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SIZE-DEPENDENT EFFECTS

# Surface modification of macroporous glycidyl methacrylate based copolymers for selective sorption of heavy metals

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**Abstract** Two samples of macroporous poly(glycidyl methacrylate-*co*-ethylene glycol dimethacrylate), poly (GMA-*co*-EGDMA), were synthesized by suspension copolymerization and modified with amines. Initial poly(GMA-*co*-EGDMA), and the samples modified with ethylene diamine [poly(GMA-*co*-EGDMA)-en], diethylene triamine [poly(GMA-*co*-EGDMA)-deta] and triethylene tetramine [poly(GMA-*co*-EGDMA)-teta], were characterized by mercury porosimetry, FTIR spectroscopy and elemental analysis. The most pronounced increase of specific surface area (75%) was observed for poly(GMA-*co*-EGDMA)-teta sample with smaller particles ($D < 150$ μm). The Cu(II) sorption was rapid, depending on porosity of amino-functionalized samples and ligand type. For poly (GMA-*co*-EGDMA)-deta and poly(GMA-*co*-EGDMA)-teta sorption half time required to reach 50% of total sorption capacity, $t_{1/2}$, were around 3 min.Sorption capacities for Cu(II), Co(II), Cd(II) and Ni(II) as well as for Cr(VI), Co(II), Cd(II) and Ni(II) ions were determined under competitive conditions as a function of pH, ligand type and porosity at room temperature. The results indicate selectivity of poly(GMA-*co*-EGDMA)-deta for Cu(II) over Cd(II) of 3:1 and for Cu(II) over Ni(II) and Co(II) of 6:1. The decrease in particle size of poly(GMA-*co*-EGDMA)-teta caused the increase of sorption capacities for all metal ions. At pH 1.8 the selectivity of poly(GMA-*co*-EGDMA)-teta with smaller particles for Cr(VI) over Ni(II), Co(II) and Cd(II) ions was 8.5:1.

## Abbreviations

| | |
|---|---|
| AIBN | 2,2′-azobisiso butyronitrile |
| $C_0$ | Concentration of the metal ions in the initial solution (mmolml$^{-1}$) |
| $C$ | Concentration of the metal ions in the aqueous phase at time t (mmolml$^{-1}$) |
| $D$ | Particle diameter (μm) |
| $d$ | Pore diameter (nm) |
| $d_m$ | Mean pore diameter (nm) |

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| | |
|---|---|
| $d_{\mathrm{mi}}$ | Mean incremental pore diameter (nm) |
| $\mathrm{d_i}$ | Incremental pore diameter (nm) |
| $d_{\mathrm{V/2}}$ | Pore diameter that corresponds to half of the pore volume (nm) |
| DETA | Diethylene triamine |
| EGDMA | Ethylene glycol dimethacrylate |
| EDA | Ethylene diamine |
| GMA | Glycidyl methacrylate |
| $L$ | Depth of the cylindrical pore (m) |
| $m$ | Amount of copolymer used in metal sorption experiments (g) |
| Poly(GMA-*co*-EGDMA) | Copolymer of glycidyl methacrylate and ethylene glycol dimethacrylate |
| Poly(GMA-*co*-EGDMA)-en | Copolymer with attached ethylene diamine |
| Poly(GMA-*co*-EGDMA)-deta | Copolymer with attached diethylene triamine |
| Poly(GMA-*co*-EGDMA)-teta | Copolymer with attached triethylene tetramine |
| $S$ | Total pore surface area ($m^2\ g^{-1}$) |
| $S_{\mathrm{i}}$ | Specific surface area ($m^2\ g^{-1}$) |
| $S_{\mathrm{Hg}}$ | Specific surface area ($m^2\ g^{-1}$) |
| $\Delta S_{\mathrm{i}}$ | Incremental specific volume ($m^2\ g^{-1}$) |
| $t_{1/2}$ | Sorption half time (min) |
| TETA | Triethylene tetramine |
| $V$ | Volume of the aqueous phase in metal sorption experiments (ml) |
| $V_{\mathrm{S}}$ | Specific pore volume ($cm^3\ g^{-1}$) |
| $V_{\mathrm{tot}}$ | Total pore volume ($cm^3\ g^{-1}$) |
| $Q$ | Metal sorption capacity ($mmolg^{-1}$) |
| $Q_{\max}$ | Maximum metal sorption capacity ($mmolg^{-1}$) |

## Introduction

The development of efficient chelating copolymers for selective removal and/or recovery of heavy metal ions from wastewater streams of hydro-metallurgical and other industries is of growing ecological and economical importance [1]. Chelating copolymers consist of crosslinked copolymer (solid support) and functional group (ligand) with N, O, S and P atoms capable for coordinating of different metal ions. The removal of heavy metals with chelating polymers is simple process, reduced only to filtration as the regeneration step. As the functional groups interacting with the metal ions are covalently bounded to an insoluble copolymer, there is no loss of extractant into the aqueous phase. Also, process neither produces waste materials, nor generates secondary pollutants. Spherical particles of macroporous crosslinked chelating copolymer prepared by suspension copolymerization are proved to be more efficient than gel type ones [2]. Among them, macroporous hydrophilic copolymers based on glycidyl methacrylate, GMA, are very attractive, since the epoxy group can be easily transformed into iminodiacetate, thiol, azole, pyrazole groups, etc. [3]. Functionalization of these copolymers with amines yields specific sorbents with high capacity, fast kinetics and good selectivity for the heavy metal ions, as well as chemical and mechanical stability [4–7]. Sorption rate and capacity, as well as selectivity, depend mainly on porosity and chemical composition of the chelating copolymer [8]. For that reason, the knowledge of the mechanism of porous structure formation and the ability of optimization of porosity parameters is needed in order to design chelating copolymer with desired sorption performances and selectivity towards individual metal ions.

In this study, samples of crosslinked poly(GMA-*co*-EGDMA) with different porosity parameters (pore volume, surface area, and pore diameter) were synthesized by suspension copolymerization of GMA and ethylene glycol dimethacrylate (EGDMA), in the presence of inert component (mixture of cyclohexanol and aliphatic alcohol). Porosity of initial poly(GMA-*co*-EGDMA) samples was adjusted by the variation of the type of aliphatic alcohol in the reaction mixture. After the synthesis, samples were amino-functionalized by ring-opening reaction of the pendant epoxy groups with ethylene diamine, diethylene triamine and triethylene tetramine. The influence of the porosity parameters, particle size and type of the ligand on the uptake of heavy metals on macroporous amino-functionalized poly(GMA-*co*-EGDMA) was studied. Sorption rates of poly(GMA-*co*-EGDMA)-en, poly(GMA-*co*-EGDMA)-deta and poly(GMA-*co*-EGDMA)-teta for Cu(II) ions were determined. Also, selectivity of poly(GMA-*co*-EGDMA)-deta and poly(GMA-*co*-EGDMA)-teta towards individual metal ions under competitive conditions were investigated as a function of pH and particle size.

