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Adsorptive features of poly(glycidyl methacrylate-*co*-hydroxyethyl methacrylate): effect of porogen formulation on heavy metal ion adsorption

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Abstract Preparation of crosslinked copolymer beads based on glycidyl methacrylate (GMA), 2-hydroxyethyl methacrylate (HEMA), and divinyl benzene for the use of heavy metal adsorption has been investigated. In our study, a series of porous copolymer beads were synthesized by suspension polymerization in the presence of porogens, 1-dodecanol, toluene, and heptane at different dilutions. The effect of the porogens on the surface appearance and the porous structure of copolymer beads was studied by scanning electron microscopy and BET method. Diethylene triamine chelating copolymers were obtained through a reaction between amine groups of diethylene triamine and epoxide pendant groups of GMA. Adsorption isotherm and quantitative analysis for adsorption capacity involving copper, chromium, manganese, cadmium, iron, and zinc ions were investigated using atomic absorption spectrophotometer. The adsorption was a function of types of metal ions, adsorption time, and solution properties including pH and metal concentration. Adsorption equilibrium was achieved in approximately 50 min with a maximum adsorption capacity at pH 5.0. The Langmuir isotherm was found to be well fitted on the adsorption behavior. The maximum metal adsorption capacities in single ion solution in mole basis were in the order Cu(II) > Cr(VI) > Mn(II) > Zn(II) > Cd (II) > Fe(II). It was found that introducing porogen in the polymerization mixture produced the copolymer beads with better adsorption capacity. The maximum Cu(II) adsorption capacity of chelating poly(GMA-*co*-HEMA) beads were 1.35 mmol/g (85.79 mg/g) measured from the beads prepared in the presence of 1-heptane with 50% dilution. Consecutive adsorption–desorption experiments showed that crosslinked poly(GMA-*co*-HEMA) micro-beads can be reused almost without any change in the adsorption capacity.

Introduction

Heavy metal ions are well known as non-biodegradable and environmental toxins because of their effects to plants, animals, and human beings. They can cause mental retardation, brain damage, and harmful diseases for human. Some ions are reported as a powerful carcinogen even at very low concentrations [1–4]. In the recent years, considerable studies have been performed for the development of various methods for the removal of toxic metals from aqueous solution such as ion exchange, neutralization, reverse osmosis, precipitation, solvent extraction, and adsorption. Most of these processes have disadvantages of high operation cost arising from the consumption of chemicals or electricity and technical problems including long time extraction, complex treatment procedures, and the production of toxic sludge that is difficult for further disposal. Among these processes, adsorption has been shown to be an economically possible alternative due to availability of different adsorbents, easy handling, and high efficiency in removing heavy ions especially at medium to low ion concentrations from wastewaters [5–7]. Considerable studies were performed in recent years for the development of polymeric adsorbents [8–11]. These materials have several distinct advantages. The availability of chemical functionalities, the easy preparations, and the

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control of desired size allow them to find a great application as adsorbents. In addition, functional polymer beads with porous structure are also widely used as precursors for the preparation of various types of ion-exchangers, supports for chromatographic separation media, and solid supports for organic synthesis and catalyst systems [12]. In order to ensure excellent performance, these polymer beads should possess the following characteristics [13]: (1) chemical stability in various solvents to provide rigid network structure in both swollen and dry state, (2) suitable particle size, (3) adequate mechanical strength to ensure repeated use capability, and (4) large specific surface area being suitable for adsorption, substrate, and product transport with the least diffuse restriction. These characteristics are consequence of the chemical structure and morphological properties which can be controlled by synthesis parameters, such as crosslinking degree. For the last requirement, the formation of porous structure in microbead polymer is generally known to provide high specific area and accessibility into the polymeric network. Porous polymer beads have been prepared by suspension polymerization of vinyl monomer and crosslinking agent in the presence of an inert diluent or a porogen [14]. Usually, the porogen is a low molecular weight substance that acts as a good solvent for monomer phase, but it rather behaves as a poor solvent for the polymer network and does not react with monomers. During the process of polymerization, crosslinking and phase separation occur, as a result a formation of porous structure polymer can be created depending on type and concentration of porogen, monomer, crosslinking agent, temperature, and stirring speed. After polymerization, the porogen can be easily extracted from the resulting polymer beads [15–18].

A number of research papers dealing with the use of poly(glycidyl methacrylate) based copolymers as functional adsorbents have been published [19–28]. These copolymers have received attentions because the epoxy functional group in glycidyl methacrylate (GMA) monomer can be chemically modified to suit variety of applications [29–31]. Although significant progress has been made on the study of GMA-based copolymers for the use as functional adsorbents, much less has been published about the influence of varying parameters of the concentrations and types of porogens on the surface appearance and adsorption behavior of these copolymers.

The aim of the present investigation was to develop heavy metal adsorbents in spherical bead form. For this purpose, we have prepared porous crosslinked poly(GMA-*co*-HEMA) beads by suspension polymerization and chemically modified the bead with an amine-containing reagent. To synthesize the efficient adsorbents, the attention was paid to the roles of different porogens on the bead morphology, such as surface area, pore size, and pore volume. The influence of adsorption conditions, such as concentration of metal ions, pH, and time on adsorption characteristics of the beads was investigated. Then, these parameters were optimized to gain the maximum adsorption capacity.

Experimental

Materials

The following chemicals were obtained from commercial sources. GMA, 2-hydroxyethyl methacrylate (HEMA), divinyl benzene (DVB), benzoyl peroxide (BPO), and diethylene triamine (DETA) were supplied from Merck. Toluene, heptane, and 1-dodecanol from Fisher Scientific were used as porogens. Sodium chloride, sodium hydroxide, and magnesium chloride were all of reagent grade. Copper nitrate trihydrate, manganese sulfate, zinc chloride, iron sulfate, cadmium nitrate tetrahydrate, and potassium dichromate (all from Aldrich) were used for the adsorption studies.

Preparation of poly(GMA-*co*-HEMA) beads

The comonomers, GMA and HEMA were copolymerized in suspension using BPO and DVB as an initiator and a crosslinker, respectively. Heptane, 1-dodecanol, or toluene was included in the recipe as a porogen. Table 1 shows the standard recipe and polymerization condition to prepare copolymer beads by suspension polymerization in a three-necked, round-bottom glass reactor fitted with a mechanical stirrer, a reflux condenser, and a nitrogen gas inlet tube. The composition of organic phase and its content were varied according to the data given in Table 2. Suspension was achieved by stirring the organic and aqueous phases under an atmosphere of nitrogen for 30 min, with the stirrer blade kept at a constant distance from the bottom of the reactor. The stirring speed was fixed during the polymerization, which was carried out at 85 °C for 7 h using a thermostated water bath. The resulting copolymer beads

Table 1 Standard recipe for poly(GMA-*co*-HEMA) microsphere preparation

Organic phase	Aqueous phase
60% mole GMA	8.6 g $MgCl_2 \cdot 6H_2O$
30% mole GMA	90 g 20%NaCl
10% mole DVB	38 mL, 5 M NaOH
1% mole BPO of monomer	
25%(v/v) porogen of monomer	
Total volume of monomer = 30 mL	

Table 2 Experimental conditions for the synthesis of poly(GMA-*co*-HEMA) beads

Exp#	Monomers in the feed (mol%)			Porogen	Porogen (vol%)	Stirring speed (rpm)
	GMA	HEMA	DVB			
Effect of stirring speed during suspension polymerization						
1	60	30	10	–	–	270
2	60	30	10	–	–	300
3	60	30	10	–	–	330
Effect of crosslinking degree						
2	60	30	10	–	–	300
4	50	25	25	–	–	300
5	33	17	50	–	–	300
6	17	8	75	–	–	300
Effect of nature and amount of porogen						
7	60	30	10	1-dodecanol	25	300
8	60	30	10	1-dodecanol	50	300
9	60	30	10	Toluene	25	300
10	60	30	10	Toluene	50	300
11	60	30	10	Heptane	25	300
12	60	30	10	Heptane	50	300

were then washed, sequentially with water, methanol, and acetone to remove porogens and any unreacted monomer. The beads were then dried under vacuum.

