Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Effect of Crosslinker Type and Embedded Magnetite on the Uptake Behavior of Amine Containing Glycidyl Methacrylate Resins towards Iron(III)

Asem A. Atia[a]; Ahmed M. Donia[a]; Mona M. El-Hawary[a]
[a] Faculty of Science, Chemistry Department, Menoufia University, Shebin El-Kom, Egypt

To cite this Article Atia, Asem A. , Donia, Ahmed M. and El-Hawary, Mona M.(2008) 'Effect of Crosslinker Type and Embedded Magnetite on the Uptake Behavior of Amine Containing Glycidyl Methacrylate Resins towards Iron(III)', Separation Science and Technology, 43: 2, 403 — 419

To link to this Article: DOI: 10.1080/01496390701787180

URL: http://dx.doi.org/10.1080/01496390701787180

Separation Science and Technology, 43: 403–419, 2008

ISSN 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390701787180

Effect of Crosslinker Type and Embedded Magnetite on the Uptake Behavior of Amine Containing Glycidyl Methacrylate Resins towards Iron(III)

Asem A. Atia, Ahmed M. Donia, and Mona M. El-Hawary

Faculty of Science, Chemistry Department, Menoufia University, Shebin El-Kom, Egypt

Abstract: Copolymerization of glycidyl methacrylate (GMA) in the presence of divinylbenzene (DVB) or N,N′-methylene bis-acrylamide (MBA) as hydrophobic or hydrophilic crosslinker was carried out. The obtained resins were immobilized with tetraethylenepentamine as active moieties. The (MBA) containing resin showed higher uptake capacity (9.0 mmol/g) towards Fe(III) compared to (DVB) containing one (8.1 mmol/g). Moreover, magnetization of (GMA/MBA) resin by embedded Fe_3O_4 dramatically improved its uptake towards Fe(III) to reach 13.0 mmol/g at 28°C. Kinetic studies indicated that the adsorption of Fe(III) by the investigated resins follows the pseudo second order kinetics. The higher efficiency of the magnetic resin towards uptake of Fe(III) was also confirmed through column studies. Regeneration of the resins was achieved using acidified thiourea with HNO_3. The durability of the resins was checked up to 5 cycles with no appreciable change in uptake capacity or durability.

Keywords: Iron, resins, glycidyl methacrylate, adsorption, kinetics, thermodynamics

INTRODUCTION

The contamination of water resources by iron become a serious issue. Many problems arise with the presence of iron in the surface and ground water.

Received 11 May 2007, Accepted 30 September 2007

Address correspondence to Ahmed M. Donia, Faculty of Science, Chemistry Department, Menoufia University, Shebin El-Kom, Egypt. Tel.: +2 010 3113697; Fax: +2 02 8356313; E-mail: ahmeddonia2003@yahoo.com

These problems affect human health as well as it causes: tastes, staining of water, discoloration of clothes, and precipitation that can reduce pipe diameter and clog valves of water distribution (1). Also growth of iron bacteria can clog strainers, pumps, and valves (2). Various technological methods have been developed to control the pollution of surface and ground water by iron. Chelating resins with different functionalities have potential applications in the selective removal of iron from waste and aqueous solutions obtained from wine, grape juice, milk, and other nutrient media (3–6). Various studies have been reported on the recovery of Fe(III) using chelating resins (7). Senkal et al. (8) removed Fe(III) using crosslinked terpolymer resins functionalized with diethylenetriamine tetraacetic acid at capacity of 1.48 mmol/g. Roy et al. (9) removed Fe(III) using crosslinked styrene/maleic acid copolymer at capacity of 0.25 mmol/g. Gurnule et al. (10) removed Fe(III) using 4-hydroxyacetophenone, biuret, and formaldehyde terpolymer resin at capacity of 2.34 mmol/g. Magnetic chelating resins are superior to the chelating resins due to their relatively fast, easy separation and collection by magnetic control (11). Glycidyl methacrylate resins and their magnetic forms have various applications in the field of separation and preconcentration (12–15). The major goal of the present study is to modify glycidyl methacrylate resins through imparting magnetic and hydrophilic properties. The modified resins were immobilized by tetraethylenepentamine and applied for Fe(III) removal from aqueous solutions. Kinetic and thermodynamic parameters of uptake process will be calculated. Column and regeneration characteristics of the investigated resins towards Fe(III) will also be clarified.

EXPERIMENTAL

Chemicals

Glycidyl methacrylate (GMA) was obtained from Fluka, Japan. Divinylbenzene (DVB, 55%) was obtained from Sigma-Aldrich, England. N,N′-methylene bis-acrylamide (MBA) and tetraethylenepentamine (en) were obtained from Fluka, Switzerland. Benzoyl peroxide (Bz_2O_2) was obtained from ALEC Co, Egypt and used after crystallization from a mixture of ethanol and methanol. All other chemicals were of analytical grade and used as received. $FeSO_4 \cdot 7H_2O$ and $FeCl_3 \cdot 6H_2O$ were obtained from Nice Co., India and used as sources for Fe(II) and Fe(III), respectively.

