



Kinetics of hexavalent chromium sorption on amino-functionalized macroporous glycidyl methacrylate copolymer

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ABSTRACT

Two samples of macroporous crosslinked poly(glycidyl methacrylate-co-ethylene glycol dimethacrylate), poly(GMA-co-EGDMA), with different porosity parameters were synthesized by suspension copolymerization and functionalized with ethylene diamine and diethylene triamine. The kinetics of Cr(VI) sorption by amino-functionalized poly(GMA-co-EGDMA) was investigated under non-competitive conditions. Competitive kinetics was studied from following multicomponent solutions: Cu(II) and Cr(VI); Cu(II), Co(II), Cd(II) and Ni(II); Cr(VI), Cu(II), Co(II) and Cd(II) solutions. Two kinetic models (the pseudo-first and pseudo-second-order) were used to determine the best-fit equation for the metals sorption by poly(GMA-co-EGDMA)-en and poly(GMA-co-EGDMA)-deta.

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1. Introduction

Due to their extreme toxicity, the effective removal of Cr(VI) from industrial waste waters is an issue of major environmental concern. Since Cr(VI) cannot be destroyed in the natural environment, development of technologies that can remove and/or recover this metal from the waste waters is in constant focus of the researchers throughout the world. Conventional methods, like precipitation, electro winning, membrane separation, evaporation and solvent extraction suffer from some drawback; since they are ineffective, expensive, generate secondary pollution, etc. [1,2]. On the other hand, chelating polymers are preferred due to their high efficiency, easy handling, reusability and cost effectiveness [3]. They consist of crosslinked copolymer as a solid support and functional group (ligand) containing N, O, S and P donor atoms capable for coordinating of different metal ions. In the relatively simple process, chelating copolymer is contacted with the contaminated solution, loaded with metal ions, and stripped with appropriate eluent.

Macroporous copolymers based on glycidyl methacrylate are very suitable for preparation of chelating sorbents, as they can be prepared by suspension copolymerization in form of spherical beads with desired size and porous structure which can be

adjusted by the variation of the type and the amount of inert component and the type and the amount of crosslinking polymer in the reaction mixture [3–6]. Additionally, the attractiveness of these copolymers originates from the fact that the epoxy group in GMA molecule can easily be transformed into a variety of groups, like iminodiacetate [7,8], thiol [9,10], dithiocarbamate [11], etc. Amino-functionalized glycidyl methacrylate copolymers have been obtained by reaction of epoxy groups of the copolymer with ammonia [12], ethylene diamine [9,12–17], diethyl amine [18], diethylene triamine [19,20], triethylene tetramine [21], etc. These copolymers possess high capacity and good selectivity for the precious and heavy metal ions, combined with chemical and mechanical stability [22].

In this study, two samples of poly(glycidyl methacrylate-co-ethylene glycol dimethacrylate) [abbreviated poly(GMA-co-EGDMA)], SGE-10/12 and SGE-10/16, with different porosity were synthesized by suspension copolymerization in the presence of inert component and additionally functionalized via ring-opening reaction of the pendant epoxy groups with ethylene diamine and diethylene triamine.

The sorption kinetics of Cr(VI) and four heavy metals: Cu(II), Co(II), Cd(II) and Ni(II), was studied under non-competitive (from single-component metal salt solutions) and competitive conditions (from mixed metal salt solutions). Kinetic data were analyzed using two sorption kinetic models (pseudo-first and pseudo-second-order) to determine the best-fit equation for heavy metal sorption onto amino-functionalized poly(GMA-co-EGDMA).

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2. Experimental

2.1. Materials and methods

All the chemicals were used as received: glycidyl methacrylate (GMA) (Merck), ethylene glycol dimethacrylate (EGDMA) (Fluka), ethylene diamine (EDA) (Fluka), diethylene triamine (DETA) (Merck), 2,2'-azobisisobutyronitrile (AIBN) (Merck), poly(N-vinyl pyrrolidone) (Kollidone 90, BASF), cyclohexanol (Merck), dodecanol and hexadecanol (Merck), copper chloride (Kemika), cobalt chloride (Carlo Erba), nickel chloride (Carlo Erba), cadmium sulphate (Kemika) and potassium dichromate (Sigma Aldrich). All solutions were prepared using deionized water.

