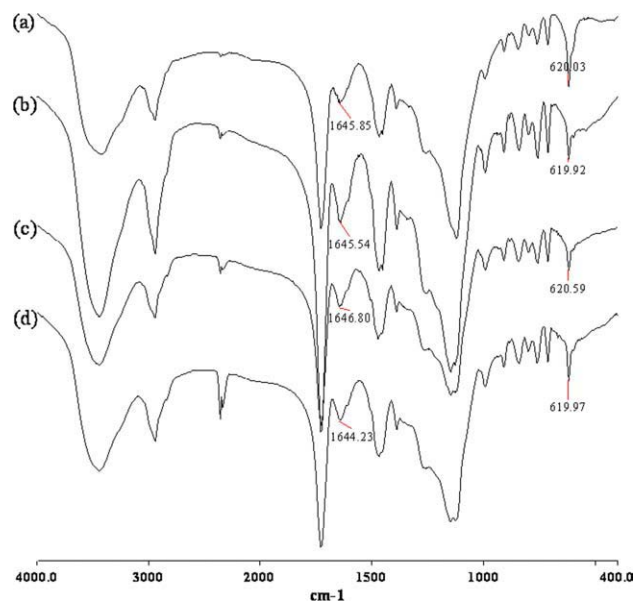


Figure 3 FTIR spectra of F-1 resin-metal ion complexes: Cu(II)(a), Co(II)(b), Ni(II)(c), and Zn(II)(d). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

GMA-DVB copolymer resin, the pore volume and porosity of the DETA-resin and F-1 resin decreases. This result indicates that anchoring large groups onto GMA-DVB resin can lead to decrease in pore volume or porosity. By comparison with DETA-resin, pore volume and porosity of F-2 resin decreases, because the diethylenetriamine mono-furfuraldehyde Schiff base group has larger volume than the DETA group.

Effect of pH of the medium

The adsorption of chelating resin towards metal ion is dependent on the pH of the metal ion solution due to the competitive reaction between chelating groups and hydrogen ions in the solution.^{14,18,35} The effects of pH on the adsorption amount of F-1 and F-2 resins towards four metal ions are shown in Figures 4 and 5 respectively. Generally, the two resins show low adsorption efficiency towards metal ions at low pH values due to protonation of chelating sites in the ligands that inhibit their binding to metal ions,³⁶ and as the pH increases, their adsorption amount increases. The highest adsorption amount

TABLE II
True Density, Pore Volume, and Porosity of Resin

Resin	d (g/cm ³)	V_P (cm ³ /g)	ϕ (%)
GMA-DVB	1.38	0.932	56.2
DETA-resin	1.36	0.632	46.5
F-1	1.25	0.622	43.7
F-2	1.32	0.484	39.1

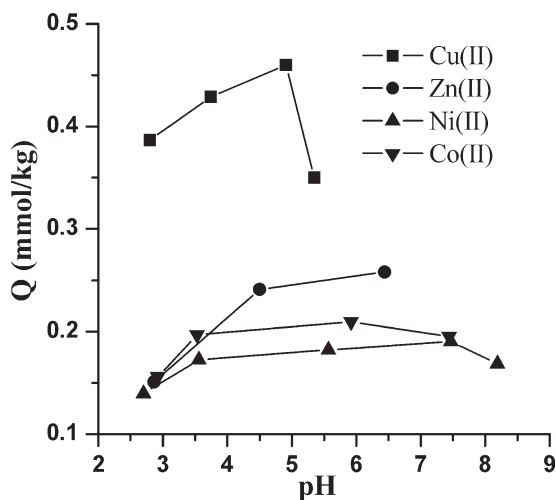


Figure 4 Dependence of adsorption amount of F-1 resin towards metal ions on pH.

are recorded at the pH before the precipitation limit for each metal ion (Cu(II) 5.3, Co(II) 7.7, Ni(II) 7.8, and Zn(II) 6.7) calculated from the ion concentration and the solubility product.³⁵ The optimum pH is 4–5 for Cu(II), 6–7 for Zn(II), 7–8 for Ni(II), and 7 for Co(II).

Metal ion adsorption capacity

The equilibrium adsorption amount (adsorption capacity) of the resin is an important factor to determine the minimum amount of resin required to adsorb a specific metal ion quantitatively from the solution. The adsorption capacities of F-1 resin towards Cu(II), Co(II), Ni(II), and Zn(II) are 0.691, 0.476, 0.396, and 0.535 mmol/g, respectively, and the adsorption capacities of F-2 resin towards Cu(II), Co(II), Ni(II), and Zn(II) are 1.01, 0.556, 0.368, and