Preparation of Magnetite (Fe_3O_4)

Magnetite was prepared following the modified Massart method (16). A 250 mL (0.2 M) of Fe(III) solution was added with stirring to a freshly prepared 250 mL (1.2 M) of Fe(II) solution. A 200 mL of ammonia solution (30%) was suddenly poured to the previously prepared Fe(III)/Fe(II) solution while stirring vigorously. A black precipitate was formed and was allowed to crystallize for 30 min with stirring. The precipitate was washed with deoxygenated water (water was boiled to repeal any gases then bubbled with nitrogen gas) under magnetic decantation until the acidity of the suspension became below pH 7.5. The precipitate was dried at room temperature to give a dry black powder.

Preparation of (GMA/DVB) and (GMA/MBA) Resins

GMA/DVB (R1) and GMA/MBA (R2) were prepared through the polymerization of GMA in the presence of DVB or MBA as crosslinkers, respectively. The ratio of GMA to the crosslinker was (9.5–0.5 w/w). A 0.1 g Bz_2O_2 (initiator) was added to the mixture with stirring. One milliliter isopropyl alcohol and 12.6 mL of cyclohexane were mixed and then added to the former solution. All the contents were poured into a flask containing 73 mL (1%) polyvinyl alcohol and refluxed on a water bath at 75–80°C with continuous stirring for 3 h. A heavy white precipitate was formed, filtered off, washed repeatedly with methanol to remove the unreacted materials, and then dried in air (12).

Preparation of (GMA/MBA) Magnetic Resin

Magnetic resin (R3) was obtained following the above polymerization method used to obtain resin (R2) in the presence of 1 g powdered Fe_3O_4. The heavy grayish precipitate formed was filtered off, washed with methanol, and then dried in air (13, 14).

Preparation of Amine Chelating Resins

The resins were loaded by tetraethylenepentamine (en) as follows: One gram of the resin (R1, R2, or R3) and 3 mL of amine were dissolved in 12 mL DMF. The reaction mixture was refluxed at 75–80°C for 72 h in an oil bath. The products obtained were filtered off, washed with methanol, and then dried in air and referred by R1-en, R2-en or R3-en, respectively (15).

Estimation of Amino Group Content

The concentration of amino group of resins was estimated using a volumetric method reported elsewhere (17). Forty milliliters of 0.05 M HCl solution was added to 0.1 g resin and conditioned for 15 h on a Vibromatic-384 shaker, Gallenkamb, England. The residual concentration of HCl was estimated through the titration against 0.05 M NaOH solution and phenolphthalein as indicator.

The number of moles of HCl interacted with amino groups and consequently the amino group concentration (in mmol/g of resin) was calculated by the following equation

$$\text{Concentration of } (\mathrm{NH_2}) \text{ group} = \frac{(\mathrm{M_1} - \mathrm{M_2}) \times 40}{0.1} (\text{mmol/g of resin}) \quad (1)$$

where M_1 and M_2 are the initial and final concentrations of HCl in mol/L.

Uptake Experiments using Batch Method

Preparation of Solutions

Stock solution (3.5×10^{-2} M) of $FeCl_3$ was prepared in distilled water and standardized using EDTA and sulfosalicylic acid as indicator (18). A stock solution of EDTA (1×10^{-3} M) was prepared and standardized against $MgSO_4 \cdot 7H_2O$ using Eriochrome Black-T (EBT) as indicator and ammonia/ammonium chloride as buffer (pH 9–10).

Iron Analysis

Iron analysis was carried out using a volumetric method reported elsewhere (18). 0.5 mL of iron solution was placed in a conical flask. 2 mL of HCl (0.5 M) was added to oxidize any species of Fe(II) to Fe(III). The acidity of the solution was then raised to pH 2–3 by adding 3 mL (5%) of sodium acetate. A 0.5 mL of sulphosalicylic acid (2%) was added where a violet red complex was formed. Then the solution was heated up to 40–50°C and titrated against EDTA (1×10^{-3}) until a pale yellow color appeared.

Effect of Contact Time on the Uptake

The effect of contacting time on the uptake of Fe(III) by resins was carried out by placing 0.1 g of dry resin in a flask containing 100 mL of Fe(III) solution at initial concentration of 3×10^{-2} M, pH 2.5 (natural). The contents of the flask were shaken on a vibromatic-384 shaker at 300 rpm and at temperature 28°C. Five milliliters of the solution was taken at different time intervals and then filtered off and used for determing the residual concentration of Fe(III). The adsorption data were treated according to the pseudo second order kinetics model

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right) t \quad (2)$$

where k_2 is the overall rate constant of the pseudo second order adsorption ($g \cdot mmol^{-1} \cdot min^{-1}$). The plot of t/q_t vs t gives a straight line with slope and intercepts equal $1/q_e$ and $1/k_2 q_e^2$, respectively.