Preparation of chelating poly(GMA-*co*-HEMA) beads

The amination of poly(GMA-*co*-HEMA) with DETA was prepared using copolymer beads with sizes in the range of 710–500 μm. One gram of the beads was added to 5 mL of amine-containing reagent and 5 mL of 3.7 M NaOH. The mixture was kept at 70 °C for 5 h with gentle stirring. The obtained product, namely poly(GMA-*co*-HEMA)-DETA, was filtrated, washed with distilled water, ethanol, and dried.

Characterization of the beads

Average size and size distribution of the beads

The copolymer beads were fractionated by sieve analysis using 106, 212, 300, 425, 500, 600, 710, and 850 μm Tyler standard sieves to yield eight fractions of the beads.

Surface area measurement

A volumetric sorption analyzer (Quantachrome) was used to determine the specific surface area, pore size, and pore volume of the beads through nitrogen adsorption. The samples were first degassed at 40 °C with nitrogen before the analysis. The specific surface areas of dry resin were determined from N_2 adsorption isotherm using the Brunauer–Emmett–Teller (BET) method. The total pore volume and the average pore diameter of the beads were derived from the Barrett–Joyner–Halenda (BJH) model.

FT-IR study

Fourier transform infrared spectroscope (FT-IR, Perkin Elmer system 2000) was used to characterize the functional groups of the beads and to confirm the effectiveness of amine grafting on the copolymer beads. The dry samples were blended with KBr, ground, and pressed into disks. The FT-IR spectra were then recorded.

Swelling ratio

The swelling behavior of the beads was determined in distilled water and toluene. The experiment was conducted as follows. Dry beads were placed in a 50 mL vial containing solvent at room temperature. The bead sample was taken out from the solvent, wiped with a filter paper, and weighed. The swelling ratio was calculated by the following expression:

$$\text{Swelling ratio} = [(W_s - W_0)/W_0] \times 100 \qquad (1)$$

where W_0 and W_s are the weights of beads before and after uptake of solvent, respectively.

SEM analysis

The morphologies of the non-porous and porous microbeads were obtained with a scanning electron microscope (SEM, LEO 1450VP). Samples were adhered onto the conductive tapes on the stubs and coated with gold before SEM observation.

Adsorption–desorption experiments

The metal ion adsorption from aqueous solution on the porous and non-porous chelating copolymer beads was investigated in a batch system. Effects of initial ion concentration, medium pH, and time on the adsorption capacity were investigated. The initial concentration of ion was varied between 0 and 900 mg/L. A series of metal solutions in the pH range 1–5 were prepared with pH being adjusted with HNO_3 or NaOH at the beginning of the experiment.

A fixed amount of copolymer beads (0.5 g) and heavy metal ion solution (100 mL) were mixed and stirred with a magnetic stirrer at room temperature. After a desired adsorption time, the concentration of metal ions in solution was measured by a flame atomic adsorption spectrophotometer (FAAS, Perkin Elmer 3300). The experiments were performed in replicates of three, and the results given were the average values. The amount of metal ions adsorbed per unit mass of the beads (q_e, mg/g) was evaluated by the following expression:

$$q_{\mathrm{e}} = \frac{(C_0 - C) \times V}{m} \tag{2}$$

where C_0 and C are the concentrations of the metal ions in the aqueous solution (mg/L) before and after the interaction with copolymer beads for a certain period of time, respectively; V is the volume of solution (L); and m is the weight of the copolymer (g).

Desorption of metal ions was performed in 50 mL of a 1% HNO_3 solution for 1 h. The metal ion loaded copolymer (0.1 g) was placed in the elution medium and stirred with a magnetic stirrer at room temperature. After treatment with the eluent, the beads were washed with distilled water and reused in the consecutive adsorption–desorption cycles. The desorption efficiency (%) was calculated from the following equation:

$$\text{Desorption efficiency}(\%) = \frac{\text{ions desorbed into the eluent}}{\text{ions adsorbed on the beads}} \times 100 \tag{3}$$

Results and discussion

Properties of the poly(GMA-*co*-HEMA) beads

Effect of stirring speed on the bead size distribution

Bead size distribution of the spherical copolymer was analyzed by the use of sieve and the weight of fractions obtained. The data are an important factor since the size of the beads influences the surface area and therefore adsorption capacity of the bead. Stirring speed in suspension is one of the primary factors affecting a heterogeneous polymerization system. The stirring speed can be used to control the size of monomer droplets. As a result, it directly influences the size and particle size distribution of copolymer beads. In this study, three different stirring speeds (270, 300, and 330 rpm) were used to prepare copolymers from reaction mixtures containing GMA: HEMA:DVB in 60:30:10 mole ratio. As expected, the size of the beads decreased with increasing stirring speed (see Fig. 1). To study the influence of the type and amount of porogens on porous structure, the 300 rpm stirring speed was used to stabilize droplets of organic phase in the reaction mixtures, and the beads in the size range of 710–500 μm were used to evaluate the specific surface, pore volume, and porous size.

Effect of DVB content on the swelling property

In preparation of copolymer beads, incorporation of crosslinking agent could both enhance the stability of macroporous structure and decrease swelling of the bead in adsorption medium [28]. The efficient beads for adsorption should be capable of swelling in aqueous solutions (waste water system), enabling the diffusion and transfer of ions towards adsorption sites and should be inert for solvents that might be contaminated with the solution [32]. In this study, the mole ratio between GMA and HEMA in organic phase was kept constant at 2:1. The effect of DVB content on the swelling ratio of copolymers is shown in Fig. 2. The swelling ratio decreased with increasing the crosslinking degree. The highest equilibrium swelling ratio was measured from the beads prepared with 60:30:10 mole ratio of GMA:HEMA:DVB. This sample also contained high content of epoxy groups which would be applied as adsorption sites for metal ions. As to the above discussion, the copolymer prepared from polymerization mixture containing 60 mol% GMA would be used for further studies on adsorption capacity.