The copolymer samples were analyzed for their carbon, hydrogen and nitrogen content using the Vario EL III device (GmbH Hanau Instruments, German) [23]. Elemental analysis was calculated from multiple determinations within $\pm 0.2\%$ agreement.

The pore size distributions of samples were previously determined by mercury porosimetry (Carlo Erba 2000, software Milestone 200) [7,23]. The metals concentration 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.

2.2. Preparation of poly(GMA-co-EGDMA)

Macroporous poly(GMA-co-EGDMA) samples were prepared by a radical suspension copolymerization [7]. The monomer phase (79.7 g) containing monomer mixture (20.7 g of GMA and 13.8 g of EGDMA), 2,2'-azobisisobutyronitrile (AIBN) as an initiator (0.8 g), and 45.2 g of inert component (40.7 g of cyclohexanol and 4.5 g of dodecanol for SGE-10/12 and hexadecanol for SGE-10/16) was suspended in the aqueous phase consisting of 240.0 g of water and 2.4 g of poly(N-vinyl pyrrolidone). In the labels letter S designates 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 (w/w) 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, kept in ethanol for 12 h, dried in vacuum at 40° C and purified by Soxhlet extraction with ethanol. The fraction with average particle diameter in the range 0.15–0.50 mm was used in subsequent reactions.

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

Four grams of poly(GMA-co-EGDMA) (sample SGE-10/12), 10.0 g of ethylene diamine and 100 cm³ of toluene were left at room temperature for 24 h [23]. The reaction mixture was heated at 80° C for 6 h. Modified sample was filtered, washed with ethanol, dried and labeled as SGE-10/12-en (-en designate sample modified with ethylene diamine).

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

A mixture of 3.6 g of poly(GMA-co-EGDMA) (sample SGE-10/16), 15.7 g of diethylene triamine and 100 cm³ of toluene was left at room temperature for 24 h, then heated at 80° C for 6 h [23]. Modified sample was filtered, washed with ethanol, dried and labeled as SGE-10/16-deta (-deta designate sample modified with diethylene triamine).

2.5. Metal sorption batch experiments

Sorption of metal ions from aqueous solutions (initial metal concentration 0.05 M, pH 1.8) was investigated in batch experiments under non-competitive and competitive conditions, at room temperature. The reproducibility of the sorption experiments results was verified in triplicate.

The amount of metal ions sorbed onto unit mass of macroporous copolymer beads (sorption capacity, mmol g⁻¹) was calculated from:

$$Q = \frac{(C_0 - C) \cdot V}{m} \quad (1)$$

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, respectively (in mmol dm⁻³), V is the volume of the aqueous phase (in dm³) and m is the amount of the poly(GMA-co-EGDMA) amino-functionalized beads used for the experiment (in g).

For determination of Cr(VI) sorption rate from single-component salt solution, 0.25 g of copolymer was contacted with 25 cm³ of metal salt solution. Cu(II) and Cr(VI) sorption rates from binary salt solutions were determined by contacting 0.5 g of copolymer with 50 cm³ of mixed metal salt solution (25 cm³ of each metal solution), while Cu(II), Cr(VI), Co(II) and Cd(II) sorption rates were determined by contacting 20 cm³ of metal salt solution (5 cm³ of each metal solution).

In each experiment, at appropriate times, 0.5 cm³ of aliquots were removed and diluted to 50 cm³. The concentrations of the metal ions in the aqueous phases were measured by atomic absorption spectrometry (AAS).

3. Results and discussion

The immobilization of low molecular compounds to homopolymers and copolymers can be achieved in two commonly used ways: copolymerization of suitable monomer that already carries the required functional group and chemical modification of synthesized polymer in order to introduce chelating groups. In this study, chemical modification was chosen as a method to introduce amino ligands into macroporous poly(GMA-co-EGDMA). On the basis of our previous results, samples SGE-10/12 ($S_{Hg} = 50 \text{ m}^2 \text{ g}^{-1}$, $V_S = 0.610 \text{ cm}^3 \text{ g}^{-1}$, $D_{V/2} = 53 \text{ nm}$) [7] and SGE-10/16 ($S_{Hg} = 33 \text{ m}^2 \text{ g}^{-1}$, $V_S = 0.755 \text{ cm}^3 \text{ g}^{-1}$, $D_{V/2} = 87 \text{ nm}$) [7] were chosen for amino-functionalization and metal sorption experiments. Porosity parameters (specific pore volume, V_S , specific pore area, S_{Hg} , and pore diameter that corresponds to the half of the pore volume, $D_{V/2}$) of amino-functionalized samples are given in Table 1 [23].