Effect of pH on the Uptake

The uptake of Fe(III) by the investigated resins was studied at different pH values. The pH was adjusted using HCl and NaOH. 0.1 g of investigated resin was placed in a series of flasks. To each flask 100 mL of Fe(III) solution (3×10^{-2} M) was added. The contents of each flask were shaken for 150 min (for R1-en and R2-en) and 120 min (R3-en) on a vibrometric 384 shaker at 300 rpm and at temperature 28°C and desired pH. Then the resin was separated from the solution by filtration. Then the residual concentration of Fe(III) was estimated as above.

Adsorption Isotherms

Complete adsorption isotherms were carried out following the above procedures. The temperature was thermostatically kept at 28, 40, or 50°C and equilibrium time 150 min for (R1-en and R2-en) and 120 min for (R3-en). Later on, the residual concentration of Fe(III) was determined. The adsorption data were treated according to Langmuir equation

$$\frac{C_e}{q_e} = \frac{C_e}{Q_{max}} + \frac{1}{K_{ads}Q_{max}} \tag{3}$$

where C_e, is the equilibrium concentration of metal ions in solution (mmol/L), q_e is the adsorbed value of metal ions at equilibrium concentration (mmol/g), Q_{max} is the maximum adsorption capacity (mmol/g), and K_{ads} is the binding constant which is related to the energy of adsorption (L/mmol). Plotting C_e/q_e against C_e gives a straight line with a slope and an intercept equal $1/Q_{max}$ and $1/K_{ads}Q_{max}$, respectively. The thermodynamic parameters of the adsorption reaction were obtained from the treatment of K_{ads} values at different temperature according to van't Hoff equation (19)

$$\ln K_{ads} = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{4}$$

where ΔH° and ΔS° are enthalpy and entropy changes, R is the universal gas constant ($8.314\ J/mol \cdot K$) and T is the absolute temperature (K). Plotting $\ln K_{ads}$ against $1/T$ gives a straight line with slope and intercept equal to $-\Delta H^\circ/R$ and $\Delta S^\circ/R$, respectively. The Gibbs free energy of adsorption (ΔG°) at different temperatures was calculated using the following relation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{5}$$

Column Experiments

Column experiments were performed in a plastic column (length 3.6 cm, diameter 1 cm). A small piece of glass wool was placed at the bottom of the column and then a known quantity of the resin under investigation was placed in the column to give a bed heights of 1, 2 and 3 cm. The metal ion solution with initial concentration of 5×10^{-3} M was allowed to flow downward through the column at different flow rates (1, 2 and 3 mL/min). The outlet metal ion concentration was analyzed at different time intervals. The experiment was terminated when the concentration of the metal ion at the outlet of the column equals the initial concentration. The data obtained were processed according to Bed Depth Service Time (BDST) model, which gives the relation between bed height (Z) and saturation time (t_s) of the column (20)

$$t_s = \frac{N_o Z}{C_o v} - \frac{1}{K_a C_o} \ln\left(\frac{C_o}{C_t} - 1\right) \tag{6}$$

where C_t is the concentration of the metal ion at the saturation time just prior equalizing the initial concentration C_o (i.e. $C_o/C_t = 100/99$), N_o is the total adsorption capacity (moles of adsorbate per liter of adsorbent), v the linear velocity (cm/min), and K_a is the rate constant of sorption (L/mmol · min). On the other hand, the critical bed height (Z_o) can be calculated using Eq. (6)

$$Z_o = \frac{v}{K_a N_o} ln\left(\frac{C_o}{C_b} - 1\right) \tag{7}$$

where C_b is the breakthrough metal ion concentration (mmol/L). The value of (C_o/C_b) was taken as ratio of (100/1).

Resins Regeneration

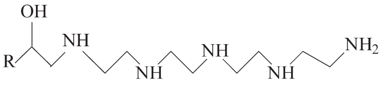
Resin regeneration was performed by placing 0.5 g of resin in the column and then loaded with an Fe(III) solution at initial concentration 5×10^{-3} M and flow rate 1 mL/min. After the maximum uptake reached in the first run, the resin was washed carefully by flowing distilled water through the column. The resin loaded by Fe(III) was then subjected for regeneration using 0.5 M thiourea acidified with 0.2 M HNO_3. After regeneration the resin was again carefully washed with distilled water to become ready for the second run of uptake. The efficiency of regeneration was calculated using the following equation

$$\text{Regeneration efficiency}(\%) = \frac{\begin{array}{c}\text{Total adsorption capacity}\\ \text{in the second run}\end{array}}{\begin{array}{c}\text{Total adsorption}\\ \text{capacity in the first run}\end{array}} \times 100 \tag{8}$$

Sorption/desorpion process was carried out for five cycles.

RESULTS AND DISCUSSIONS

The structure of the active moiety of the studied resins can be represented as follows



R= Resin matrix

The values of amino group concentration of R1-en, R2-en and R3-en resins were found to be 9.0, 11.2, or 17.0 mmol/g, respectively. The observed higher value of R3-en may be attributed to the formation of extended film of the resin over the magnetite particles (13).