Effect of porogen on the porous structure

In this study, we are particularly interested in surface area and porosity because adsorption of metal ions occurs at surface of the beads. As a consequence, the surface properties have much influence on the binding behavior. Increasing specific surface area and pore volume should facilitate the binding between the beads and the metal ions. The role of different types and amounts of porogens on the bead morphology was investigated. The SEM images shown in Fig. 3 suggest that the surface characteristics of

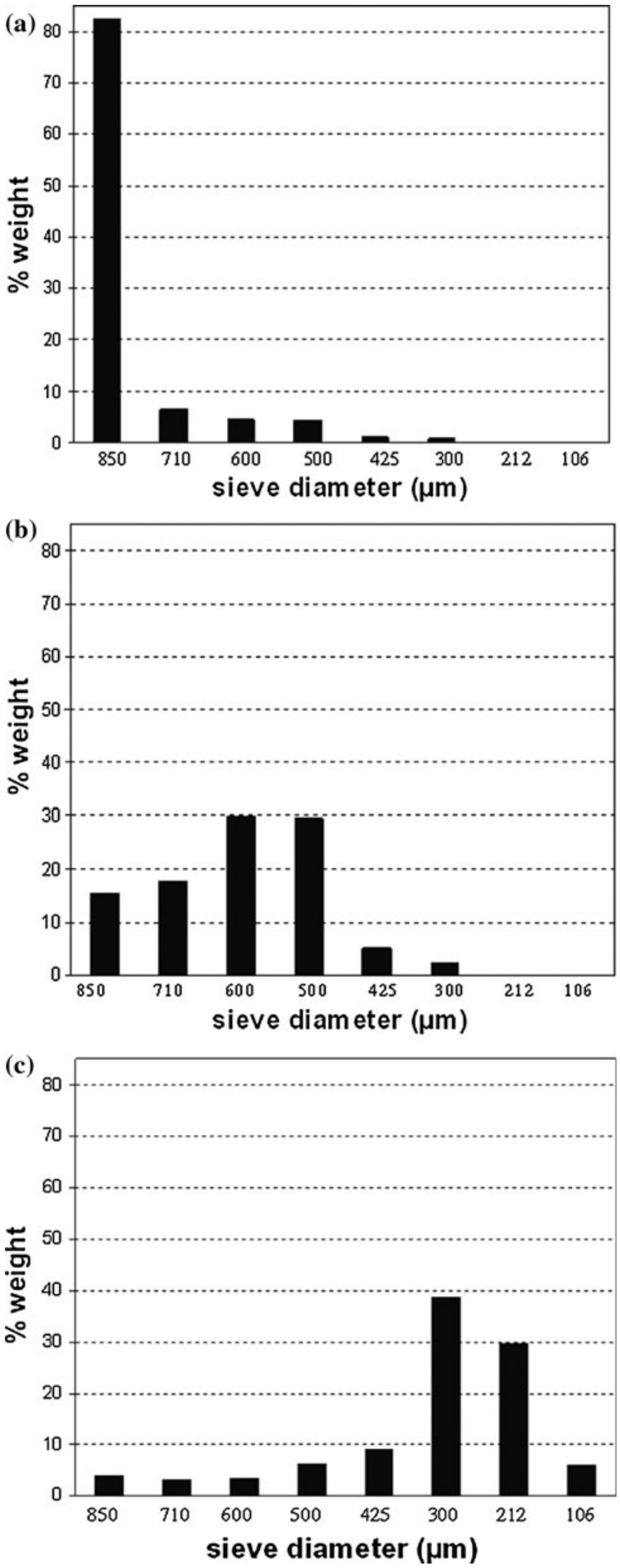


Fig. 1 Influence of the stirring speed during polymerization on the particle size distribution of poly(GMA-*co*-HEMA) beads; **a** 270 rpm; **b** 300 rpm, and **c** 330 rpm

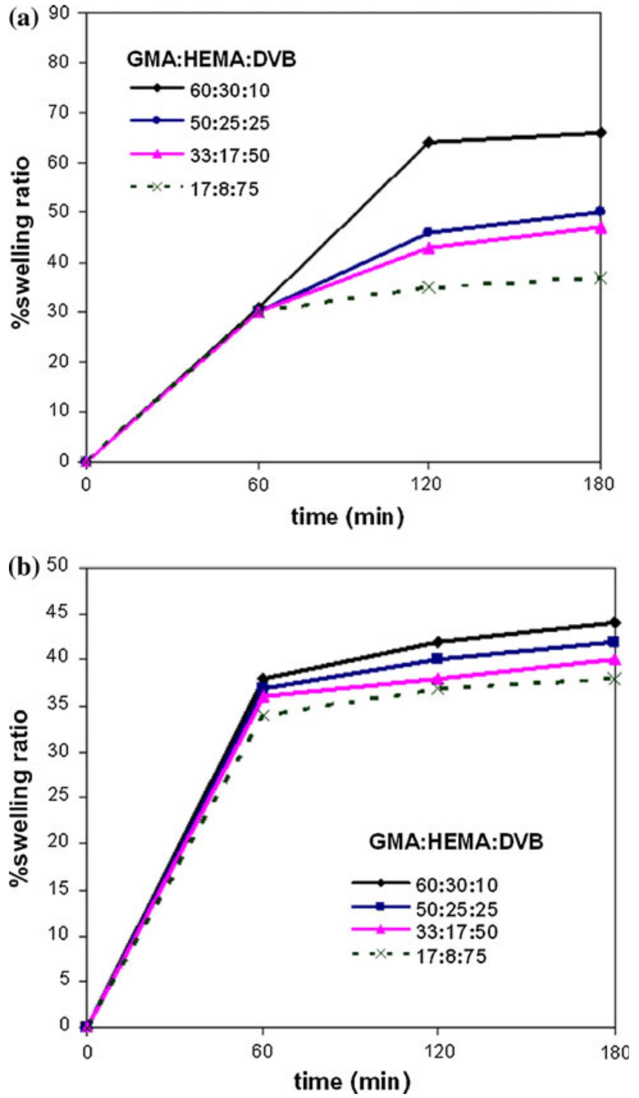


Fig. 2 Swelling ratios of poly(GMA-*co*-HEMA) beads in **a** water and **b** toluene

the network copolymers and their porous structure varied considerably depending on the organic phase composition. Without an addition of porogen, the bead was spherical with smooth surface, Fig. 3. Other samples exhibit different structures. The SEM micrographs of the beads in Figs. 4, 5, and 6 indicate that they possess spherical structure with rough surfaces and porous structures. Among the three types of porogen used in this study, heptane was found to be a good porogen for poly(GMA-*co*-HEMA). Porous structure of the beads prepared with 50% heptane can be clearly seen on its surface and cross-sectioned images, Fig. 6.

According to the results from surface area measurement, different porogens were found to leave different pore

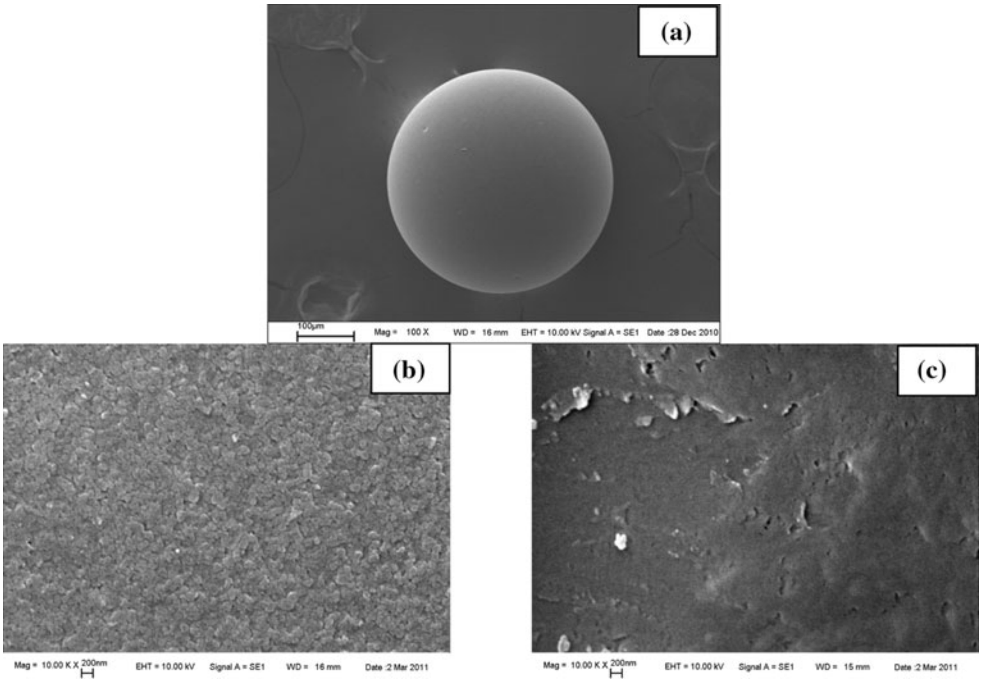


Fig. 3 SEM photographs of the beads, Exp#2, nonporous: **a** surface 100×, **b** surface 10,000×, and **c** cross-sectioned 10,000×

