Polyacrylate anion exchangers in sorption of heavy metal ions with non-biodegradable complexing agents

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A B S T R A C T

The polyacrylate anion exchangers are widely used in purification of heavy metal ions from wastewaters and different accompanying complexing agents. Such effluents containing the chelators (EDTA, NTA, HEDTA, DTPA, and IDA) are discharged from relevant industries such as printed circuits boards, plating on plastics, metal finishing and others. The sorption was studied as a function of phase contact time and pH by the batch technique. It was found that the removal of heavy metal ions in the presence of EDTA, NTA and IDA strictly depends on the phase contact time and pH values. Various kinetic models such as the pseudo first-order and the pseudo second-order as well as the intraparticle one were also tested to estimate the sorption rate. The equilibrium capacities of the studied anion exchangers for Cu(II), Zn(II), Co(II), Ni(II), Pb(II) and Cd(II) in the presence of EDTA were the highest for Pb(II) and Cd(II). The order of sorption for Amberlite IRA 458, Amberlite IRA 958 as well as Amberlite IRA 67 can be as follows: Pb(II) > Cd(II) > Zn(II) > Cu(II) > Ni(II) > Co(II). The stability of forming complexes was also compared. The estimation of the capacities of anion exchangers under investigation by the continuous column studies was also carried out.

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1. Introduction

Aminopolycarboxylic acids (APCAs) are one of the most important groups of organic compounds which are able to bind metal ions. As they form strong and water soluble complexes with various cations, they are also known as chelating agents or just chelators. Chelating agents containing several carboxylate groups linked to one or several nitrogen atoms form one or more heteroatomic rings, which decides about higher stability of the complexes as compared to those in which such rings are not present.

The wastewaters containing heavy metal ions as well as complexing agents constitute a particular group of wastewaters. For example, ethylenediaminetetraacetic acid (EDTA) and nitrilotriacetic acid (NTA) are widely applied in many industries where industrial, pharmaceutical and agricultural purposes including metal, textile, leather, rubber, food, cosmetic, paper and textile production are the most important [1,2]. In these processes, they control the availability and accessibility of metal ions to prevent from formation of precipitates, metal-catalysed reactions. They are also used for removing metal ions and in some cases increasing metal ions availability. Therefore they are present in almost all anthropogenically influenced streams and rivers in industrialized countries. Many of the investigated synthetic complexing
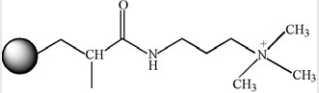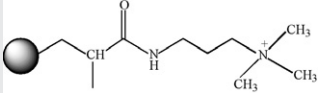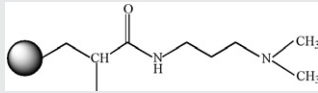
agents can be classified as environmentally relevant, since they are poorly microbiologically degradable and exhibit excellent water solubility. According to Sỳkora and Nowak [3,4], EDTA has been measured in rivers at mean concentrations ranging from 0.01 to 0.1 μM. One important process for the fate of EDTA is the photodegradation of the [Fe(edta)]⁻ complex [5–7]. The rapid photodegradation of this complex results in a mean half-life of EDTA in river waters for a few hours in summer and for several days in winter [8,9]. Under successive decarboxylation a stepwise degradation leads to ethylenediaminetriacetate, ethylenediaminediacetate and ethylenediaminemonoacetate. Complexes of EDTA with metal ions such as Zn(II), Cu(II), Ca(II), Mg(II), Ni(II) and Mn(II), are either stable in sunlight or occur at concentrations too low to contribute significantly to the overall degradation of EDTA in surface waters [10].

Contrary to EDTA, NTA is readily biodegradable. In the countries using NTA to replace sodiumtripolyphosphate, concentrations of NTA in domestic sewages are between 10 and 20 mg/L, even as high as 35 mg/L in the areas of hard water. The rate of biodegradability is largely influenced by microorganisms, temperature, dissolved oxygen concentration in water, NTA concentration and water hardness [11–13]. In the paper by Bolton et al. [14], the order of degradation rates was: Hnta²⁻ (40% h⁻¹) > [Co(nta)]⁻ = [FeOH(nta)]⁻ = [Zn(nta)]⁻ > [AlOH(nta)]⁻ > [Cu(nta)]⁻ > [Ni(nta)]⁻ (2% h⁻¹). Although NTA appears not to be of such concern to the environment because of being readily biodegradable, its presence in many products excludes the award

Table 1
The physicochemical properties of studied anion exchangers.