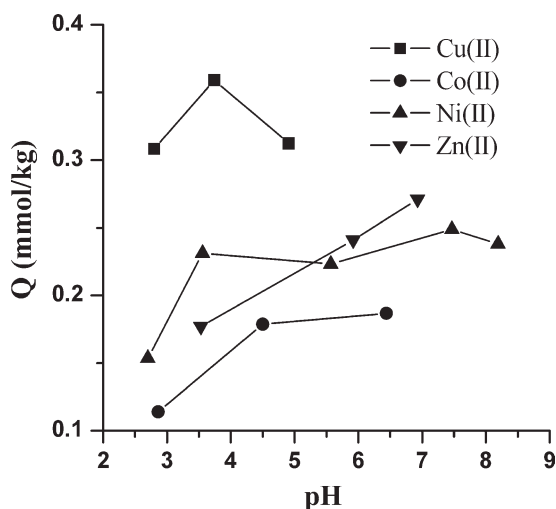


Figure 5 Dependence of adsorption amount of F-2 resin towards metal ions on pH.

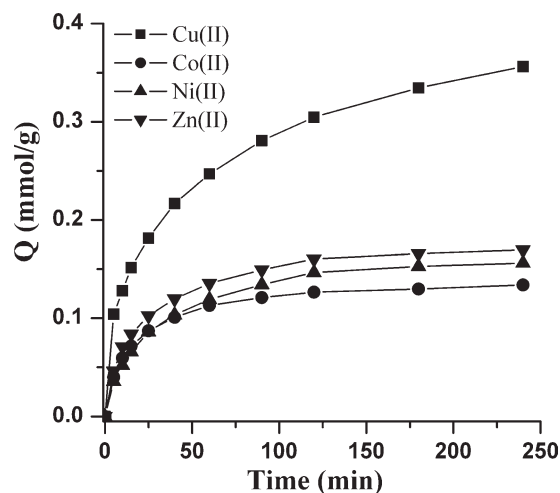


Figure 6 Effect of contact time on adsorption amount of F-1 resin.

0.531 mmol/g, respectively. The results show that F-1 and F-2 resins have much higher adsorption capacity towards Cu(II).

Metal ion adsorption kinetics

The effects of contact times on the adsorption amount of F-1 and F-2 resins towards four metal ions are shown in Figures 6 and 7, respectively. It is seen that the adsorption rates towards Cu(II) are much higher than those towards other ions similar with the results reported in some literatures,^{12,14,36} and the order of adsorption rate is Cu(II) > Zn(II) > Ni(II) > Co(II) for F-1 resin and Cu(II) > Zn(II) > Co(II) > Ni(II) for F-2 resin. It is further noted that the adsorption rates of F-1 resin are higher than those of F-2 resin due to their differences in structure, particle diameter, pore volume, and porosity. F-1 resin has higher pore volume and porosity and

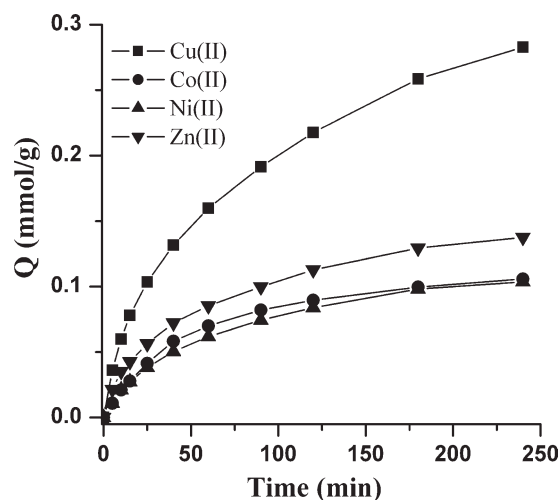


Figure 7 Effect of contact time on adsorption amount of F-2 resin.

smaller particle diameter as mentioned earlier, which leads to a higher adsorption rate, because the metal adsorption of the resin depends not only on the nature of the ligand groups (such as complexing capacity, steric hindrance, and hydrophobicity) but also the accessibility towards the metal ions.¹²

It is known that the adsorption of the chelating resin towards metal ions must be considered as a liquid–solid phase reaction which includes the diffusion of the ions from the solution to the resin surface, the diffusion of the ions within the solid resin beads, and the coordination reaction between the ions and the chelating groups of the resin. The adsorption kinetics is governed by the slowest of these processes. Generally, intraparticle diffusion of ions is the slowest step, the rate-determining step^{37–39} and the intraparticle diffusion model can be applied to treat the adsorption-time data according to the following equation³⁹:

$$Q_t = x_i + k_p t^{1/2}$$

where Q_t (mmol/g) is the adsorption amount at contact time t (min), k_p ($\text{mmol g}^{-1} \text{min}^{-0.5}$) the intraparticle diffusion rate constant, and x_i the intercept of the straight line which is proportional to the boundary layer thickness.