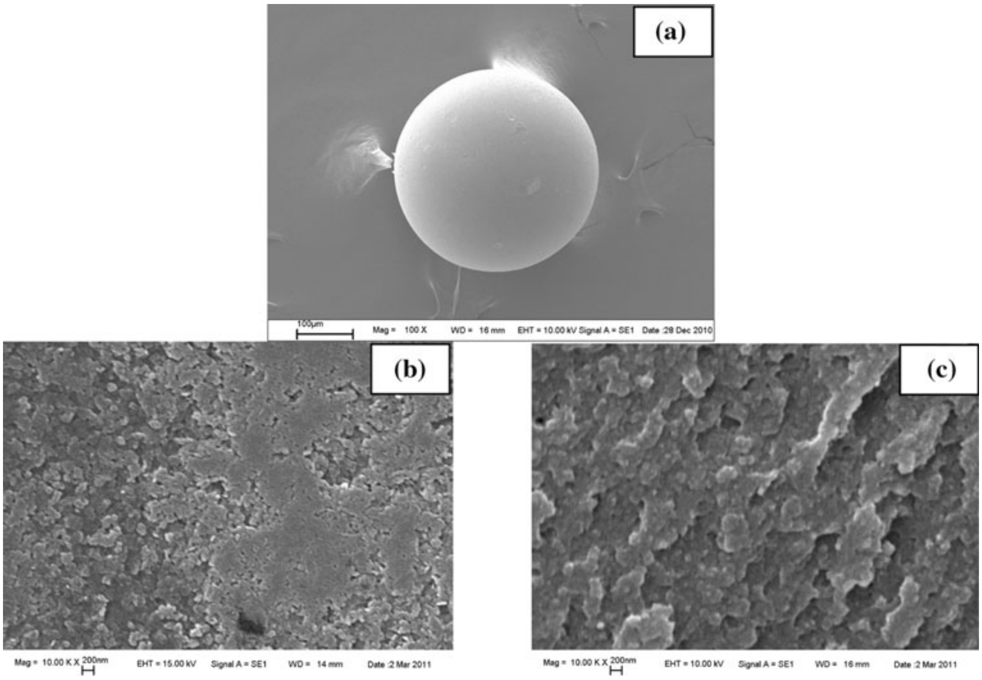


Fig. 4 SEM photographs of the beads, Exp#10, 50% toluene: **a** surface 100×, **b** surface 10,000×, and **c** cross-sectioned 10,000×

volumes, and hence surface areas (Fig. 7). These results were in accordance with the literature on related porous copolymers [12, 18]. Heptane was the most effective among the porogens used in this study. The porous characteristic of the copolymer prepared from a monomer phase composed of heptane can be attributed to the non-solvating property of heptane. The pore volume, pore diameter, and specific surface area of the beads increased with increasing the proportion of heptane in polymerization mixture. The specific surface areas of 0.13, 0.63, and 0.95 m^2/g were measured from the beads prepared with addition of 0, 25, and 50% heptane, respectively.

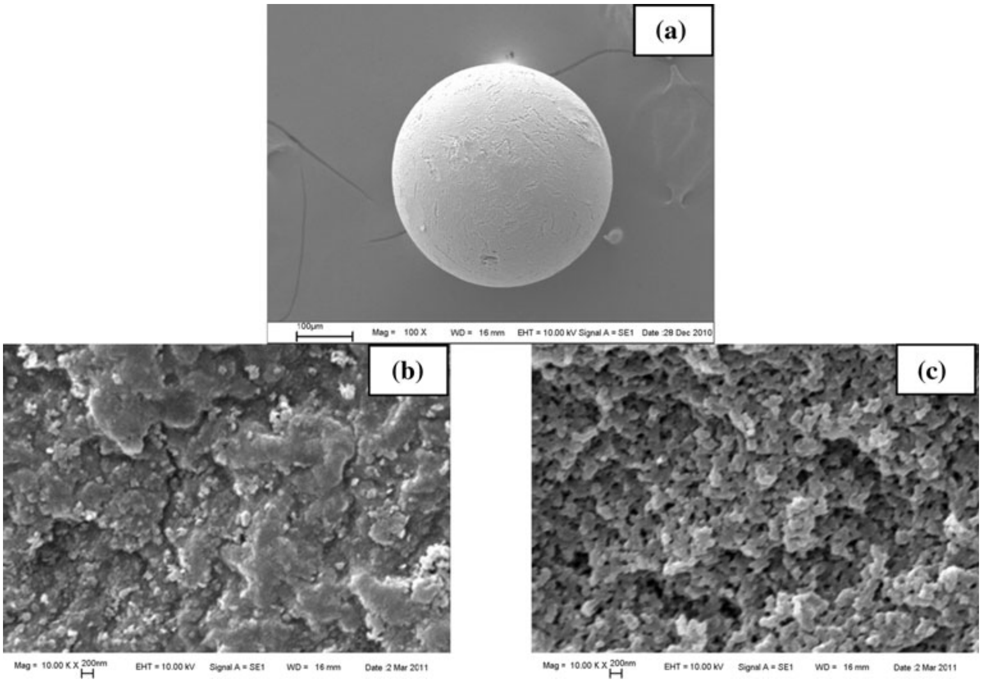


Fig. 5 SEM photographs of the beads, Exp#8, 50% dodecanol: **a** surface 100×, **b** surface 10,000×, and **c** cross-sectioned 10,000×