The elemental analysis data of amino-functionalized samples, as well as degree of conversion of epoxy groups, ligand concentration, C_{LIG} , and amino group concentration, C_{AG} , were given in Table 2. The lower degree of conversion was obtained for sample functionalized with diethylene triamine, probably due to a steric effect, which is one of the main problems in polymer functionalization with larger groups [24].

3.1. Kinetics

The important physicochemical aspects for the evaluation of applicability of chelating copolymers are specific and fast complex-

Table 1
Porosity parameters of amino-functionalized samples [23].

Sample	S_{Hg} , m ² /g	V_S , cm ³ /g	$D_{V/2}$, nm
SGE-10/12-en	70 ± 0.4	1.18 ± 0.01	42 ± 0.6
SGE-10/16-deta	50 ± 0.3	0.66 ± 0.005	60 ± 0.4

Table 2

Elemental analysis of amino-functionalized poly(GMA-co-EGDMA) samples, as well as the degree of conversion of epoxy groups, ligand concentration, C_{LIG} , and amino group concentration, C_{AG} [23].

Sample	Found			Calculated			C_{LIG} , mmol g ⁻¹	Conv., %	C_{AG} , mmol g ⁻¹
	% C	% H	% N	% C	% H	% N			
SGE-10/12-en	52.6	8.5	6.1	56.3	8.2	8.4	2.2 ± 0.004	52 ± 0.08	4.4 ± 0.009
SGE-10/16-deta	50.2	10.1	6.8	56.3	8.2	8.4	1.6 ± 0.003	38 ± 0.08	4.9 ± 0.008

^a Elemental analysis was calculated from multiple determinations within ±0.2% agreement.

Table 3

The sorption half time, $t_{1/2}$, sorption capacities after 5 min (Q_5) and 30 min (Q_{30}), maximum sorption capacities (Q_{max}) and maximum ligand occupation (L_{max}) for metal sorption on amino-functionalized poly(GMA-co-EGDMA) samples.

Copolymer sample	pH	$t_{1/2}$, min	Q_5 , mmol g ⁻¹ (%) ^a	Q_{30} , mmol g ⁻¹ (%) ^a	Q_{max} , mmol g ⁻¹	Q_{max} , g g ⁻¹	L_{max} , %
Non-competitive conditions							
Cr(VI) single-component solution							
SGE-10/12-en	1.8	1.0	1.84 (90)	2.11 (100)	2.11	0.110	96.8
SGE-10/16-deta	1.8	0.4	1.15 (78)	1.37 (93)	1.48	0.094	67.9
Competitive conditions							
Cr(VI) and Cu(II) binary solution							
SGE-10/16-deta							
Cr(VI)	1.8	11	0.26 (26)	0.76 (76)	1.00	0.052	61.7
Cu(II)	1.8	45	0.072 (13)	0.22 (40)	0.55	0.035	33.9
Cr(VI), Cu(II), Co(II) and Cd(II) multi-component solution							
SGE-10/16-deta							
Cr(VI)	1.0	1.6	0.27 (63)	0.22 (63)	0.43	0.024	26.5
Cu(II)	1.0	2.5	0.22 (63)	0.26 (74)	0.35	0.022	21.6
Co(II)	1.0	1.2	0.11 (79)	0.14 (100)	0.14	0.008	8.6
Cd(II)	1.0	1.2	0.11 (73)	0.11 (100)	0.15	0.017	9.3

^a Calculated in relation to Q_{max} .

ation of the metal ions, as well as their regeneration and reusability [25]. Consequently, the rapid sorption of metal ions by functionalized poly(GMA-co-EGDMA) would be beneficial for practical use, providing a short solution–sorbent contact time in the actual process.