## Experimental

### Materials and characterization

All the chemicals used were analytical grade products and used as received: glycidyl methacrylate (GMA) (Merck), ethylene glycol dimethacrylate (EGDMA) (Fluka), ethylene diamine (EDA) (Fluka), diethylene triamine (DETA), (Merck), triethylene tetramine (TETA), (Merck), 2,2′-azobisiso-butyronitrile (AIBN) (Merck), poly(*N*-vinyl pyrrolidone) (Kollidone 90, BASF), cyclohexanol (Merck) and dodecanol (Merck). All solutions were prepared using deionized water.

The epoxy group content in synthesized poly(GMA-*co*-EGDMA) samples was determined by HCl-dioxane method [9]. The copolymer samples were analyzed for their carbon, hydrogen and nitrogen content using the Vario EL III device (GmbH Hanau Instruments, German). Elemental analysis was calculated from multiple determinations within ±0.2% agreement.

The pore size distributions were determined by mercury porosimetry (Carlo Erba 2000, software Milestone 200). The concentration of metals was determined by atomic absorption spectrometry (AAS, SpektrAA Varian Instruments). Standard statistical methods were used to determine the mean values and standard deviations for each set of data.

The FTIR spectra were recorded in KBr pellets on a Perkin–Elmer FTIR 1725X spectrophotometer (4,000–400 $\text{cm}^{-1}$) with DGTS detector and IRDM software.

### Preparation of poly(GMA-co-EGDMA)

Two samples of macroporous poly(GMA-*co*-EGDMA) with different porosity parameters were prepared by a radical suspension copolymerization [10]. The monomer phase (79.7 g) containing monomer mixture (20.7 g of GMA and 13.8 g of EGDMA), azobisisobytironitrile (AIBN) as an initiator (0.3 g), and 45.2 g of inert component (cyclohexanol and aliphatic alcohol) was suspended in the aqueous phase consisting of 240.0 g of water and 2.4 g of poly(*N*-vinyl pyrrolidone).

The inert component consisted of 40.7 g of cyclohexanol and 4.5 g of aliphatic alcohol (dodecanol for SGE-10/12 and hexadecanol for SGE-10/16). In the labels of copolymer samples, letter S designate suspension copolymerization, G and E stand for monomers (GMA and EGDMA). The first number in a sample labels stands for the share of aliphatic alcohol in the inert component (in wt.%) and the second one for the number of C-atoms in the aliphatic alcohol.

The copolymerization was carried out at 70 °C for 2 h and at 80 °C for 6 h with a stirring rate of 200 rpm. After completion of the reaction, the copolymer particles were washed with water and ethanol, then kept in ethanol for 12 h and dried in vacuum (10 mm Hg) at 40 °C. The resulting crosslinked beads were sieved and purified by Soxhlet extraction with ethanol. Fractions with average particle diameter ($D$) in the range $150 < D < 500$ μm and $150\ \mu\text{m} > D$, were used in subsequent reactions.

### Functionalization of poly(GMA-co-EGDMA) with ethylene diamine

Four grams of poly(GMA-*co*-EGDMA) (samples SGE-10/12 and SGE-10/16, with particle size $150 < D < 500$ μm), 10.0 g of ethylene diamine and 100 ml of toluene was left at room temperature for 24 h. The reaction mixture was heated at 80 °C for 6 h. Modified samples were filtered, washed with water and ethanol, dried and labeled as SGE-10/12-en and SGE-10/16- en (additional label -en designate sample modified with ethylene diamine).

### Functionalization of poly(GMA-co-EGDMA) with diethylene triamine

A mixture of 3.6 g of poly(GMA-*co*-EGDMA) (sample SGE-10/16, with particle size $150 < D < 500$ μm), 15.7 g of diethylene triamine and 100 ml of toluene was left at room temperature for 24 h, then heated at 80 °C for 6 h. Modified sample was filtered, washed with water and ethanol, dried and labeled as SGE-10/16-deta (additional label -deta designate sample modified with diethylene triamine).

### Functionalization of poly(GMA-co-EGDMA) with triethylene tetramine

A mixture of 5.0 g of poly(GMA-*co*-EGDMA), 7.75 g of triethylene tetramine and 30 ml of toluene was left at room temperature for 24 h, then heated at 80 °C for 6 h. Modified sample was filtered, washed with water and ethanol, dried and labeled as SGE-10/16-teta-**a** and SGE-10/16-teta-**b** (additional label -teta designate sample modified with diethylene triamine, while **a** and **b** designate fractions with particle diameters in the range 150–500 μm and beyond 150 μm, respectively).

### Metal-uptake experiments

Sorption of metal ions from aqueous solutions was investigated in batch experiments at room temperature. At appropriate times, the samples were filtered, washed subsequently with water and ethanol, and dried. The concentration of metal ions in the filtrate was determined by AAS. The reproducibility of the sorption experiments results was verified in triplicate.

For the determination of Cu(II) sorption rate, 0.5 g of copolymer was contacted with 50 ml of metal salt solution (0.05 M). At appropriate times, 1 ml of aliquots were removed and diluted to 100 ml.

Metal-uptake capacities under competitive conditions were determined as a function of pH for two mixed solutions: Cu(II), Co(II), Cd(II) and Ni(II) as well as for Cr(VI), Co(II), Cd(II) and Ni(II). Modified copolymer (0.1 g) was contacted with 10 ml of mixed metal salt solution (0.05 M) and 10 ml of NaCl/HCl (pH 0.2–2.3) or NaOAc/HOAc (pH 2.5–5.5) solution.