Figure 8 shows that the plots of the adsorption amount of F-1 and F-2 resins versus $t^{1/2}$ are basically straight lines during 60 min. This indicates that the adsorption kinetics is governed by intraparticle diffusion within the pores of the resin beads. The values of k_p for Cu(II), Co(II), Ni(II), and Zn(II) are cal-

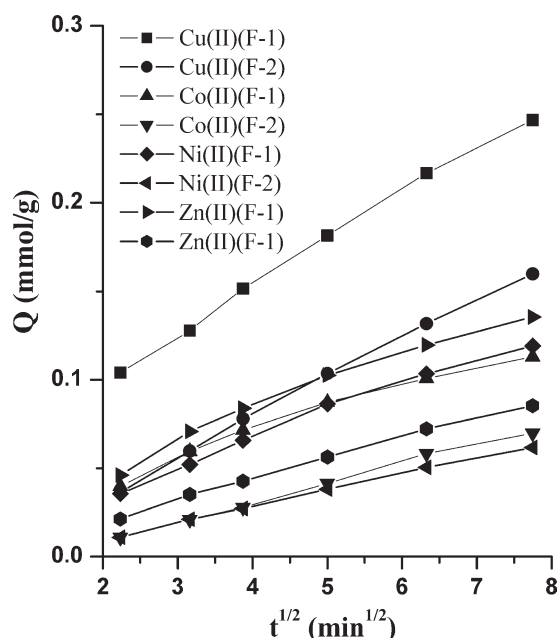


Figure 8 Adsorption amount of F-1 and F-2 resins as a function of square root of time.

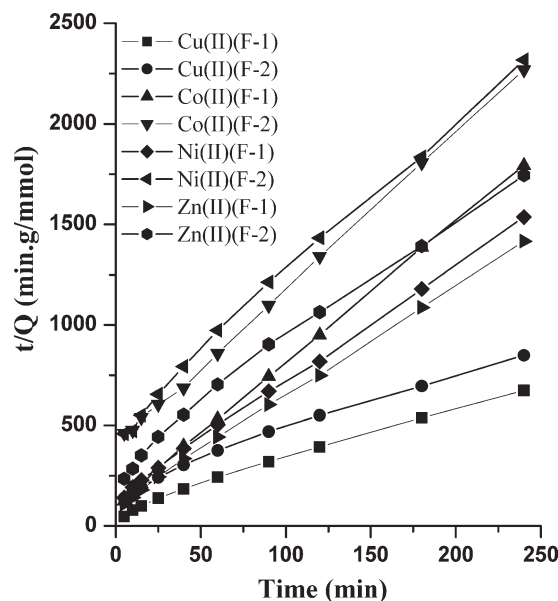


Figure 9 t/Q_t for F-1 and F-2 resins as a function of time.

culated from the slope values of the straight lines and found to be 0.053, 0.026, 0.031, and 0.032 $\text{mmol g}^{-1} \text{min}^{0.5}$ for F-1 resin and 0.045, 0.022, 0.018, and 0.023 $\text{mmol g}^{-1} \text{min}^{0.5}$ for F-2 resin, respectively. The values of x_i are found to be near zero and positive for F-1 resin and negative for F-2 resin.

$$\frac{t}{Q_t} = \frac{1}{kQ_e^2} + \frac{t}{Q_e}$$

where k (g/mmol) is the rate constant of pseudo second-order adsorption, and Q_e (mmol/g) the adsorption amount at equilibrium. The results are shown in Figure 9. As can be seen, the plots of t/Q_t for F-1 and F-2 resins versus t are good linear during whole experimental time. This indicates that pseudo second-order model is more suitable for fitting the adsorption kinetics. The values of Q_e for Cu(II), Co(II), Ni(II), and Zn(II) are calculated from the slope values of the straight lines and found to be 0.77, 0.28, 0.34, and 0.36 mmol g^{-1} for F-1 resin and 0.67, 0.26, 0.25, and 0.32 mmol g^{-1} for F-2 resin, respectively. The values of k for Cu(II), Co(II), Ni(II), and Zn(II) are also calculated from the intercept values of the straight lines and found to be 0.051, 0.24, 0.12, and 0.15 g mmol^{-1} for F-1 resin and 0.027, 0.074, 0.068, and 0.074 mmol g^{-1} for F-2 resin, respectively.

The adsorption amount-time data obtained from Figures 6 and 7 are also treated according to pseudo second-order rate equation given as⁴⁰

CONCLUSIONS

Two new chelating resins are prepared by the reaction of epoxy groups with diethylenetriamine bis-furfuraldehyde Schiff base and the reaction of diethylenetriaminated GMA-DVB resin with furfuraldehyde, and

utilized for the adsorption towards Cu(II), Co(II), Ni(II), and Zn(II). The chelating resins show a higher adsorption capacity toward Cu(II). The conductivity method can be used for determining the adsorption kinetics of the resins towards metal ions, the results show that the adsorption rates towards Cu(II) are much higher than those towards other ions and pseudo second-order and the intraparticle diffusion models can be applied to treat the adsorption amount-time data. Some kinetic parameters are obtained.

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