3.2. Non-competitive conditions

The sorption rates for Cr(VI) ions by SGE-10/12-en and SGE-10/16-deta are presented in Fig. 1. Since those samples have different ligand concentrations, in order to provide a more appropriate comparison, maximum ligand occupation, L_{max} , was

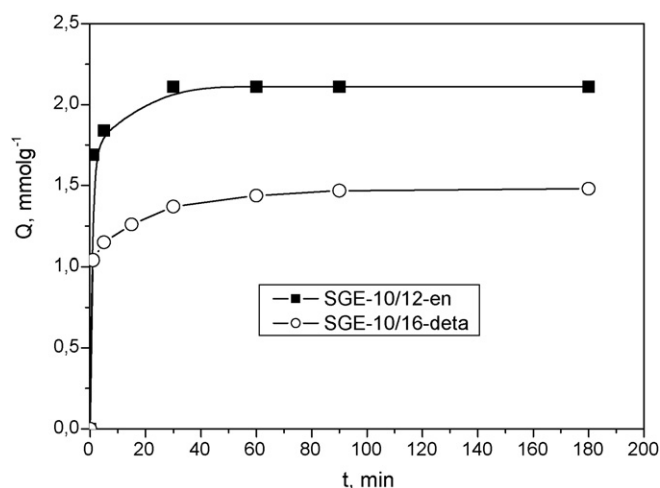


Fig. 1. Sorption of Cr(VI) ions vs. time under non-competitive conditions, on SGE-10/12-en and SGE-10/16-deta.

calculated [26]:

$$L_{max} = \frac{Q_{max}}{C_{LIG}} \cdot 100 \quad (2)$$

From the experimental data, sorption half time, $t_{1/2}$ (time required to reach 50% of the total sorption capacity) and maximum ligand occupation (L_{max}) were calculated and given in Table 3, with the values of the maximum sorption capacities (Q_{max}), sorption capacities after 5 min (Q_5) and 30 min (Q_{30}), taken from Fig. 1.

The uptake of Cr(VI) ions was very rapid, with $t_{1/2}$ value of ≤1 min. Somewhat faster sorption was observed for SGE-10/12-en for which after 30 min maximum sorption capacity was attained. Also, ligand occupation was lower for SGE-10/16-deta (68%) than for SGE-10/12-en (97%), i.e. for the sample with 1.4 times higher surface area (the values of specific surface area for SGE-10/12-en and SGE-10/16-deta as given in Table 1 were 70 and 50 m² g⁻¹, respectively). It is in accordance with literature data, which suggest that when the initial sorption rate is high, the sorption process occurs predominantly at the surface of the highly crosslinked amino-functionalized beads [27]. 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.

Here must be mentioned that poly(GMA-co-EGDMA) was functionalized with two different amines, i.e. ethylene diamine (sample SGE-10/12-en) and diethylene triamine (sample SGE-10/16-deta), so the assumption was that we cannot exclude the influence of the ligand, especially if we bear in mind previous results [23]. Indeed, sorption capacity seems to be influenced by the ligand type and this is clear when the values of specific surface area and pore diameters are the same, like in case of samples SGE-10/16-en, SGE-10/16-deta and the sample functionalized with triethylene tetramine, SGE-10/16-teta (S_{Hg} around 50 m² g⁻¹, $D_{V/2}$ 30 nm). According to the previously obtained results, maximum capacities for Cu(II) ions on

SGE-10/16-deta and SGE-10/16-teta were 1.75 times higher than for SGE-10/16-en [23]. On the other hand, sorption rates were similar, with $t_{1/2}$ value for SGE-10/16-en around 4 min, and slightly lower $t_{1/2}$ for SGE-10/16-deta and SGE-10/16-teta, of around 3 min. However, in the case of samples with different surface area used in this study, like SGE-10/12-en ($70 \text{ m}^2 \text{ g}^{-1}$) and SGE-10/16-deta ($50 \text{ m}^2 \text{ g}^{-1}$) it seems that influence of surface area on the sorption rate and capacity becomes dominant.