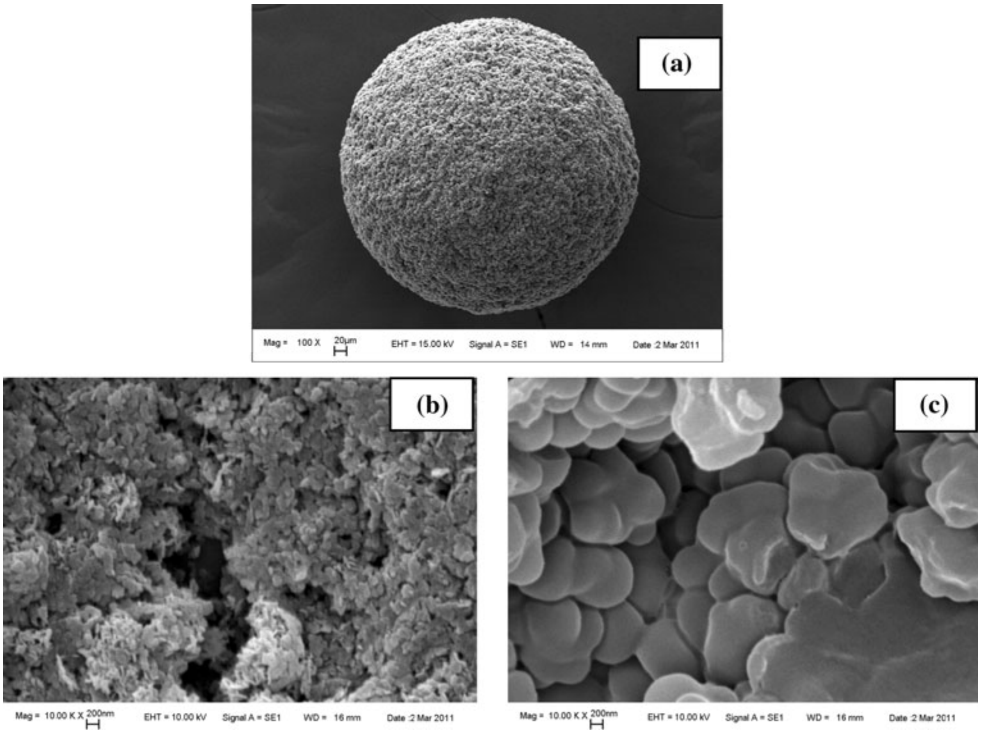


Fig. 6 SEM photographs of the beads, Exp#2, 50% heptane: **a** surface 100×, **b** surface 10,000×, and **c** cross-sectioned 10,000×

The corresponding pore size and volume also showed a similar pattern. According to our experience, the spherical morphology was lost when the content of heptane was increased to 100% dilution. Moreover, the beads were fragile and deficient for adsorption application.

Characterization of amine-containing poly(GMA-*co*-HEMA) beads

The chelating copolymers, poly(GMA-*co*-HEMA)-DETA, were synthesized via a reaction between epoxy group of

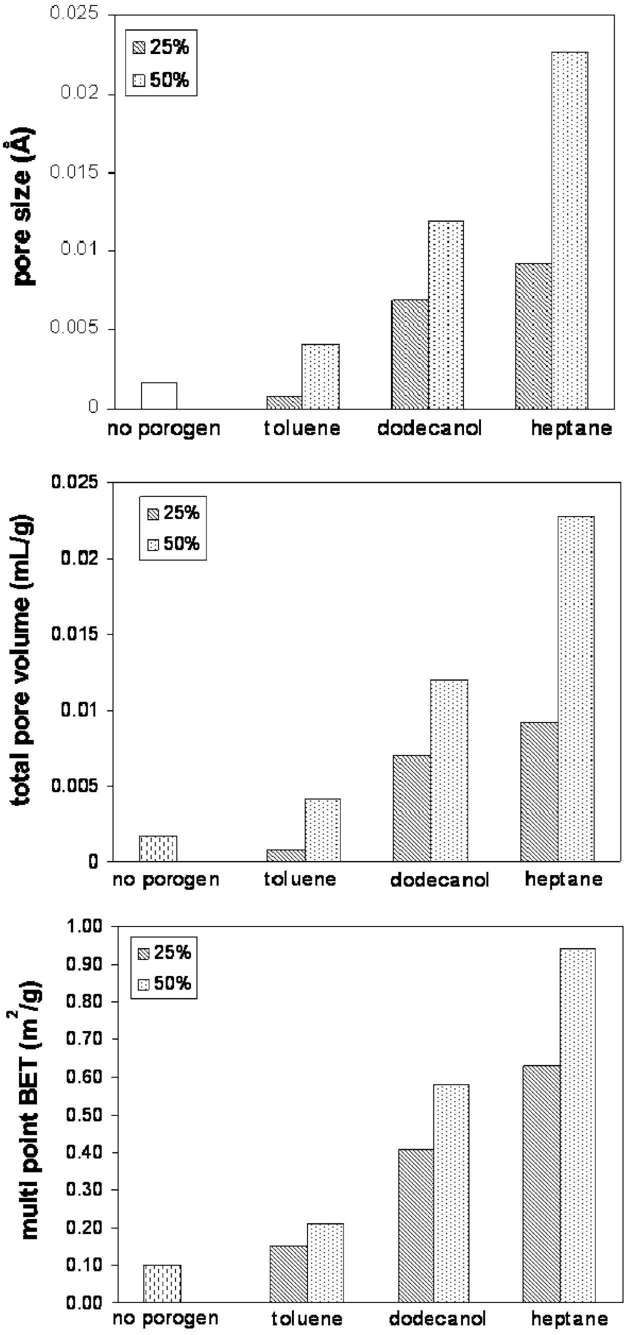


Fig. 7 Surface characteristics of copolymers synthesized from monomer phases containing different types and amounts of porogens, Exp# 2, 7–12

poly(GMA-*co*-HEMA) and DETA (see Fig. 8). Figure 9 presents the FT-IR spectra of poly(GMA-*co*-HEMA) and chelating poly(GMA-*co*-HEMA)-DETA copolymers. For poly(GMA-*co*-HEMA), the peaks at 3417 and 1722 cm^{-1} can be assigned to the O–H of HEMA and C=O of carboxyl groups of HEMA and GMA. The characteristic peaks at 907 and 845 cm^{-1} were caused by the epoxy groups of GMA. The weak band around 755 cm^{-1} corresponded to the vibration of C–H bonds of bi-substituted phynylene in DVB link [7, 28]. After grafting of DETA on poly(GMA-*co*-HEMA), a strong broad band appeared around 3426 cm^{-1}, expressing the N–H stretching vibrations of amine groups. The new peak at 1450 cm^{-1} for the methylene groups and the strong peaks at 1152 cm^{-1} for the C–N stretching vibration were observed. The spectrum confirmed that amination of poly(GMA-*co*-HEMA) with DETA to form poly(GMA-*co*-HEMA)-DETA was carried out successfully. The band of the epoxy groups at 907 cm^{-1} disappeared; however, the peak at 845 cm^{-1} still existed, indicating that epoxy groups in poly(GMA-*co*-HEMA) were not completely utilized to couple with DETA [6].

Adsorption studies

Effect of adsorption time

Figure 10 shows the amount of Cu(II) ions adsorbed on poly(GMA-*co*-HEMA)-DETA beads as a function of time. High adsorption rate was observed at the beginning of adsorption and adsorption tended towards equilibrium at 50 min. Accordingly, other adsorption studies were examined for 60 min to ensure a complete equilibrium between copolymer and metal ions.

Effect of pH

The effect of solution pH is one of the most important parameters controlling the metal ion adsorption process. The study of Cu(II) ion adsorption on poly(GMA-*co*-HEMA)-DETA beads was investigated in acidic solution with the range of pH 1–5 to avoid the precipitation of metal hydroxide by OH^-. At low pH value, the beads exhibited a remarkable decrement of adsorption capacities (Fig. 11), because of the protonation of amine groups on the beads so Cu(II) ions did not react with them. In another word, H^+ can compete with metal ions for adsorption sites and decrease the adsorption capacity [25].