Effect of pH

The higher uptake capacity of Fe(III) was achieved at pH 2.5. In such acidic medium the uptake may be explained to proceed through interaction between the aquo-iron complex with high positive charge $[Fe(H_2O)_4\ (OH)_2\ Fe\ (H_2O)_4]^{+4}$ and the resin active sites (nitrogen atom). It is noteworthy to refer that, the above positively charged (+4) aquo complex of iron competes and overcome the protonation of a lone pair of nitrogen atom by the protons in acid medium giving iron(III)-amine complex. This type of competition decreases at higher concentration of H^+ (lower pH) giving a lower uptake value (Fig. 1).

Adsorption Isotherms

Figure 2 show the adsorption isotherms of Fe(III) by R1-en, R2-en and R3-en at pH 2.5 and at different temperatures. At 28°C the maximum uptakes for R1-en, R2-en, or R3-en resins are 8.1, 9.2, or 13.0 mmol/g, respectively. Generally, the uptake values of Fe(III) for all studied resins were found to be higher than those early reported by others (8–10). The values of K_{ads} and Q_{max} for adsorption of Fe(III) on all resins were obtained and reported in (Table 1). The values of Q_{max} are comparable with the experimental ones. The values of K_{ads} follows the order R3-en > R2-en > R1-en, indicating different nature of interaction between metal ion and active sites. The suggested nature of interaction can be represented as shown in Scheme 1. This suggested mole ratio (N:Fe) was obtained from the matching between the experimentally obtained uptake values at for example 28°C and the expected ones from the amine content (Table 2). Both expected and experimental uptake values of R2-en and R3-en (with hydrophilic crosslinker) are closely similar to a great extent confirming the suggested nature of interaction in Scheme 1. The observed decrease in the uptake value of R1-en (with

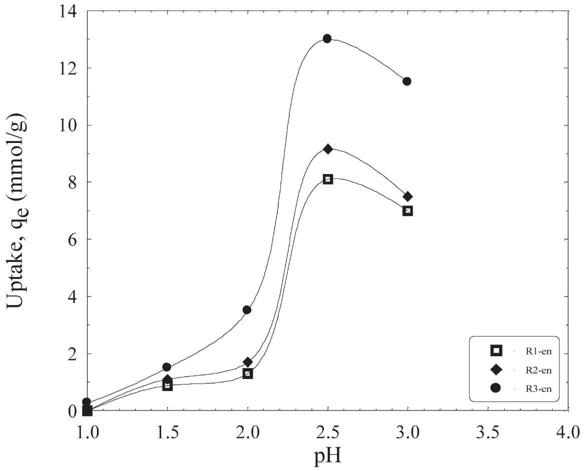


Figure 1. Effect of pH on the uptake of Fe(III) by resins at initial concentration of 3×10^{-2} M; contact time 150 min for (R1-en and R2-en) and 120 min for (R3-en) at temperature 28°C.

hydrophobic crosslinker) than the expected one can be attributed to the incomplete coverage of the active sites by large size dimeric aquo-iron(III) complex as a result of hindered diffusion inside the pores. This behavior confirms the effect of textural properties on the nature of binding as well as the uptake capacity. It is well known that the strength of binding increases as the number of chelating rings around metal ion increase (21). As shown in Scheme 1 no chelate ring was obtained in the case of R1-en, two chelate rings for R2-en and two fused chelate rings along with one chelate ring for R3-en. These different nature of interactions are reflected in the different values of K_{ads}.

The calculated values of ΔH° and ΔS° were obtained from (Fig. 3) and reported in (Table 3). The positive value of ΔH° indicates an endothermic adsorption process. The values obtained of ΔG° and TΔS° are given in (Table 3). It is seen that negative value of ΔG° increases as the temperature increases. This implies that, the adsorption becomes more favorable at higher temperature (22). The thermodynamic behavior may be attributed to the increased number of active sites as well as the partial dehydration of both metal ions and active sites at elevated temperature (23). At all temperatures, $|\Delta H^\circ| < |T\Delta S^\circ|$ indicating that the adsorption process is dominated by entropic rather than enthalpic changes (24).

Adsorption Kinetics

Figure 4 shows the adsorption time of Fe(III) as function of time at pH 2.5 (natural) and 28°C. It is seen that the equilibrium is 150 min for (R1-en and R2-en) and