The reported literature data on Cr(VI) removal with commercial and synthetic polymer sorbents are in a wide range, but they were obtained under different experimental conditions. However, just for the sake of comparison we will mention some of those results. For example, Saha et al. obtained $t_{1/2} \approx 3$ min for Cr(VI) sorption on highly crosslinked acrylic resin Amberlite XAD-7 impregnated with Aliquat 336 [28]. Hydrophilic methacrylic based polymer HP-2MG impregnated with Aliquat 336 sorbed more than 50% of Cr(VI) within the first 10 min [29]. Baran et al. reported that sorption of Cr(VI) attained an optimum at 30 and 40 min for macroporous strongly acidic poly(styrene-co-divinylbenzene) based ion-exchangers Purolite CT-275 and Purolite MN-500; and 30 min for Amberlite XAD-7 [30]. The high sorption rates of hexavalent chromium at the onset, and then plateau values gradually reached within 15 min were observed for macroporous basic anion exchange resins containing tertiary amine groups, Lewatit MP 62 and Lewatit M 610 [31]. Bayramoglu et al. also observed high initial Cr(VI) sorption rate at pH 2, with time required to attain the equilibrium of 120 min both for crosslinked poly(glycidyl methacrylate-co-methyl methacrylate) with attached ethylene diamine [17] and magnetic poly(GMA-co-EGDMA) with immobilized poly(ethyleneimine) [32].

3.3. Competitive conditions

The metal ion uptake capacities and selectivity under competitive conditions, besides agitation (static experiments) or flow rate (column experiments), structural properties of the chelating copolymers (particle size, porosity parameters), sorption conditions (pH, initial concentration of metal ions), ligand type, kinetic and thermodynamic stability of the formed metal complexes with the chemically bonded amine ligands; strongly depend on the presence of the other metal ions which they compete for the active sites in the copolymer [25]. For that reason, it is almost impossible to generalize the order of metal sorption (selectivity) or to predetermine the amount of the adsorbed metal ions on the basis of the results obtained under non-competitive conditions. The decisive role in determination whether polymer could be used for selective sorption or not, has the experiments under comparative conditions.

3.4. Metal sorption from binary solutions

The sorption rates for Cr(VI) and Cu(II) ions under competitive conditions from binary metal solutions were determined for poly(GMA-co-EGDMA)-deta (sample SGE-10/16-deta) and the results are presented in Fig. 2 and Table 3.

It can be seen that Cr(VI) is preferably taken up by SGE-10/16-deta. The main reason could lie in the fact that the experiment was performed at pH 1.8, which is favorable for maximum Cr(VI) sorption. The Cr(VI) exists in anionic forms ($\text{Cr}_2\text{O}_7^{2-}$, HCrO_4^- , CrO_4^{2-} and HCr_2O_7^-) in aqueous solution, and the fraction of any particular species is dependent on chromium concentration and pH [17]. At low pH, protonated amino groups attached to the crosslinked copolymer attract the negatively chromium species, leading to higher sorption. On the other hand, the protonation of amine group leads to a strong electrostatic repulsion to the copper ions and lower sorption capacities for Cu(II) at low pH [17,19]. The curve for Cr(VI) sorption has higher slope comparing with

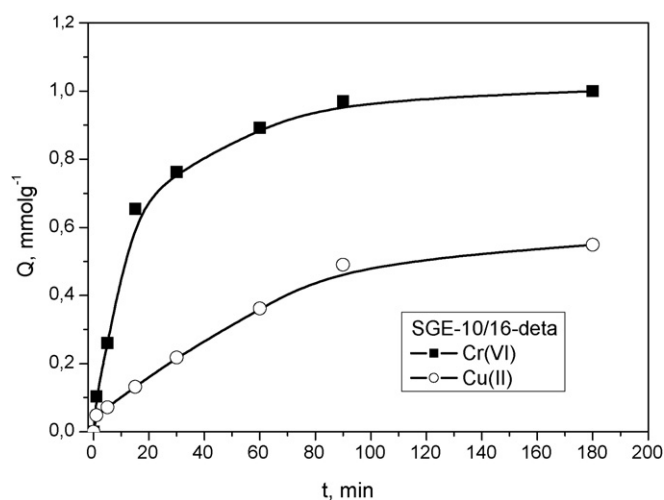


Fig. 2. Sorption of Cr(VI) and Cu(II) ions, vs. time under competitive conditions, on SGE-10/16-deta.

curve for Cu(II), especially within 30 min from the start of the experiment.