Adsorption isotherm

The adsorption isotherm of the poly(GMA-*co*-HEMA)-DETA beads was presented as a function of the initial concentration of Cu(II) ions in aqueous solution between 100 and 900 ppm (Fig. 12). The amount of Cu(II) ion adsorbed per unit mass of the beads increased significantly with the ion concentrations in solution and then reached a plateau value, which represented saturation of the active adsorption sites.

Two adsorption isotherm models (the Langmuir and the Freundlich) have been used to fit the experimental

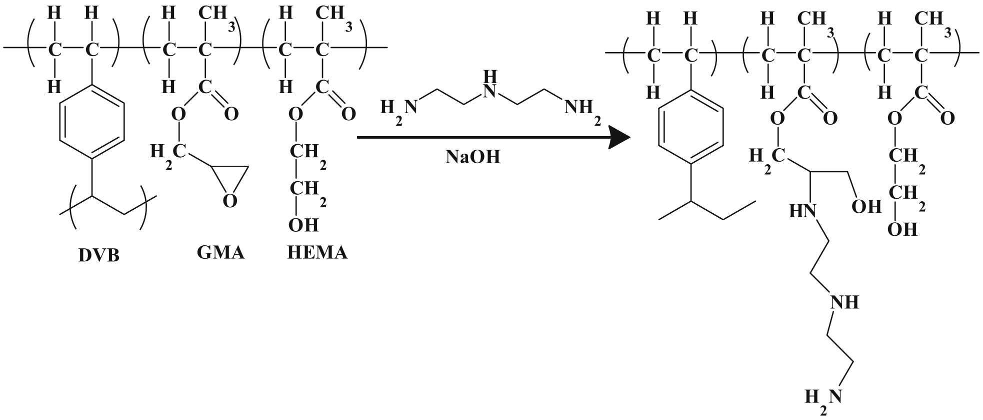


Fig. 8 Preparation of chelating resin, poly(GMA-*co*-HEMA)-DETA

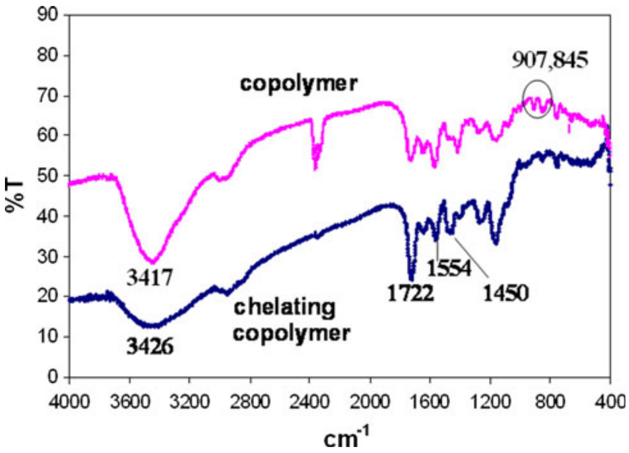


Fig. 9 FT-IR spectra of poly(GMA-*co*-HEMA) and chelating poly(GMA-*co*-HEMA)-DETA

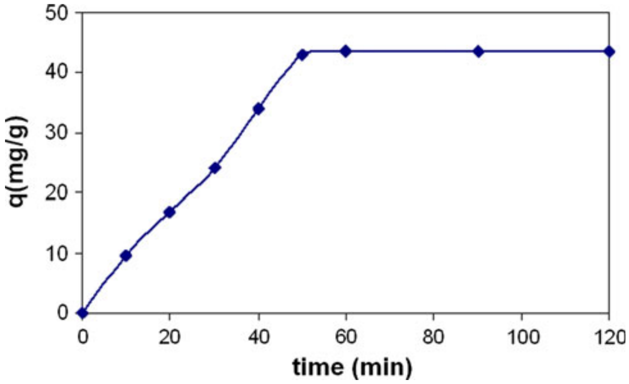


Fig. 10 Adsorption curve of Cu(II) ions onto poly(GMA-*co*-HEMA)-DETA beads, Exp# 7: pH 5, initial concentration of Cu(II) ion 500 ppm

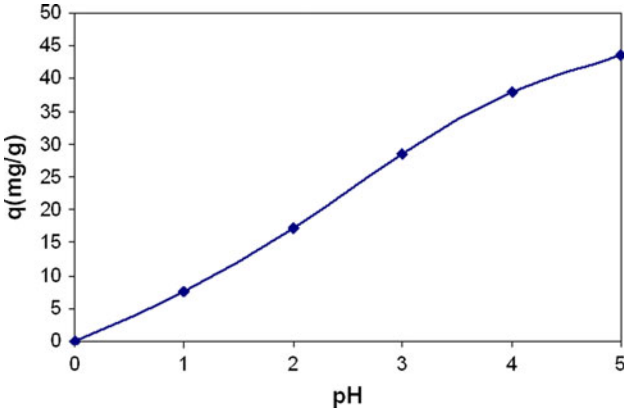


Fig. 11 Effect of pH on the adsorption capacity of poly(GMA-*co*-HEMA)-DETA beads, Exp# 7: 60 min, initial concentration of Cu(II) ion 500 ppm

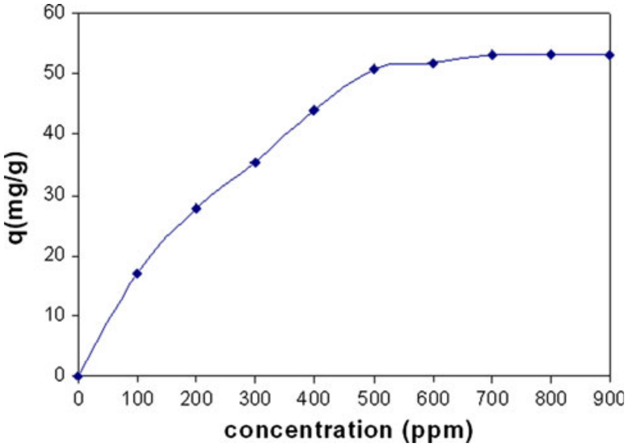


Fig. 12 Effect of concentration on the adsorption capacity of poly(GMA-*co*-HEMA)-DETA, Exp# 7: 60 min, initial concentration of Cu(II) ion 500 ppm

Table 3 Isotherm constants and correlation coefficients for the adsorption of Cu(II) from aqueous solutions

Langmuir constant			Freundlich constant		
b_L (L/mmol)	K_L(L/g)	R^2	K_F(L/g)	n	R^2
0.161	0.214	0.996	0.215	0.606	0.981

$q_{max} = 1.33$ mmol/L

adsorption data in this study. The Langmuir isotherm model assumes monolayer adsorption with equal energy and enthalpy for all adsorption sites [7, 33]. This model can be written as follows:

$$q_e = (K_L C_e)/(1 + b_L C_e) \tag{4}$$

This expression can be linearized to give

$$1/q_e = 1/K_L C_e + b_L/K_L \tag{5}$$

where C_e (mmol/L) and q_e (mmol/g) show the equilibrium metal ion concentration in the solution and the amount of the metal ions adsorbed on the adsorbent at adsorption equilibrium, respectively. K_L (L/g) and b_L (L/mmol) are the Langmuir isotherm constants of the system. The ratio of K_L/b_L is the maximum adsorption capacity, q_{max}. A plot on $1/q_e$ versus $1/C_e$ would result in a straight line with a slope of $1/K_L$ and intercept of b_L/K_L. The calculated data are given in Table 3.