The amount of metal ions sorbed onto unit mass of macroporous copolymer beads (sorption capacity, mmol/g) were calculated by using the following expression:

$$Q = \frac{(C_0 - C) \times V}{m} \tag{1}$$

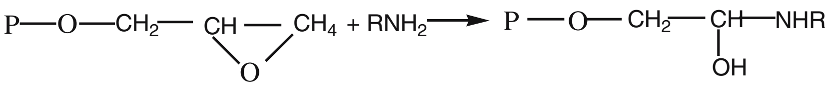
where $C_0$ and $C$ are the concentrations of the metal ions in the initial solution and in the aqueous phase after treatment for certain period of time (in mmolml$^{-1}$), respectively, $V$ is the volume of the aqueous phase (in ml) and $m$ is the amount of the poly(GMA-*co*-EGDMA) amino-functionalized beads used for the experiment (in g).

## Results and discussion

### Synthetic aspects

Macroporous crosslinked copolymers are obtained by radical suspension copolymerization in the shape of regular beads of required size, when the inert component is present in the mixture of monomer and initiator [3, 11, 12]. Among other factors, sorption capacity, selectivity, diffusion and flow properties of macroporous chelating copolymers to a great extent depend on their porosity. Therefore, for the practical use, it is necessary to optimize porosity parameters of macroporous crosslinked copolymers. Formation of macroporous copolymers have been extensively investigated and described in the literature [3, 10–16]. Macroporous structure appears as a result of the phase separation that occurs during the polymerization of a monomer mixture containing appropriate amounts of both crosslinking monomer and inert component being a good solvent, a poor solvent for synthesized copolymer, or a linear polymer [3, 11, 12]. Švec et al. showed that macroporous copolymer of glycidyl methacrylate and EGDMA, poly(GMA-*co*-EGDMA), can be obtained by suspension copolymerization when an inert component (mixture of cyclohexanol as solvent and dodecanol as non-solvent for copolymer) is present in the monomer mixture [12, 17]. Recently, Jovanović et al. showed that variation in the type and the amount of aliphatic alcohol in the inert component as well as the chemical structure and size of crosslinking monomer significantly influences the porosity parameters of glycidyl methacrylate based copolymers [10, 14]. The choice of inert component plays an important role in the design of the porous structure; the larger pores are obtained in a poor solvent due to an earlier onset of the phase separation.

Two samples of macroporous crosslinked poly(GMA-*co*-EGDMA), SGE-10/12 and SGE-10/16, were chosen according to previous studies [10, 14]. The initial samples were further amino-functionalized by ring opening reaction of the pendant epoxy group with ethylene diamine, diethylene triamine and triethylene tetramine, yielding products with favorable exchange kinetics for transition metals, as a result of the hydrophilic character of the resultant chelating copolymer, due to the hydroxyl group on the carbon atom $\beta$ to the incoming amine [18]. Detailed studies regarding the reaction of macroporous poly(GMA-*co*-EGDMA) with ammonia, primary and secondary amines, diamines and hydroxyalkylamines were published by Švec et al. [19, 20]. Scheme 1 shows amination reaction.



where R is:

| | |
|---|---|
| Ethylene diamine | $-(CH_2)_2-NH_2$ |
| Diethylene triamine | $-(CH_2)_2-NH-(CH_2)_2-NH_2$ |
| Triethylene tetramine | $-(CH_2)_2-NH-(CH_2)_2-NH-(CH_2)_2-NH-(CH_2)_2-NH_2$ |

**Scheme 1.** Chemical modification of poly(GMA-*co*-EGDMA) with ethylene diamine, diethylene triamine and triethylene tetramine

The pore size distributions for all initial and amino-functionalized samples were determined by mercury porosimetry. As an illustration, in Fig. 1 are presented cumulative pore distribution curves for samples SGE-10/16, SGE-10/16-en, SGE-10/16-deta with particle size 150 < *D* < 500 μm and two fractions of SGE-10/16-teta with different particle size (150 < *D* < 500 μm and 150 μm > *D*).

The values of specific pore volume, $V_S$, and pore diameter that corresponds to half of the pore volume, $d_{V/2}$, were read from Fig. 1. The calculation of specific surface area, $S_{Hg}$, of initial and amino-functionalized samples is based on cylindrical pore model [10, 21]. The wall area of cylinder is πdL, where *d* and *L* are pore diameter and the depth of the pore, respectively. The volume of a cylindrical pore is therefore, $\pi d^2 L/4$. Thus, for a cylinder, total pore surface area, *S*, is given by the relation between volume and wall area:

$$S = \frac{4V_{tot}}{d_m} \tag{2}$$

where $V_{tot}$ is total pore volume, i.e., the total intruded volume of mercury at the highest pressure determined, and $d_m$ is the mean pore diameter.

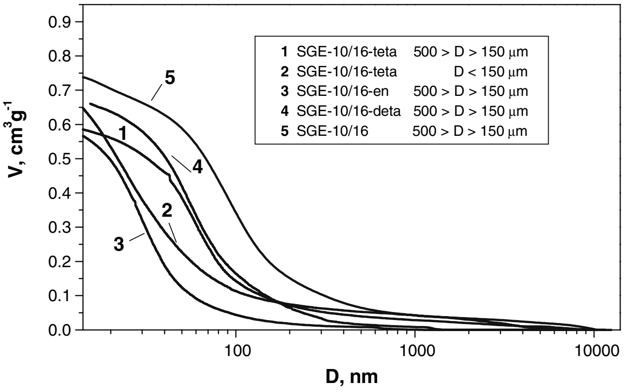


**Fig. 1** Cumulative pore size distribution curves for samples SGE-10/16, SGE-10/16-en, SGE-10/16-deta (particle size 150 < *D* < 500 μm) and SGE-10/16-teta (particle size 150 < *D* < 500 μm and 150 μm > *D*)

Specific surface area, $S_{Hg}$, was calculated from the mercury porosity data, as the sum of incremental specific surface area:

$$S_{Hg} = \sum_{i=1}^{n} \Delta S_i \tag{3}$$

Incremental specific volume, $\Delta S_i$, was calculated from changes in cumulative volumes over each pressure (diameter) increment, multiplying specific volume by 4,000 (for the sake of the units agreement) and dividing by the mean pore diameter, $d_{mi}$, over which the volume increment was determined, i.e., $d_{mi}= (d_i + d_{i+1})/2$.

$$\Delta S_i = \frac{4000(V_{i+1} - V_i)}{(d_i + d_{i+1})/2} \tag{4}$$

where and $V_i$, is the volume of the pores with diameter $d_i$. Porosity parameters for initial and amino-functionalized samples are presented in Table 1.