It is very important to emphasize that Cr(VI) and Cu(II) sorption for SGE-10/16-deta was much slower from their binary solutions ($t_{1/2}$ values for the uptake of Cr(VI) and Cu(II) ions of 11 and 45 min), than from single-component solutions ($t_{1/2}$ values for Cr(VI) and Cu(II) ions were 0.5 and 3 min [23]). It seems that two highly sorbed metals, Cr(VI) and Cu(II), compete for the active sites (ligands) on the beads and at the same time hinder the metal coordination of concurrent ion from their binary solution. Even though the sorption of both metals was very slow, total ligand occupation for SGE-10/16-deta was 96%.

3.5. Metal sorption from multicomponent solutions

In our previous study, kinetics of competitive sorption of Cu(II), Cd(II), Ni(II) and Co(II) on poly(GMA-co-EGDMA)-deta (sample SGE-10/16-deta) was studied at pH 4, which was favorable for maximum sorption of these metals [33]. Poly(GMA-co-EGDMA)-deta was selective for Cu(II) over other ions present in the mixed salt solution. Namely, maximum capacity for Cu(II) from Cu(II), Cd(II), Ni(II) and Co(II) mixed solution (at pH 4) on poly(GMA-co-EGDMA)-deta was 1.15 mmol g^{-1} , i.e. 1.7; 4.8 and 5.7 times higher than that of Cd(II), Co(II) and Ni(II), respectively.

Due to the fact that non-competitive experiments on poly(GMA-co-EGDMA)-deta showed fast kinetics and high sorption capacity for Cr(VI) ions, Ni(II) ions were replaced with Cr(VI), and metal uptake was investigated from the multicomponent solution of Cr(VI), Cu(II), Cd(II) and Co(II) (Fig. 3, Table 3).

It should be noted that this experiment was performed at pH 1.80, which is not favorable for Cu(II), Co(II) and Cd(II) sorption, as already mentioned. On the contrary, the maximum sorption capacities of amino-functionalized poly(GMA-co-EGDMA) for these metals were observed for pH 5.5 [15,33]. Namely, with the pH increase more amino groups exist in the neutral form, reducing the electrostatic repulsion to the copper, cobalt and cadmium ions [19]. As a result, at higher pH values there is an increase in Cu(II), Co(II) and Cd(II) sorption. The main reason for choosing pH 1.80 was our intention to study Cr(VI) sorption by amino-functionalized macroporous poly(GMA-co-EGDMA) as well as to investigate the influence of Cr(VI) on the sorption of other metal ions, and to compare the results of Cr(VI) sorption from single and Cr(VI)/Cu(II) binary solution, so we have chosen pH at which the maximum Cr(VI) sorption capacity was observed [23].

Table 4
Kinetic data for heavy metals sorption on poly(GMA-co-EGDMA)-en and poly(GMA-co-EGDMA)-deta.

Sample	Pseudo-first-order kinetics				Pseudo-second-order kinetics		
	$Q_{e,exp}$, mmol g ⁻¹	k_1 , min ⁻¹	Q_{eq} , mmol g ⁻¹	R^2	k_2 , gmmol ⁻¹ min ⁻¹	Q_{eq} , mmol g ⁻¹	R^2
Non-competitive conditions							
Cr(VI) single-component solution							
SGE-10/12-en	2.11	0.325	5.69	0.632	1.508	2.11	0.999
SGE-10/16-deta	1.48	0.004	0.57	0.916	0.362	1.49	0.999
Competitive conditions							
Cr(VI) and Cu(II) binary solution							
SGE-10/16-deta							
Cr(VI)	1.00	0.037	0.84	0.979	8.23·10 ⁴	1.07	0.999
Cu(II)	0.55	0.023	0.57	0.961	0.034	0.68	0.931
Cr(VI), Cu(II), Co(II) and Cd(II) multi-component solution							
SGE-10/16-deta							
Cr(VI)	0.43	0.048	0.23	0.963	0.761	0.44	0.999
Cu(II)	0.35	0.020	0.18	0.813	0.409	0.35	0.993
Co(II)	0.14	0.085	0.07	0.853	5.25	0.14	0.999
Cd(II)	0.15	0.047	0.05	0.779	4.90	0.15	0.999