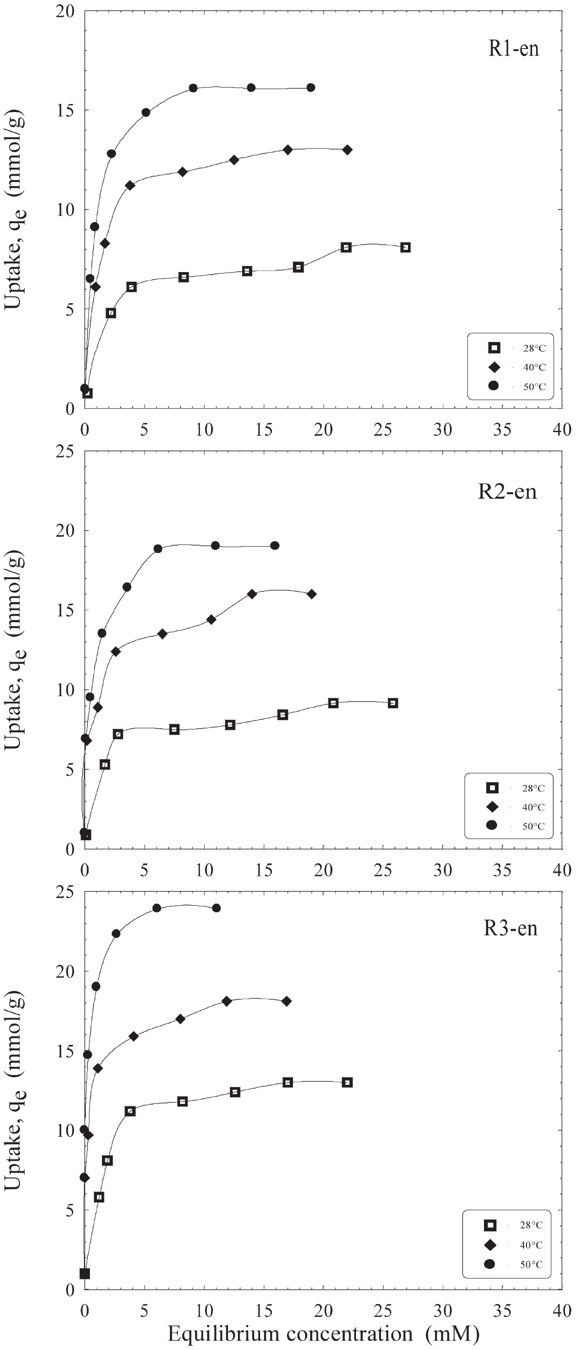
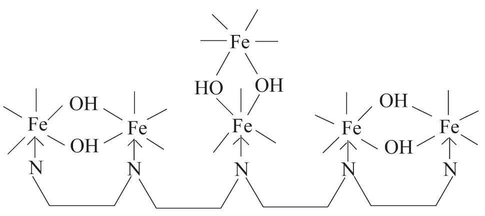


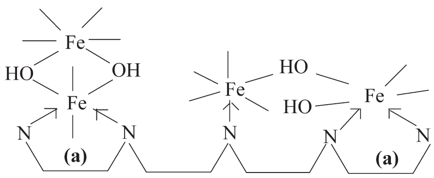
Figure 2. Adsorption isotherms of Fe(III) on resins at different temperatures; pH 2.5; contact time 2.5 h.

Table 1. Values of Langmuir parameters for the adsorption of Fe(III) on resins at different temperatures

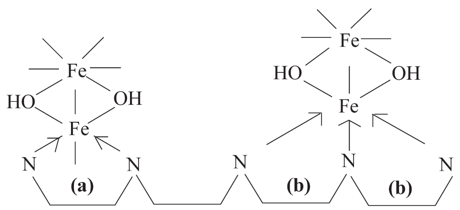
	R1-en				R2-en				R3-en			
	Q_{max} mmol/g		K_{ads}(L/mmol)	R^2	Q_{max} mmol/g		K_{ads}(L/mmol)	R^2	Q_{max} mmol/g		K_{ads}(L/mmol)	R^2
Temp (°C)	Exp.	Calc.			Exp.	Calc.			Exp.	Calc.		
28	8.1	8.5	0.43	0.9862	9.0	9.5	0.69	0.9945	13.0	13.5	1.09	0.9963
40	13	13.5	1.21	0.9993	16.0	16.2	1.74	0.9944	18.1	18.2	5.16	0.9987
50	16.2	16.7	1.6	0.9997	19.0	19.5	3.48	0.9982	23.9	24.0	11.28	0.9993



R1-en: 5 N (donor atoms) interact with 5 Fe(III); no formation of chelate rings.



R2-en: 5 N (donor atoms) interact with 3 Fe(III); formation of two chelate rings of type (a).



R3-en: 5 N (donor atoms) interact with 2 Fe(III); formation of one chelate ring of type (a) and two fused chelate rings of type (b).

Scheme 1. Proposed modes of interactions between the resin active sites and Fe ions.