From the pore size distribution curves presented in Fig. 1 and the porosity data in Table 1, it can be concluded that amino-functionalization causes considerable alteration of porosity parameters of poly(GMA-*co*-EGDMA). The specific surface area of SGE-10/12-en increased 40% (from 50 $m^2$ $g^{-1}$ to 70 $m^2$ $g^{-1}$) while

**Table 1** Porosity parameters of initial and amino-functionalized poly(GMA-*co*-EGDMA) samples

| Sample | $S_{Hg}$, $m^2$/g | $V_S$, $cm^3$/g | $d_{V/2}$, nm |
|---|---|---|---|
| SGE-10/12[a] | 50 ± 0.3 | 0.61 ± 0.005 | 53 ± 0.3 |
| SGE-10/16[a] | 33 ± 0.2 | 0.75 ± 0.006 | 87 ± 1.4 |
| SGE-10/12-en | 70 ± 0.4 | 1.18 ± 0.01 | 42 ± 0.6 |
| SGE-10/16-en | 55 ± 0.2 | 0.65 ± 0.006 | 31 ± 0.3 |
| SGE-10/16-deta | 50 ± 0.3 | 0.66 ± 0.005 | 29 ± 0.4 |
| SGE-10/16-teta-**a**[b] | 53 ± 0.3 | 0.61 ± 0.005 | 30 ± 0.3 |
| SGE-10/16-teta-**b**[b] | 93 ± 0.5 | 0.84 ± 0.007 | 25 ± 0.4 |

[a] Porosity parameters for initial samples were taken from [12]

[b] Fractions with particle size 150 < *D* < 500 μm (**a**) and 150 μm > *D* (**b**)

specific pore volume increases 93% (from 0.61 $cm^3 g^{-1}$ to 1.18 $cm^3 g^{-1}$) in comparison with the initial sample, SGE-10/12. Paredes et al. reported the similar [22]. According to these authors, functionalization of poly(GMA-*co*-EGDMA) with ammonia promotes the formation of smaller mesopores and consequently, the increase in specific surface area.

In order to investigate the influence of the type of the ligand attached to poly(GMA-*co*-EGDMA) on the porosity parameters, sample SGE-10/16 was modified with ethylene diamine (SGE-10/16-en), diethylene triamine (SGE-10/16-deta) and triethylene tetramine (SGE-10/16-deta). It was shown that functionalization with ethylene diamine causes significant increase in specific surface area of 67% (from 33 $m^2g^{-1}$ to 55 $m^2g^{-1}$). Also, for sample SGE-10/16-en pore diameter that corresponds to half of the pore volume, $d_{V/2}$ decreased 2.81 times (from 87 nm to 31 nm), compared with the initial sample SGE-10/16. However, no differences in porosity parameters of samples functionalized with different amines were observed. On the other hand, the most pronounced influence of amino-functionalization on the porosity was observed in the case of two poly(GMA-*co*-EGDMA)-teta samples with different particle size. For example, sample with smaller particles, SGE-10/16-teta-**b**, has 75% higher specific surface area than SGE-10/16-teta-**a**.

FTIR spectra of initial poly(GMA-*co*-EGDMA) (sample SGE-10/16) and sample modified with triethylene tetramine (sample SGE-10/16-teta) were recorded and presented in Figs. 2 and 3, respectively.

The epoxy peaks found in spectra of initial poly (GMA-*co*-EGDMA) sample, at 848, 908 $cm^{-1}$ (epoxy ring vibrations), 1,261 and 1,455 $cm^{-1}$ [$\delta$(CH) epoxy] have not totally disappeared from spectra of sample modified with triethylene tetramine, poly(GMA-*co*-EGDMA)-teta, indicating incomplete conversion of the epoxy groups. Namely, some parts of epoxy groups usually remain inside the crosslinked polymer, being inaccessible for subsequent reactions. The similar was observed for poly(GMA-*co*-EGDMA) modified with ethylene diamine [6].

The bands for ester vibrations at 1,729 $cm^{-1}$ [$\nu$(C=O)], as well as the bands characteristic for the crosslinked copolymer at 2,955 $cm^{-1}$ [$\delta$ (CH)] and at 1,161 $cm^{-1}$ [$\nu$(C–O)], were not changed in modified sample. However, the bands found in the spectra of poly(GMA-*co*-EGDMA)-teta at 3,400 $cm^{-1}$ [$\nu(NH_2)$], 1,643 $cm^{-1}$ [$\delta$ ($NH_2$), $\delta$(NH)], 1,567 $cm^{-1}$ [$\delta$(NH)] and 1,394 $cm^{-1}$ [$\nu$(NH)], indicate presence of –NH and –$NH_2$ groups as a result of modification of poly(GMA-*co*-EGDMA) with triethylene tetramine. A strong band occurs at 3,500 $cm^{-1}$, where the valence vibrations for –NH, –$NH_2$ and –OH groups overlap. The