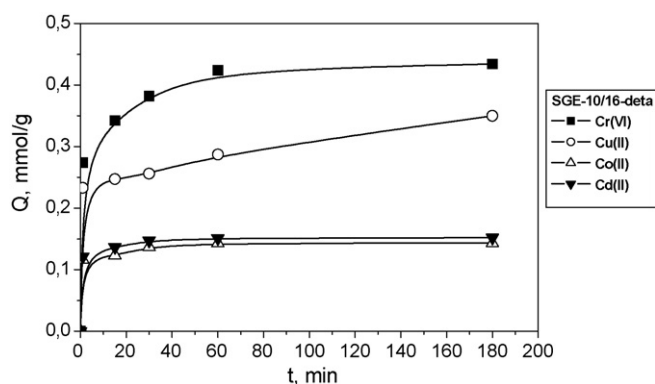


Fig. 3. Sorption of Cr(VI), Cu(II), Co(II) and Cd(II) vs. time under competitive conditions on SGE-10/16-deta.

Sorption of all metals was very fast, with $t_{1/2} \leq 2$ min for Cr(VI), Co(II) and Cd(II) and 2.5 min for Cu(II). It can be seen that $t_{1/2}$ values and maximum capacities were quite different comparing with the results obtained with Cu(II), Cd(II), Ni(II) and Co(II) mixed solution. In that case, the $t_{1/2}$ values for the uptake of Cu(II) and Cd(II) on poly(GMA-co-EGDMA)-deta were approximately 8 and 3.5 min, while $t_{1/2}$ values for Ni(II) and Co(II) were similar, i.e. around 5 min [33]. Also, Cu(II) and Cr(VI) sorption was considerably faster from multicomponent Cr(VI), Cu(II), Cd(II) and Co(II), than from binary Cr(VI) and Cu(II) solution. The presence of Co(II) and Cd(II) that are not preferentially taken by SGE-10/16-deta

enhances Cr(VI) and Cu(II) sorption compared with the sorption from their binary solution. Inversely, the presence of Cr(VI) promotes the sorption of cobalt and cadmium which are not so fast bound from the mixed Cu(II), Co(II), Cd(II) and Ni(II) solution. Although metals were sorbed slower from mixed Cu(II), Co(II), Cd(II) and Ni(II) solution, the total amount of bonded metals was twice higher (2.22 mmol g⁻¹) than from Cr(VI), Cu(II), Cd(II) and Co(II) solution (1.07 mmol g⁻¹). It seems that in the case of competitive sorption, pH and the presence of other metals have the most pronounced influence on the values of sorption rate and capacities.

3.6. Kinetic models

Two kinetic models were used to determine the best-fit equation for the metals sorption by poly(GMA-co-EGDMA)-en and poly(GMA-co-EGDMA)-deta.

The most commonly used is Lagergren's equation for pseudo-first-order rate [34]:

$$\log(Q_{eq} - Q_t) = \log Q_{eq} - \frac{(k_1 t)}{2.303} \quad (3)$$

where k_1 is the rate constant of pseudo-first-order sorption (min⁻¹), Q_{eq} and Q_t denote the amounts of sorbed metal ions at equilibrium and at time t (mmol g⁻¹), respectively. A plot of $\log(Q_{eq} - Q_t)$ versus t should give a straight line to confirm the applicability of the kinetic model. In a true first-order process, $\log(Q_{eq} - Q_t)$ should be equal to the intercept of a plot $\log(Q_{eq} - Q_t)$ against t .