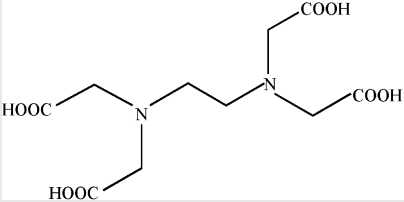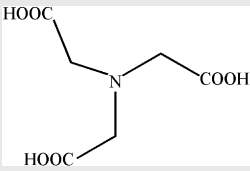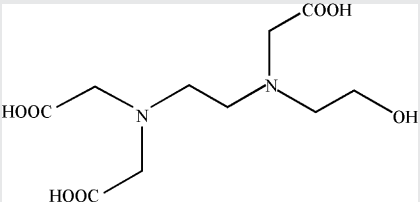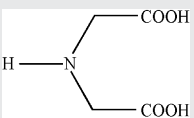| Properties	Amberlite IRA 458	Amberlite IRA 958	Amberlite IRA 67
Appearance	White, translucent	White, translucent	Yellow, translucent
Matrix	A-DVB, gel, type 1	A-DVB, macroporous, type 1	A-DVB, gel, type 1
Structure			
Bead size	600–900 µm	675–875 µm	550–750 µm
Capacity	1.25 meq/mL	0.80 meq/mL	1.6 meq/mL
Operating pH range	0–14	0–14	0–7
Thermal stability	373 K	373 K	343 K

of an eco-label due to its potential carcinogenicity. In 2006 the Commission's Working Group on the Classification and Labelling of Dangerous Substances decided to classify NTA and its salts as a Category 3 Carcinogen with an R 40 label (limited evidence of a carcinogenic effect) [15].

Nowadays the most common treatment method for effective removal of heavy metal ions as well as complexing agents in one step is sorption using ion exchangers. The studies carried out in the USA in the end of the seventies of the past century showed that among anion exchange resins, those with the acrylic polymer skeleton have better qualities than the polystyrene ones, for example, high anion exchange capacities and the resistance to the fall. They are also characterised by high resistance to the osmotic shock, quick kinetic exchange and greater basicity. As follows from the literature data, introduction of the acrylic molecule (acrylic acid and methacrylic acid, acrylic acid esters, acrylonitrile) for the preparation of this type of ion exchangers eliminates the interaction of an aromatic matrix with the aromatic moieties, e.g. pollutants.

Owing to their unique properties, polyacrylate anion exchangers can be applied for deacidification, deionization and desalination of water where the removal of strong mineral acids and adsorption of organics are desired [16–19]. Anion exchangers of this type are successfully used for removal of potentially carcinogenic chlorinated hydrocarbons such as trihalomethanes (THMs) when disinfection is carried out with chlorine [19]. It was found that strongly basic polyacrylate anion exchangers, e.g. Amberlite IRA 458 are more effective for removal of trace organic compounds from drinking water than adsorbents. Weakly basic polyacrylate anion exchangers are also of significant importance. Because of their low basicity, they exchange efficiently only anions of strong acids. They have higher values of anion exchange capacities and fall to a much lower degree than polystyrene resins do when applied where high levels of organic compounds are present [19]. As follows from the literature data, the resins of 60% water content or more, namely Amberlite IRA 458 and Amberlite IRA 958 possess more polar structures than type 1 of polystyrene resins of low water content used in common ion exchange applications. Because of the presence of heteroatoms in the bridge between the exchange site and the polymer backbone, a secondary amino group as the exchange site, or else a low ratio of carbon to quaternary nitrogen, the resins are of more polar char-

Table 2
The structural formula and the basic information concerning the complexing agents used in the paper.

Chelator	Name	Structure	CAS No.
EDTA (H_4edta)	Ethylenediaminetetraacetic acid		60-00-4
NTA (H_3nta)	Nitrilotriacetic acid		139-13-9
HEDTA (H_3hedta)	N-(2-hydroxyethyl)ethylenediamine-triacetic acid)		139-89-9
IDA (H_2ida)	Iminodiacetic acid		142-73-4

Fig. 1. Comparison of the recovery factor (%R) values for Cu(II), Zn(II), Co(II), Ni(II), Pb(II) and Cd(II) complexes with EDTA (a–c) and HEDTA (d–f) on Amberlite IRA 458, Amberlite IRA 958 and Amberlite IRA 67.

acter. This behaviour fits the selectivity theory, that in weak base resins the charge on the $-NH_2$ exchange site is more concentrated, so the site is more polar than that of $-N(CH_3)_3$ of strong base resins. Therefore larger size and lower charge density of the $-N(CH_3)_2$ sites result in greater affinity for hydrophobic counter ions [18,19]. Hence the higher charge density of the protonated secondary amino sites provides greater affinity for hydrophilic counter ions. Weakly basic anion exchangers are cost advantageous in terms of regen-

erant usage: a strongly basic resin requires salt and alkali well in excess of the stoichiometric amounts, whereas a weakly basic resin has lower chemical requirements in the form of lime and mineral acid at only slightly above equivalent levels.