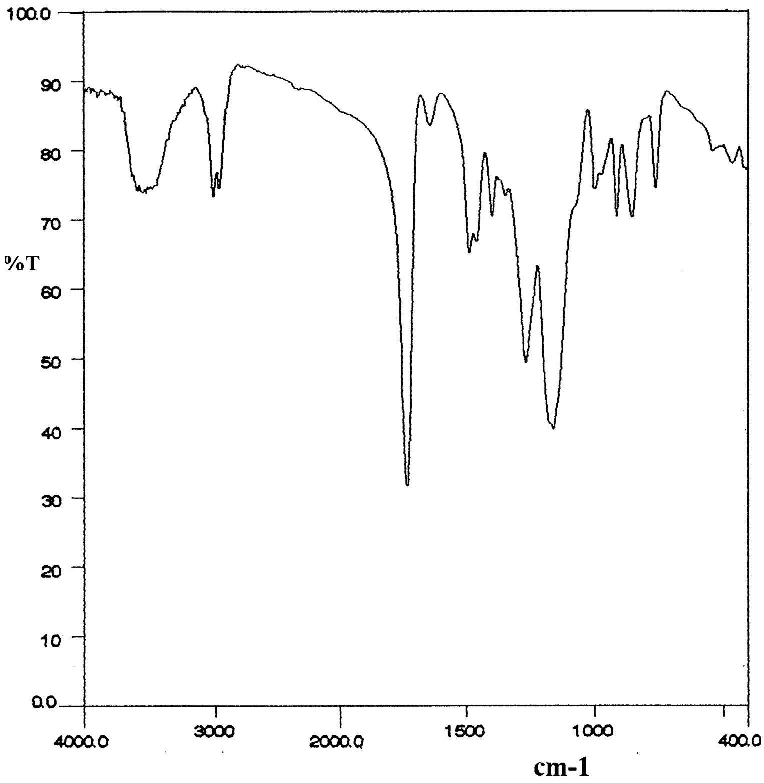
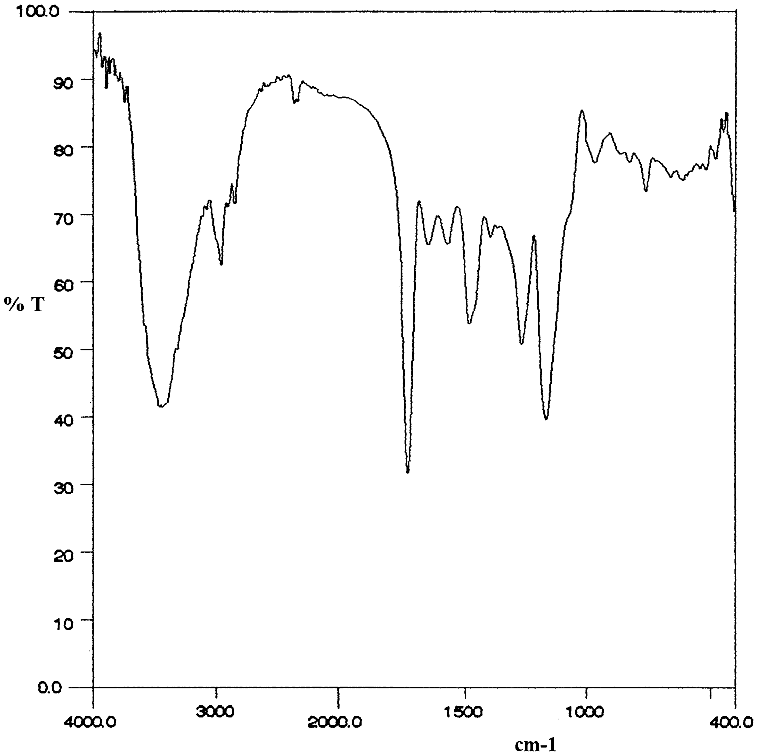


**Fig. 2** FTIR spectra of poly(GMA-*co*-EGDMA) (sample SGE-10/16)

**Fig. 3** FTIR spectra of poly(GMA-*co*-EGDMA)-teta (sample SGE-10/16-teta)



similar bands were observed in FTIR spectra of poly(GMA-*co*-EGDMA)-deta samples.

The elemental analysis data for initial copolymer samples, poly(GMA-*co*-EGDMA), samples modified with ethylene diamine, diethylene triamine, and triethylene tetramine were presented in Table 2. The theoretical content of epoxy groups in synthesized poly(GMA-*co*-EGDMA) samples, calculated on the basis of the feed composition, was 4.22 mmol/g. The elemental analysis data for the sample (Table 2) are in fair agreement with the theoretical value. The difference is within the limits for suspension polymerization. The epoxy group content in copolymer sample is therefore as designed.

**Table 2** Elemental analysis of initial and amino-functionalized poly(GMA-*co*-EGDMA) samples

| Sample | Elemental analysis[a] | | | | | |
|---|---|---|---|---|---|---|
| | Found | | | Calculated | | |
| | % *C* | % *H* | % *N* | % *C* | % *H* | % *N* |
| SGE-10/12 | 57.29 | 7.42 | – | 59.85 | 7.06 | – |
| SGE-10/16 | 57.57 | 8.35 | – | | | |
| SGE-10/12-en | 52.60 | 8.46 | 6.11 | 56.29 | 8.18 | 8.38 |
| SGE-10/16-en | 49.38 | 10.75 | 6.24 | | | |
| SGE-10/16-deta | 50.21 | 10.11 | 6.82 | 56.23 | 11.14 | 8.58 |
| SGE-10/16-teta | 51.20 | 10.73 | 7.28 | 56.2 | 8.89 | 13.33 |

[a] Elemental analysis was calculated from multiple determinations within ±0.2% agreement

The content of epoxy groups on the surface of crosslinked copolymer samples SGE-10/12 and SGE-10/16, determined by HCl-dioxane method were 2.08 ± 0.02 and 2.20 ± 0.03 mmolg$^{-1}$, respectively, and differs from the theoretical value. This discrepancy is understandable, since some part of epoxy groups usually remains inside the crosslinked copolymer, being not accessible for subsequent reactions and analytical determinations [6].

From elemental analysis data, the degree of conversion of epoxy groups, ligand concentration and amino group concentration in the samples SGE-10/12-en, SGE-10/16-en, SGE-10/16-deta and SGE-10/16-teta were calculated and presented in Table 3.

For samples SGE-10/12-en and SGE-10/16-en, functionalized with ethylene diamine, similar values for degree of conversion of epoxy groups, ligand

**Table 3** Conversion of epoxy groups, ligand concentration and amino group concentration in amino-functionalized poly(GMA-*co*-EGDMA) samples

| | Conversion of epoxy groups, % | Ligand concentration, mmolg$^{-1}$ | Amino group concentration, mmolg$^{-1}$ |
|---|---|---|---|
| SGE-10/12-en | 52 ± 0.08 | 2.18 ± 0.004 | 4.36 ± 0.008 |
| SGE-10/16-en | 53 ± 0.07 | 2.23 ± 0.005 | 4.46 ± 0.009 |
| SGE-10/16-deta | 38 ± 0.08 | 1.62 ± 0.003 | 4.86 ± 0.008 |
| SGE-10/16-teta | 31 ± 0.06 | 1.30 ± 0.002 | 5.20 ± 0.01 |

concentration and amino group concentration were observed.

However, the type of the ligand has pronounced influence on the conversion and ligand concentration. At the same reaction conditions, the degree of conversion of epoxy groups decreases in order: SGE-10/16-en > SGE-10/16-deta > SGE-10/16-teta. This could be expected, since the limitation of the reaction due to a steric effect is one of the main problems in polymer functionalization with larger groups [23]. For example, considerably lower degree of conversion was obtained for pyrazole containing ligand with two bulky 3,5 dimethylpyrazole substituents (23%) than for ligand with one bulky group (51%) [4]. Another limitation in the case of macroporous poly(GMA-*co*-EGDMA) is inaccessibility of all epoxy groups for chemical reaction due to high crosslinking degree. Namely, amines predominantly react with epoxy groups on the surface of copolymer beads. The similar was observed for reaction of azole ligands on the sulfure analogue of GMA based macroporous crosslinked copolymers [24].