The Freundlich isotherm model assumes that the adsorption energy of a metal binging to a site on an adsorption depends on whether or not the adjacent sites are already occupied. The adsorption occurs on heterogeneous surfaces and possibly in multilayer adsorption. The isotherm is as follow: [5, 33]

$$q_e = K_F C_e^n \tag{6}$$

The equation may be linearized by taking logarithms

$$\ln q_e = n \ln C_e + \ln K_F \tag{7}$$

where K_F (mmol^{1-n} L^n/g) is the Freundlich constant depicting adsorption capacity, n is a constant indicating adsorption intensity, and C_e (mmol/L) and q_e (mmol/g) have the same definitions as before. Therefore, a plot of ln q_e versus ln C_e would result in a straight line and enable the constants n and K_F to be determined. These constants are listed in Table 3.

It can be concluded from the correlation regression coefficients that the Langmuir model best fitted to the experimental data. According to the Langmuir model, adsorption occurs uniformly on the active sites of the adsorbent, and stops at one monolayer consistent with specific and strong adsorption onto specific binding sites [34, 35].

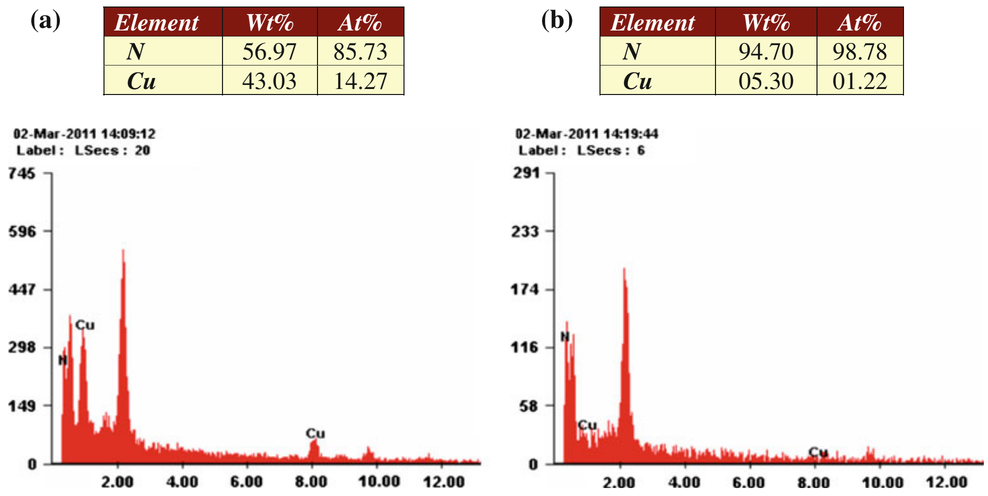
Adsorption from synthetic wastewater

Effect of porogen on the adsorption capacity. In this study, porous polymeric adsorbents were synthesized through suspension polymerization in the presence of different types and contents of porogens such as 1-docedanol, toluene, and heptane. These agents are removed from the polymer beads after polymerization resulting in porous structure of the beads. Surface area and pore structure of a given polymeric adsorbent which significantly affect the adsorption behavior depend on the usage of the crosslinking agent and the porogen. In order to study the effect of porogens on the adsorption of poly(GMA-*co*-HEMA) and their chelating beads, the content of crosslinking agent was fixed at 10%mol. The results are listed in Table 4. With increasing the surface area of copolymer beads, the Cu(II) adsorption capacity increased as expected. The non-porous chelating beads achieved 0.29 mmol/g (18.43 mg/g), while porous chelating beads prepared in the presence of 50% heptane (Exp#12) showed maximum adsorption capacity of 1.35 mmol/g (85.79 mg/g).

Figure 13 shows the energy dispersive X-ray analysis (EDX) of the chelating porous and nonporous poly(GMA-*co*-HEMA)-DETA beads (Exp#12 and 2) after adsorption. The higher adsorption capacity of the chelating porous bead was confirmed by the elemental composition and the strong signal caused by the presence of Cu(II) on the

Table 4 Surface area and Cu(II) adsorption capacities of copolymers, initial concentration of Cu(II) ion 700 ppm

Porogens		Surface area (m^2/g)	Cu(II) Adsorption (mmol/g)	
Type	Content (%V)		P(GMA-*co*-HEMA)	Chelating P(GMA-*co*-HEMA)-DETA
No porogen	0	0.13	0.14	0.29
1-Dodecanol	25	0.42	0.22	0.66
1-Dodecanol	50	0.62	0.43	0.72
Toluene	25	0.47	0.29	0.51
Toluene	50	0.79	0.51	1.08
Heptane	25	0.63	0.36	0.68
Heptane	50	0.95	0.72	1.35



(a)

Element	Wt%	At%
N	56.97	85.73
Cu	43.03	14.27

(b)

Element	Wt%	At%
N	94.70	98.78
Cu	05.30	01.22

Fig. 13 EDX analysis of the chelating polymers after adsorption **a** porous bead, Exp#12: 50% heptane and **b** nonporous bead, Exp#2: no porogen

surface of the bead. (The unlabeled signal around 2.3 was due to the gold coating before EDX-SEM observation).

Recently, numerous approaches have been investigated for the development of heavy metal adsorbents. In the literature, different binding capacities of various adsorbents have been reported. Krishnapariya and Kandaswamy prepared chitosan derivative by the chemical modification of chitosan with vanillin-based complexing agent. The binding capacities of the polymer were found to be 56.5, 46.1, and 19.8 mg/g for Cu(II), Cd(II), and Mn(II), respectively [36]. Deng et al. used diethylene triamine-modified polyacrylonitrile fibers for heavy metal removal. They reported $q_{\max}$ for adsorption to be 76 and 31 mg/g for Pb(II) and Cu(II), respectively [37]. Duran et al. prepared poly(vinyl pyridine-poly ethylene glycol methacrylate-ethylene glycol dimethacrylate) beads by suspension polymerization. The maximum chelation capacities of the beads were 18.3, 17.4, and 16.5 mg/g for Cu(II), Cr(VI), and Cd(II), respectively [5]. Jiang and Kim developed Cu(II) ion-imprinted macroporous particles from two functional monomers, methacrylic acid, and vinyl pyridine by forming a complex with the template Cu ion by ionic interactions. The maximum adsorption capacity of Cu(II) was about 22.2 mg/g [38]. Wang and Wang studied the adsorption characteristics of metal complexes by chelated copolymers with amino group. Pentaethylenehexamine was grafted onto GMA copolymer to obtain chelating copolymer via suspension polymerization. The maximum adsorption capacity for Cu ion was 79.4 mg/g [23]. The selective removal of metal ions by DETA-functionalized GMA-trimethylopropane trimethacrylate copolymer was investigated. It was observed that adsorption uptake of Cu(II) was 73.66 mg/g copolymer [24]. Chen et al. used crosslinked poly(GMA-aspartic acid) for the recovery of metal ions from aqueous solutions. In single metal ion solution, the adsorption capacities were 88.9 and 81.28 mg/g for Cu(II) and Cd(II), respectively [39]. Nastasovic et al. [40] investigated metal adsorption on macroporous poly(GMA-*co*-ethylene glycol dimethacrylate). The maximum adsorption capacity of the beads was 69.85 mg/g for Cu(II). PHEMA nanobeads containing imidazole groups were investigated for removal of metal ions. The reported adsorption capacities were 61.4 and 34.9 mg/g for Cu(II) and Cd(II), respectively [41]. Comparing the results in literature, it seems that the poly(GMA-*co*-HEMA)-DETA beads prepared in this study may competitively and effectively be used for the removal of heavy metal ions from aqueous solutions.