120 min for (R3-en). Within the first 15 min, the uptake of Fe(III) by R1-en, R2-en, and R3-en resins reached 4.2, 5.6 and 8.2 mmol/g, respectively. These values represent about 51.3, 60.5, and 63.0% from the total uptake values of R1-en, R2-en and R3-en, respectively. The pseudo second order rate constant, k_2 and

Table 2. Expected values of uptake at 28°C according to the suggested mode of interaction between Fe(III) and active sites

Resin code	Suggested mole ratio of (N:Fe)	Amine content (mmol/g)	Expected uptake (mmol/g)	Experimental uptake (mmol/g)
R1-en	5:6	9.0	10.8	8.1
R2-en	5:4	11.2	9.0	9.0
R3-en	5:4	17.0	13.6	13.0

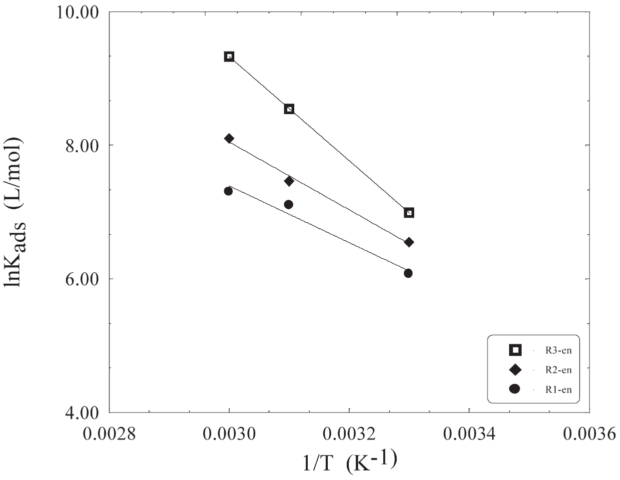


Figure 3. Van't Hoff plots for adsorption of Fe(III) on resins.

equilibrium sorption capacity, q_e, were calculated and reported in (Table 4). Obviously, a satisfactory agreement was obtained between the calculated and the experimental values of q_e. This implies that the adsorption process proceeds according to pseudo second order kinetics and depends upon both metal ion concentration and the textural properties of the resin. It is also seen that the values of k_2 follow the order R3-en > R2-en > R1-en. This could be attributed to the presence of hydrophilic crosslinker MBA in R2-en and R3-en (along with embedded magnetite particles) which enhances the interaction between hydrated metal ions and active sites giving a faster rate of uptake. On the other hand, the presence of oxide particles makes the resin to be stretched as a thin film over the oxide particles giving a higher concentration of active sites as well as lower diffusion properties. This behavior together with the hydrophilicity of MBA reflects the faster rate of R3-en compared to R1-en and R2-en.

COLUMN EXPERIMENTS

Effect of Flow Rate

Breakthrough curves of the studied resins towards adsorption of Fe(III) at different flow rates (1, 2, and 3 mL/min) and a fixed bed height indicate that at the same bed height and flow rate, the breakthrough time follows the order R3-en > R2-en > R1-en. For example, for the flow rate of 1 mL/min and bed height of 2 cm, the breakthrough time are 310, 430, and 840 min for R1-en, R2-en and R3-en, respectively. This behavior of breakthrough time values is consistent with the active site concentration on the resins. It is also noticed that breakthrough and exhaustion time of all resins occur faster at

Table 3. Thermodynamic parameters of adsorption of Fe(III) on resins

Resin	ΔH° (kJ/mol)	ΔS° (kJ/mol . K)	Temperature (K)	ΔG° (kJ/mol)	TΔS° (kJ/mol)
R1-en	35.30	0.16	301	−12.9	48.2
			313	−14.8	50.1
			323	−16.4	51.7
R2-en	42.20	0.19	301	−15.0	57.2
			313	−17.3	59.5
			323	−19.2	61.4
R3-en	64.80	0.27	301	−16.5	81.3
			313	−19.7	84.5
			323	−22.4	87.2

higher flow rate. This can be explained on the basis of the amount of metal ion solution passed over the resin. In the case of higher flow rate large amount of metal ion solution passes achieving early saturation of active sites.

Effect of Bed Height

The effect of bed height (1, 2, and 3 cm) on the breakthrough time at constant flow rate (1 mL/min) was studied. It is seen that for all resins as the bed height increases the breakthrough time increases. For example the breakthrough time of R1-en were found to be 140, 310, and 695 min at bed heights of 1, 2, and 3 cm, respectively. On the other hand, at bed height 1 cm and flow rate 1 mL/

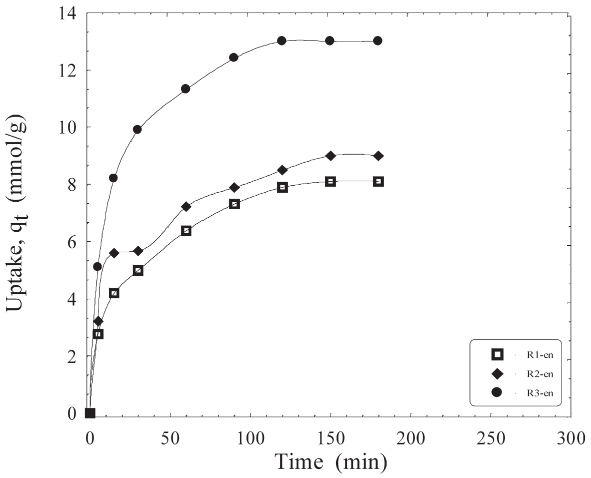


Figure 4. Uptake of Fe(III) by resins as a function of time at 28°C; pH 2.5; initial concentration 3×10^{-2} M.