## Metal sorption on amino-functionalized poly(GMA-co-EGDMA)

The numerous studies of sorption capacity and selectivity of poly(GMA-*co*-EGDMA) functionalized with different functional groups was reported in literature [6, 7, 25–31]. The hydrophilic character of amino-functionalized groups macroporous poly(GMA-*co*-EGDMA) facilitates the access of metal ions to the ligands immobilized on the copolymer, enhancing sorption of noble and heavy metals from aqueous solutions [23, 29]. However, there are few data regarding chelating properties of macroporous poly(GMA-*co*-EGDMA) modified with diethylene triamine and triethylene tetramine. Also, there is a lack of comparative studies concerning metal sorption macroporous GMA based copolymers functionalized with various amines.

The separation of metal ions by macroporous copolymers depends on the structural properties of the chelating copolymers (copolymer particle size, specific surface area, pore diameter, specific pore volume), chemical structure of chelating copolymer and attached ligand, pH, presence of other ions which compete for the active sites, as well as on the different kinetic and thermodynamic stability of the formed metal complexes with the chemically bonded amine ligands [4, 26, 32].

From the standpoint of potential application, one of the most important properties of the chelating polymers is the rate of establishing of the equilibrium metal sorption. Consequently, the rapid sorption of metal ions by functionalized poly(GMA-*co*-EGDMA) would be beneficial for practical use. For this purpose, sorption rate for Cu(II) ions on poly(GMA-*co*-EGDMA)-en, poly(GMA-*co*-EGDMA)-deta and poly(GMA-*co*-EGDMA)-teta was determined.

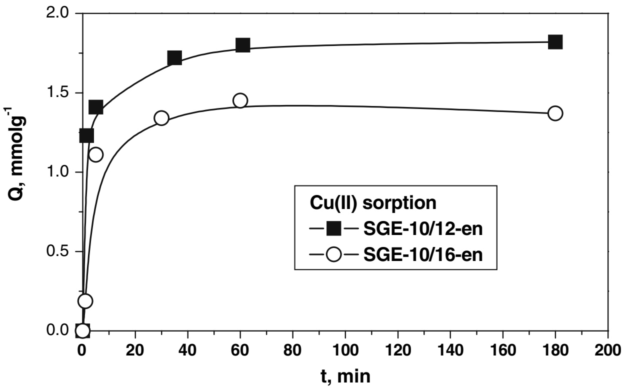


**Fig. 4** Sorption of Cu(II) ions vs. time, on poly(GMA-*co*-EGDMA)-en samples with different porosity parameters (metal ions initial concentration 0.05 M, pH = 4)

The influence of porosity on the Cu(II) sorption rate on poly(GMA-*co*-EGDMA) functionalized with ethylene diamine is presented in Fig. 4.

The sorption of Cu(II) for both samples with attached ethylene diamine was found to be rapid. The sorption half time, $t_{1/2}$, defined as the time required to reach 50% of the total sorption capacity, was of the order of 1 min and 5 min for SGE-10/12-en and SGE-10/16-en, respectively. Already after 5 min, SGE-10/12-en and SGE-10/16-en sorbed 75% and 81% of Cu(II) ions, respectively. After 30 min, the amount of sorbed Cu(II) ions was around 90% for both amino-functionalized samples. The maximum Cu(II) sorption capacity for SGE-10/12-en is 1.3 times higher than for SGE-10/16-en. Bearing in mind that samples SGE-10/12-en and SGE-10/16-en have almost equal values of ligand concentration, it could be concluded that porosity parameters predominantly affect the sorption rate and capacity of Cu(II) ions on poly(GMA-*co*-EGDMA) functionalized with ethylene diamine. Also, fast sorption of Cu(II) ions can be ascribed to the hydrophilicity of the macroporous copolymer, which facilitate the interaction of the copolymer with the solution, as well as the coordination of the metal ions due to the presence of heteroatoms (N and O) [33].

The effect of the type of amino-ligand on the Cu(II) sorption rate is presented in Fig. 5.

The sorption of Cu(II) ions on samples functionalized with diethylene triamine and triethylene

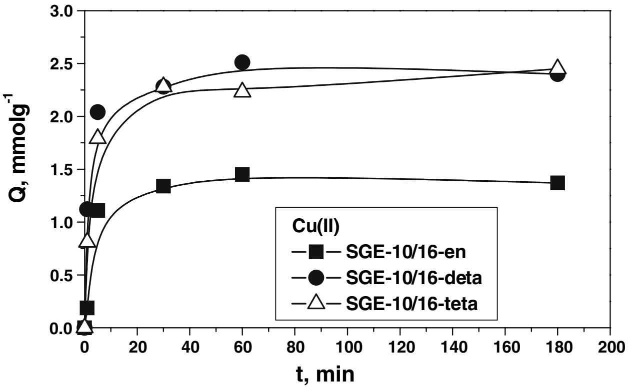


**Fig. 5.** Sorption of Cu(II) ions vs. time, on poly(GMA-*co*-EGDMA)-en, poly(GMA-*co*-EGDMA)-deta and poly(GMA-*co*-EGDMA)-teta (metal ions initial concentration 0.05 M, pH = 4)

tetramine was found to be rapid compared with sample SGE-10/16-en with attached ethylene diamine. Namely, $t_{1/2}$ values for SGE-10/16-deta and SGE-10/16-teta were around 3 min. All samples sorbed approximately 90% of Cu(II) ions after 30 min. The results obtained for Cu(II) sorption on macroporous amino-functionalized poly(GMA-*co*-EGDMA) are comparable with literature data and seems to be rather good. Lindsay and Sherrington noticed that poly(GMA-*co*-EGDMA) with pyridine containing ligands show remarkably enhanced kinetic behavior in the sorption of Cu(II) ions ($t_{1/2}$ value of 8 min) and superior selectivity for particular metal ions from mixed salts solutions than poly(styrene) analogue [29, 30]. For poly(GMA-*co*-EGDMA) with attached 2-(3,5-dimethylpyrazolyl)ethylamine, a $t_{1/2}$ value of 13 min for Cu(II) sorption was obtained [4]. Verweij et. al. observed $t_{1/2}$ value of 13 min for Cu(II) sorption on poly(GMA-*co*-TMPTMA) with immobilized pyrazole ligand [27]. According to the literature data, high initial rate for Cu(II) uptake suggests that the sorption process occurs predominantly at the surface of the highly crosslinked amino-functionalized beads [34]. After that, the sorption rate becomes slower and saturation was gradually reached. The mechanism of intrapore diffusion is represented by the slower sorption rate, which was noticed after 30 min of the initial sorption.