Adsorption capacity in single metal ion solution. Table 5 shows the adsorption data of poly(GMA-*co*-HEMA)-DETA beads prepared in the presence of 50% heptane from the experiments conducted with six different heavy metal ion solutions. The concentration of these single metal solutions was fixed at 700 ppm. The adsorption capacities are presented on the basis of mole and mass

Table 5 Non-competitive metal ion adsorption capacity of poly(GMA-*co*-HEMA)-DETA, Exp#12, in single metal solution

Metal ions	Adsorption capacity	
	Mole basis (mmol/g)	Mass basis (mg/g)
Cu(II)	1.35	85.79
Cr(VI)	1.14	59.28
Mn(II)	0.50	27.47
Zn(II)	0.46	30.07
Cd(II)	0.32	35.97
Fe(II)	0.13	7.26

Table 6 Competitive metal ion adsorption capacity of poly(GMA-*co*-HEMA)-DETA, Exp#12, in mixed metal solution 700 ppm

Metal ions	Adsorption capacity	
	Mole basis (mmol/g)	Mass basis (mg/g)
Cu(II)	0.82	52.11
Cr(II)	0.56	29.12
Mn(II)	0.15	8.24
Cd(II)	0.10	11.24

(mg) metal adsorption per gram copolymer. However, the adsorption on molar basis is more effective for the indication of total number of binding sites available on the adsorbent and for the comparing of adsorption in mixed ion solution [35]. The highest equilibrium adsorption capacity was 1.35 mmol/g for Cu(II). It can be clearly seen from Table 5 that the adsorption capacities (mole basis) of poly(GMA-*co*-HEMA)-DETA beads follow the order Cu(II) > Cr(VI) > Mn(II) > Zn(II) > Cd(II) > Fe(II). This corresponds well with the finding reported by Say and his research team. They reported that histidine-containing copolymer beads showed more affinity to Cu(II) ions and the binding of ions was achieved by exploiting the Lewis base donor properties of the nitrogen free electron pair of *N*-π-electrons of the side chains of histidine [6, 11].

Adsorption capacity in mixed metal ion solution. The competitive adsorptions of the copolymer for Cu(II), Cr(VI), Mn(II), and Cd(II) in mixed metal ion solutions are shown in Table 6. It was found that the adsorption capacities of the beads for mixed heavy metal ions were lower than those of the single solutions. The adsorption capacities on a mole basis of poly(GMA-*co*-HEMA)-DETA follow the order Cu(II) > Cr(VI) > Mn(II) > Cd(II). A number of parameters are important in adsorption experiments besides the ones that we reported, pH, concentration, and time. We found that the ratio between volume of the metal solution and mass of the copolymer (V/m) used in the experiment, the content of GMA in the copolymer, and the size of the copolymer beads are substantial factors affecting the adsorption capacity (data not shown here). However, the affinity order was not altered by adjusting the above parameters [35].

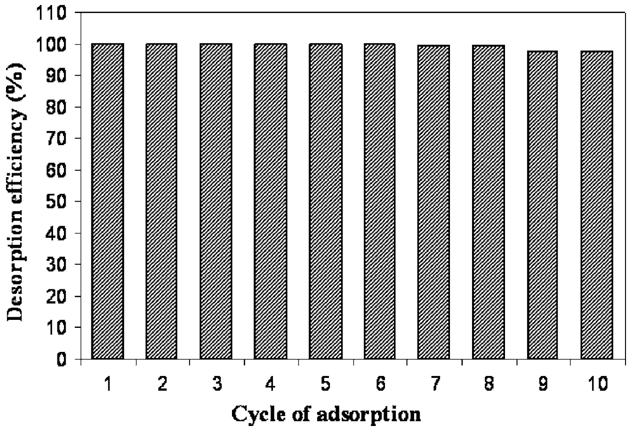


Fig. 15 The desorption efficiency of poly(GMA-*co*-HEMA)-DETA beads after repeated adsorption–desorption cycles

Desorption and repeated use

For potential application, the practical consideration of adsorbent depends not only on the adsorption capacity, but also on its capability for regeneration and reuse which are key factors in improving process economics. Cross-sectioned SEM images of the porous chelating beads shown in Fig. 14a and b suggest that after adsorption–desorption cycle the bead morphology has remained unchanged. The regenerated bead shows the similar morphology comparable to that of the fresh one. The effect of ten adsorption–desorption consecutive cycles on the adsorption of Cu(II) was also studied. The results are shown in Fig. 15. It was found that an aqueous solution of 1% nitric acid was effective to elute the heavy metal ions from the poly(GMA-*co*-HEMA)-DETA beads. The desorption efficiency reached up to 97% for the tenth adsorption–desorption cycle. These crosslinked beads showed good reusability without losing

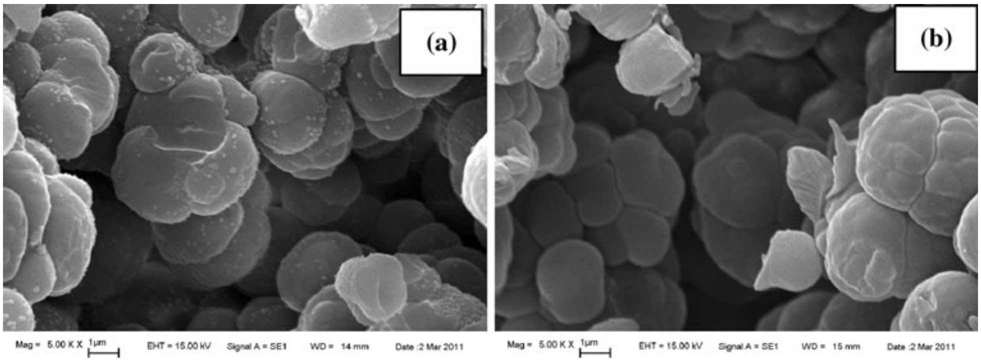


Fig. 14 SEM photographs of the beads, Exp#12, 50% heptane cross sectioned: **a** Cu(II)-containing, after adsorption and **b** Cu(II)-removed, after desorption with HNO_3 solution

significant adsorption capacity after ten times of repeated uses.

Conclusions

Polymeric adsorbent was synthesized by suspension polymerization of GMA, HEMA, and DVB in aqueous medium. Adsorption capacities and kinetics of the poly(GMA-*co*-HEMA) were greatly influenced by the polymeric physical and physicochemical characteristics of the beads, such as surface area, swelling property, and chemical structure of the chelating groups. In our study, by incorporation of porogens, 1-dodecanol, toluene, and heptane, into the reaction mixture, the surface area and porosity of the beads were increased, and the adsorption capacity was improved. The maximum adsorption capacities of poly(GMA-*co*-HEMA)-DETA beads performed on single metal ion solution were 1.35, 1.14, 0.50, 0.46, 0.32, and 0.13 mmol/g for Cu(II), Cr(VI), Mn(II), Zn(II), Cd(II), and Fe(II), respectively. As for the environmental concerns, this adsorbent exhibited perfect strength and endured repeated adsorption–desorption cycles. After ten cycles of repeated use, the re-adsorption capacity could attain 97% of initial value. The beads can be regenerated under mild condition of acid rinsing and reused.

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