Table 4. Pseudo second order adsorption parameters at initial concentration 3×10^{-2} M of Fe(III) and temperature 28°C

Resin code	q_e (exp) (mmol/g)	k_2 (g/mmol · min)	q_e (calc) (mmol/g)	R^2
R1-en	8.1	0.088	8.6	0.9954
R2-en	9.0	0.090	9.5	0.9938
R3-en	13.0	0.097	13.5	0.9991

min, the breakthrough time of the investigated resins were found to be 140, 180 and 240 min for R1-en, R2-en and R3-en, respectively. This behavior can be again related to the active site concentrations. The values of N_o were calculated from the slope of the BDST plots, (Fig. 5). The calculated values of N_o for the resins were found to be 8.05, 9.03 and 12.88 mmol/g for R1-en, R2-en and R3-en, respectively. These values are comparable with the experimental values of Q_{max}, (Table 1). This indicates the validity of BDST model for the investigated resins. The values of K_a were also calculated from the intercept of BDST plots. The observed values of K_a are 18.38, 22.97, and 70.69 L/mol · min for R1-en, R2-en and R3-en, respectively. This confirms the above results obtained from batch method about the kinetics of adsorption of Fe(III) by the investigated resins (The rate of adsorption follows the order R3-en > R2-en > R1-en). The calculated values of the critical bed height Z_o are 0.04, 0.03, and 0.007 cm for R1-en, R2-en, and R3-en, respectively. These very small values of critical bed height indicate the higher efficiency of the investigated resins towards the removal of Fe(III).

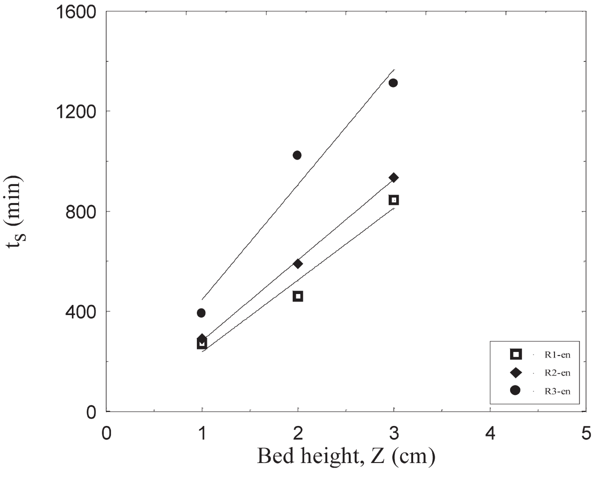


Figure 5. Variation of saturation time with the bed height of resin.

RESIN REGENERATION

Regeneration of the resins was carried out using 0.5 M thiourea acidified with 0.2 M HNO_3. The regeneration efficiency was found to be 91.5%, 89.6%, and 80.3% for R1-en, R2-en, and R3-en, respectively. The observed values of regeneration efficiency are related to the langmuir binding constant values, (Table 1). As the binding constant value increases the amount of metal eluted decreases. This also confirms the suggested different mode of binding of the resins with Fe(III). The regeneration process was repeated for five cycles without considerable changes in the durability of the resins.

CONCLUSIONS

Glycidyl methacrylate resins with hydrophobic DVB (R1) and hydrophilic MBA (R2) crosslinker were prepared. The magnetic beads of these resins (R3) were obtained. The resins were loaded by tetraethylenepentamine chelating moiety to give the corresponding amine containing resins R1-en, R2-en, and R3-en. The maximum uptake value as well as the rate of sorption of the resins towards Fe(III) follows the order R3-en $>$ R2-en $>$ R1-en. The adsorption process was found to be endothermic and proceeded according to pseudo second order kinetics. Column studies indicated that the critical bed heights (Z_o) are 0.04, 0.03, and 0.007 cm for R1-en, R2-en, and R3-en, respectively. The regeneration of the resins was performed using thiourea acidified with HNO_3 without loss of durability over five cycles. The regeneration efficiency was found to be in the range 80.3–91.5%.

REFERENCES

1. Ali, A., Shawky, H., Abd El Rehim, H., and Hegazy, E. (2003) Synthesis and characterization of PVP/AAc copolymer hydrogel and its applications in the removal of heavy metals from aqueous solution. *Europe. Polym. J.*, 39: 2337–2344.
2. Vaaramaa, K. and Lehto, J. (2003) Removal of metals and anions from drinking water by ion exchange. *Desalination*, 155: 157–170.
3. Gurnule, W.B., Juneja, H.D., and Paliwal, L.J. (2002) Ion-exchage properties of a salicylic acid-melamine-formaldehyde terpolymer resin. *React. & Funct. Polym.*, 50: 95–100.
4. Lasanta, C., Caro, I., and Perez, L. (2005) Theoretical model for ion exchange of iron(III) in chelating resins: application to metal ion removal from wine. *Chem. Eng. Sci.*, 60: 3477–3486.
5. Benitez, P., Castro, R., and Barroso, C.G. (2002) Removal of iron, copper and manganese from white wines through ion exchange techniques: effects on their

organoleptic characteristics and susceptibility to browning. *Anal. Chim. Acta.*, 458: 197–202.