Further, obtained results imply that maximum sorption capacity of amino-functionalized poly(GMA-*co*-EGDMA) depends on the type of the ligand. Namely, the maximum capacites for Cu(II) ions on SGE-10/16-deta and SGE-10/16-teta are 1.75 times higher then for SGE-10/16-en. It seems that further improvement in sorption kinetics was not achieved by functionalization with triethylene tetramine, since no difference in maximum sorption capacities between samples SGE-10/16-deta and SGE-10/16-teta was observed.

Also, the development of highly selective ligands will be ineffective if characteristics of chelating copolymer (support) have negative effect on the selectivity, or reduce the uptake capacity [26]. Therefore, optimization of porosity and ligand chelating characteristics is needed.

## *Competitive sorption*

According to the literature data, besides pH, the selectivity of chelating copolymers depends on the nature of the ligand immobilized on the crosslinked copolymer and characteristics of the chelating copolymer (porosity parameters of the copolymer, diffusion, particle size) [4, 6, 7, 26, 27, 35]. Also, metal uptake under competitive conditions, i.e., uptake from mixed metal salt solutions, is influenced by the presence of other metal ions competing for the active sites in the modified copolymer [32]. In general, chelating GMA based copolymers with amino groups are selective towards multivalent metal ions over the alkali and alkali earth metals. Despite the fact that numerous papers regarding metal sorption on amino-functionalized GMA based macroporous copolymers were published, only few dealt with competitive sorption of heavy metal sorption [5, 6, 36].

In the first series of experiments, competitive sorption of Cu(II), Ni(II), Co(II) and Cd(II) ions was performed on poly(GMA-*co*-EGDMA) functionalized with diethylene triamine and triethylene tetramine. The results are presented in Figs. 6 and 7. The maximum capacities of SGE-10/16-deta (particle size $150 < D < 500$ μm) and SGE-10/16-teta (two fractions

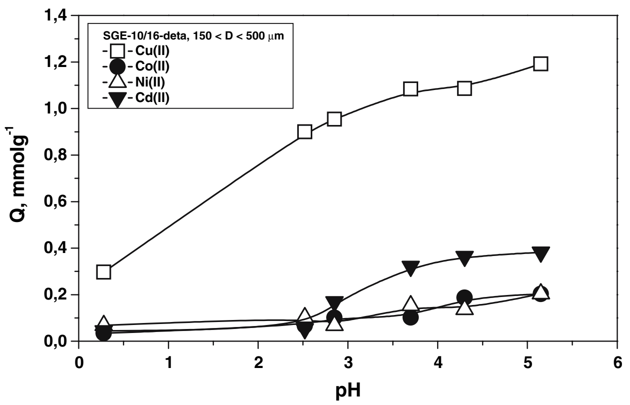


**Fig. 6** Competitive sorption of Cu(II), Co(II), Ni(II) and Cd(II) ions on poly(GMA-*co*-EGDMA)-deta (particle size $150 < D < 500$ μm)

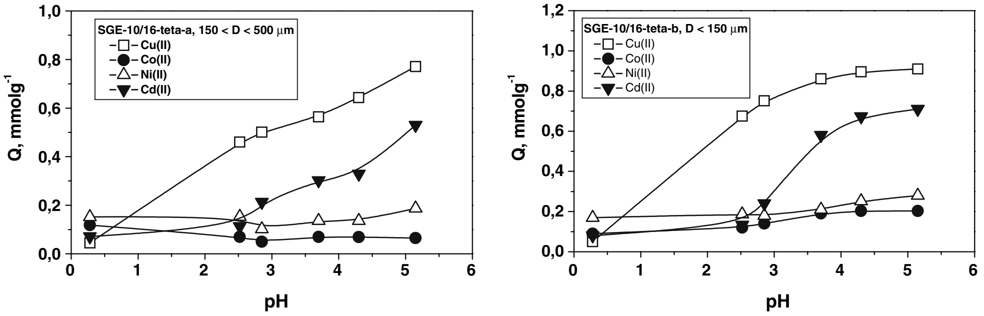


**Fig. 7** Competitive sorption of Cu(II), Co(II), Ni(II) and Cd(II) ions on poly(GMA-*co*-EGDMA)-teta with particle size 150 < *D* < 500 µm (left) and *D* < 150 µm (right)

with particle size 150 < *D* < 500 µm and *D* < 150 µm) for Cu(II), Ni(II), Co(II) and Cd(II) ions under competitive conditions are listed in Table 4.

The uptake of SGE-10/16-deta for all ions increases with increasing pH. In the whole pH range SGE-10/16-deta is highly selective for Cu(II) over other metal ions ions. At pH 5 the selectivity for Cu(II) over Cd(II) was 3:1 and for Cu(II) over Ni(II) and Co(II) was 6:1. It is obvious that ligand type influences the sorption capacity and selectivity of amino-functionalized poly(GMA-*co*-EGDMA). Namely, although the sorption capacity of SGE-10/16-teta is higher for Cu(II) than for Ni(II), Co(II) and Cd(II), it is obvious that SGE-10/16-deta is far more selective for Cu(II) ions. The maximum sorption capacities of all metal ions are considerably higher for SGE-10/16-deta in comparison with SGE-10/16-teta (Table 4).

High selectivity for Cu(II) over other heavy metal ions at higher pH values was observed for poly(GMA-*co*-EGDMA)-en [6], as well for glycidyl methacrylate based copolymers with pyrazole and bis(benzimidazole) ligands [4, 26, 27]. Competitive experiments on poly(GMA-*co*-EGDMA) with imidazole, 1,2,4-triazole and tetrazole ligands also showed high selectivity for Cu(II) ions in the whole pH range [24].