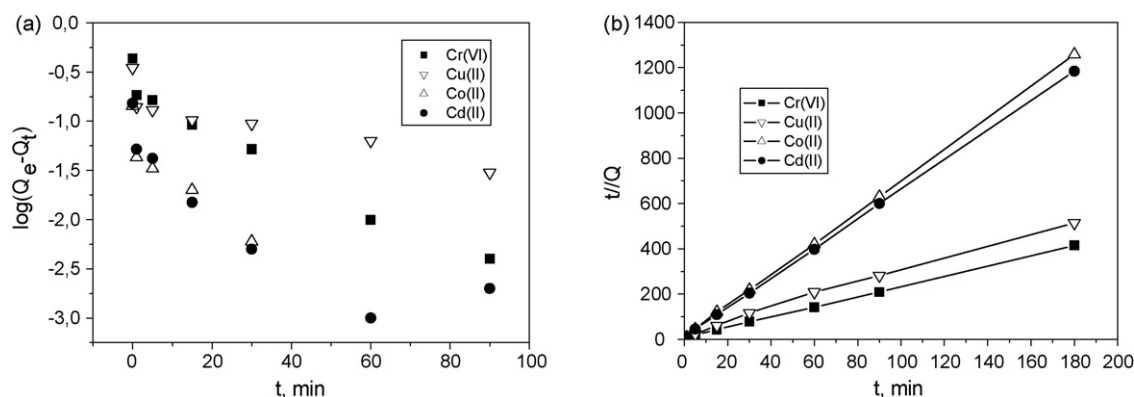


Fig. 4. Pseudo-first (a) and pseudo-second-order kinetics (b) of the Cr(VI), Cu(II), Cd(II) and Co(II) solution ions uptake by SGE-10/16-deta.

A pseudo-second-order equation is given as [34]:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_{eq}^2} + \frac{1}{Q_{eq}} t \quad (4)$$

where k_2 ($\text{g}^{-1} \text{mmol}^{-1} \text{min}^{-1}$) is the rate constant of pseudo-second-order sorption. A plot of t/Q_t versus t should give a linear relationship for the second-order kinetics.

The rate constants k_1 and k_2 , equilibrium sorption capacity, Q_{eq} , and the correlation coefficient, R^2 , calculated from the values of intercepts and slopes of corresponding plots for pseudo-first and second-order equations are given in Table 4. As an illustration, plots $\log(Q_{eq} - Q_t) - t$ (pseudo-first-order) and $t/Q_t - t$ (pseudo-second-order) for competitive sorption of Cr(VI), Cu(II), Cd(II) and Co(II) ions by SGE-10/16-deta were shown in Fig. 4.

The theoretical Q_{eq} values estimated from the first-order kinetic model gave significantly different values compared to experimental ones, and correlation coefficients are found to be rather low. The only exception is competitive Cu(II) sorption from binary Cr(VI)/Cu(II) solution on SGE-10/16-deta, for which the correlation coefficient is slightly lower and Q_{eq} value higher than experimental one for pseudo-second-order. This indicates that the first-order kinetic model is not applicable to the sorption of tested metals on amino-functionalized samples.

On the other hand, theoretical Q_{eq} values for metal ions show good agreement with the experimental data for second-order kinetics, with correlation coefficients higher than 0.99 (with one exception, already mentioned). This suggests that heavy metals sorption under competitive conditions on poly(GMA-co-EGDMA)-deta obeys pseudo-second-order kinetics, meaning that sorption depends both on the properties of the metal and chelating copolymer.

4. Conclusions

Macroporous crosslinked samples of poly(GMA-co-EGDMA) with different porosity were synthesized by suspension copolymerization and functionalized with ethylene diamine and diethylene triamine. The uptake of Cr(VI) ions under non-competitive conditions was very rapid ($t_{1/2} \leq 1$ min), presumably because the sorption process occurs predominantly at the surface of amino-functionalized beads. In such a case, the influence of surface area on the sorption rate and capacity becomes dominant. The Cr(VI) and Cu(II) sorption was much slower from their binary solutions ($t_{1/2}$ for Cr(VI) and Cu(II) were 11 and 45 min) than from single-component solutions ($t_{1/2}$ for Cr(VI) and Cu(II) were 0.5 and 3 min) probably due to their mutual competition for the active sites on the copolymer beads. In the case of competitive sorption, pH and the presence of other metals have the most pronounced influence on the values of sorption rate and capacities. From the analysis of two kinetic models it was concluded that sorption of investigated heavy metals by amino-functionalized poly(GMA-co-EGDMA) obeys pseudo-second-order kinetics, meaning that sorption depends both on the properties of the metal and chelating copolymer.

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