6. Feng, M., Does, L.V., and Bantjes, A. (1995) Iron removal from milk and other nutrient media with a chelating resin. *J. Dairy Sci.*, 78: 55–61.
7. Lohan, M.C., Isias, A.M.A., Franks, R.P., and Bruland, K.W. (2005) Determination of iron and copper in seawater at pH 1.7 with a new commercially available chelating resins. *Anal. Chim. Acta.*, 530: 121–129.
8. Senkal, B.F. and Bicak, N. (2001) Glycidyl methacrylate based polymer resins with diethylene triamine tertaacetic acid functions for efficient removal of Ca(II) and Mg(II). *React & Funct. Polym.*, 49: 151–157.
9. Roy, P.K., Rawat, A.S., Choudhary, V., and Rai, P.K. (2004) Synthesis and analytical application of a chelating resin based on a crosslinked styrene/malic acid copolymer for the extraction of trace metal ions. *J. Appl. Polym. Sci.*, 94: 1771–1779.
10. Gurnule, W.B., Rahangdale, P.K., Paliwal, L.J., and Kharat, R.B. (2003) Synthesis, characterization and ion exchange properties of 4-hydroxyacetophenone, biuret and formaldehyde terpolymer resins. *React & Funct. Polym.*, 55: 255–265.
11. Yamaura, M., Camilo, R.L., and Felinto, M.C.F. (2002) Synthesis and performance of organic-coated magnetite particles. *J. Alloys Compd.*, 344: 152–156.
12. Atia, A.A., Donia, A.M., and Yousif, A.M. (2005) Comparative study on the recovery of silver(I) from aqueous solutions using different chelating resins derived from glycidyl methacrylate. *Appl. Polym. Sci.*, 97 (3): 806–816.
13. Atia, A.A., Donia, A.M., and Shahin, A.E. (2005) Studies on the uptake behavior of a magnetic Co_3O_4-containing resin for Ni(II), Cu(II) and Hg(II) from their aqupus solutions. *Sep. Purif. Technol.*, 46: 208–213.
14. Donia, A.M., Atia, A.A., El-Boraey, H.A., and Mabrouk, D. (2006) Uptake studies of copper(II) on glycidyl methacrylate chelating resin containing Fe_2O_3 particles. *Sep. Purif. Technol.*, 49: 64–70.
15. Atia, A.A., Donia, A.M., and Yousif, A.M. (2007) Effect of chain length of aliphatic amines immobilized on a magnetic glycidyl methacrylate resin towards the uptake behavior of Hg(II) from aqueous solutions. *Sep. Sci. & Technol.*, 42: 403–420.
16. Sun, Y.K., Ma, M., Zahag, Y., and Gu, N. (2004) Synthesis of nanometer-size maghemite particles from magnetite. *Coll. & Surf. A*, 245: 15–19.
17. Atia, A.A., Donia, A.M., Abou-Ei-Enein, S.A., and Yousif, A.M. (2003) Studies on uptake behaviour of copper(II) and lead(II) by amine chelating resins with different textural properities. *Sep. & Purif. Technol.*, 33: 295–301.
18. West, T.S. (1969) *Complexmetry with EDTA and Related Reagents*, 3rd edn.; BDH Chemicals Ltd.
19. Boonamnuayvitaya, V., Chaiya, C., Tanthapichakoon, W., and Jarudilkkul, S. (2004) Removal of heavy metals by adsorbent prepared from pyrolyzed coffee residues and clay. *Sep. & Purif. Technol.*, 35: 11–22.
20. Vijayaaraghavan, K., Jegan, J., Palanivelu, K., and Velan, M. (2005) Biosorption of cobalt(II) and nickel(II) by seaweeds: batch and column studies. *Sep. & Purif. Technol.*, 44/1: 53–59.
21. Nicholls, D. (1974) *Complex and First-Row Transition Elements*, 1st edn.; Macmillan Education: Great Britain, London.
22. Tahir, S.S. and Rauf, N. (2003) Thermodynamic studies of Ni(II) adsorption onto bentonite from aqueous solution. *J. Chem. Therm.*, 35: 2003–2009.

23. Bicak, N., Senkal, B.F., and Melekaslan, D. (2002) Poly (styrene sulfonamides) with EDTA-like chelating groups for removal of transition metal ions. *J. Appl. Polym. Sci.*, 77: 2749–2755.
24. Mpofu, P., Mensah, J.A., and Ralston, J. (2004) Temperature influence of nonionic polyethylene oxide and anionic polyacrylamide on flocculation and dewatering behavior of kaolinite dispersions. *J. Colloid & Interf. Sci.*, 271: 145–156.