It was shown that particle size of poly(GMA-*co*-EGDMA) functionalized with triethylene tetramine affects sorption capacities. Namely, decrease in the particle size from 150 < *D* < 500 µm to *D* < 150 µm resulted in the increase of sorption capacities for all metal ions. Bearing in mind that sorption of metal ions predominantly occurs on the surface of amino-functionalized particles, enhanced sorption capacities of sample SGE-10/16-teta-**b** can be ascribed to the higher available specific surface area (Table 1) and consequently, higher concentration of amino groups on the particle surface.

**Table 4** Maximum capacities of poly(GMA-*co*-EGDMA)-deta and poly(GMA-*co*-EGDMA)-teta for Cu(II), Ni(II), Co(II) and Cd(II) ions under competitive conditions (sorption time: 30 min, pH 5.1)

| Metal ions | $Q_{max}$, mmolg$^{-1}$ | | |
|---|---|---|---|
| | SGE-10/16-deta 150 < *D* < 500 µm | SGE-10/16-teta-**a** 150 < *D* < 500 µm | SGE-10/16-teta-**b** *D* < 150 µm |
| Cu(II) | 1.19 ± 0.01 | 0.77 ± 0.005 | 0.91 ± 0.01 |
| Ni(II) | 0.20 ± 0.01 | 0.19 ± 0.01 | 0.27 ± 0.02 |
| Co(II) | 0.20 ± 0.01 | 0.068 ± 0.006 | 0.20 ± 0.01 |
| Cd(II) | 0.38 ± 0.03 | 0.53 ± 0.004 | 0.71 ± 0.004 |

In the second series of experiments, the influence of the presence of different metal ions on the selectivity of poly(GMA-*co*-EGDMA)-teta was studied. Competitive sorption of Cr(VI), Ni(II), Co(II) and Cd(II) ions were performed on SGE-10/16-teta-**b** (fraction with particle size *D* < 150 µm). The results are given in Fig. 8. The maximum capacities under competitive conditions and corresponding pH values are listed in Table 5.

As seen from Fig. 7, the replacement of Cu(II) with Cr(VI) in the mixed salt solution resulted in the changed selectivity of poly(GMA-*co*-EGDMA) functionalized with triethylene tetramine. Namely, in the pH range 1.8–6, Cr(VI) is preferentially taken up by SGE-10/16-teta-**b**, with maximum sorption at pH 1.8.

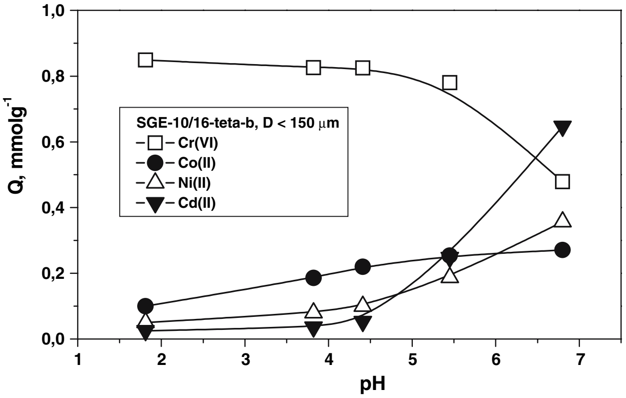


**Fig. 8** Competitive sorption of Cr(VI), Co(II), Ni(II) and Cd(II) ions on poly(GMA-*co*-EGDMA)-teta (particle size *D* < 150 µm)

**Table 5** Maximum capacities of poly(GMA-*co*-EGDMA)-teta for Cr(VI), Ni(II), Co(II) and Cd(II) ions under competitive conditions (sorption time: 30 min)

| Metal ions | pH | $Q_{\max}$, mmolg$^{-1}$ |
|---|---|---|
| | | SGE-10/16-teta-**b** $D < 150$ µm |
| Cr(VI) | 1.8 | 0.85 ± 0.02 |
| Ni(II) | 6.8 | 0.35 ± 0.03 |
| Co(II) | 6.8 | 0.26 ± 0.01 |
| Cd(II) | 6.8 | 0.64 ± 0.02 |

At pH 1.8 the selectivity for Cr(VI) over Ni(II), Co(II) and Cd(II) ions was 8.5:1.

The results indicate that if the sorption conditions are suitably chosen, metal ions of interest can be separated from mixed solutions. Previous experiments showed that poly(GMA-*co*-EGDMA)-en has high selectivity for Pt(IV) of 13:1 over Cu(II), Co(II), Ni(II) and Pb(II) ions at pH 2.1 [6].

## Conclusions

Macroporous crosslinked poly(GMA-*co*-EGDMA) with attached ethylene diamine, dietylene triamine and triethylene tetramine was used for the removal of heavy and precious metals from aqueous solutions. Additional reaction with amines causes considerable alternation of porosity parameters of poly(GMA-*co*-EGDMA). The most pronounced increase of specific surface area (75%) was observed for poly(GMA-*co*-EGDMA)-teta sample with smaller particles ($D <$ 150 µm). The sorption of Cu(II) ions was found to be very rapid and depends on porosity of amino-functionalized samples and type of ligand. For poly(GMA-*co*-EGDMA)-deta and poly(GMA-*co*-EGDMA)-teta, $t_{1/2}$ values were around 3 min.

Experiments under competitive conditions indicate selectivity of poly(GMA-*co*-EGDMA)-deta for Cu(II) over Cd(II) of 3:1 and for Cu(II) over Ni(II) and Co(II) of 6:1. Functionalization of poly(GMA-*co*-EGDMA) with bulkier ligand, triethylene tetramine, showed no improvement in sorption performances of poly(GMA-*co*-EGDMA)-teta in comparison with poly(GMA-*co*-EGDMA)-deta. The decrease in particle size of poly(GMA-*co*-EGDMA)-teta from $150 < D < 500$ µm to $D < 150$ µm resulted in the increase of sorption capacities for all metal ions.

The replacement of Cu(II) with Cr(VI) ions in the mixed salt solution resulted in the changed selectivity of poly(GMA-*co*-EGDMA)-teta. Namely, in the pH range 1.8–6, Cr(VI) is preferentially taken up by SGE-10/16-teta-**b**, with maximum sorption at pH 1.8. At pH 1.8, the selectivity of poly(GMA-*co*-EGDMA)-teta with particle size of $D < 150$ µm for Cr(VI) over Ni(II), Co(II) and Cd(II) ions was 8.5:1.

The results presented in this study indicate that amino-functionalized macroporous poly(GMA-*co*-EGDMA) can be used as effective and environmental friendly chelating copolymer for sorption of heavy metal ions from aqueous solutions.

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