In the presented paper the possibility of removal of heavy metal ions Cu(II), Zn(II), Co(II), Ni(II), Pb(II) and Cd(II) in the presence of complexing agents with the aminopolycarboxylic acid groups namely EDTA, NTA, HEDTA and IDA on polyacrylate anion
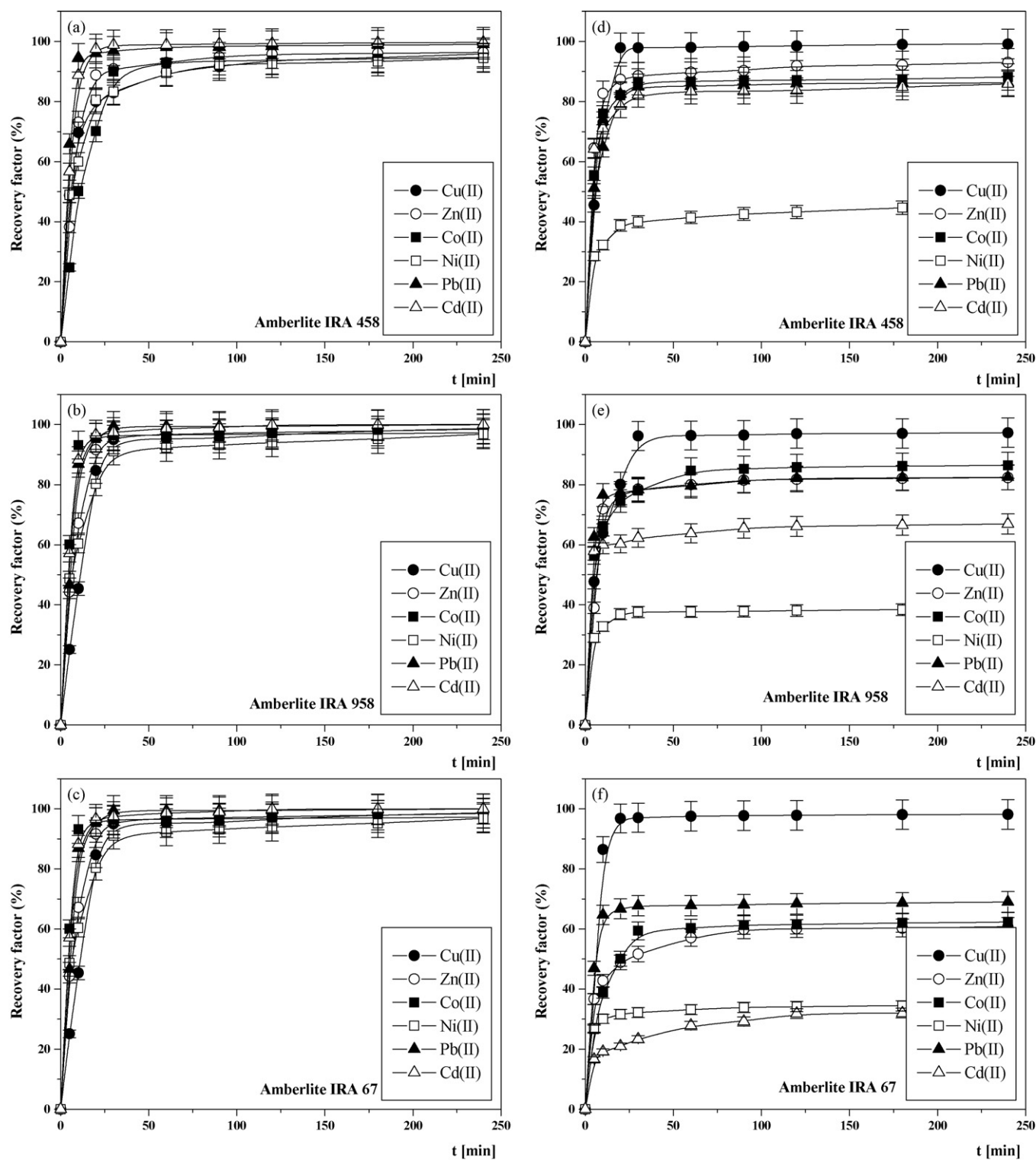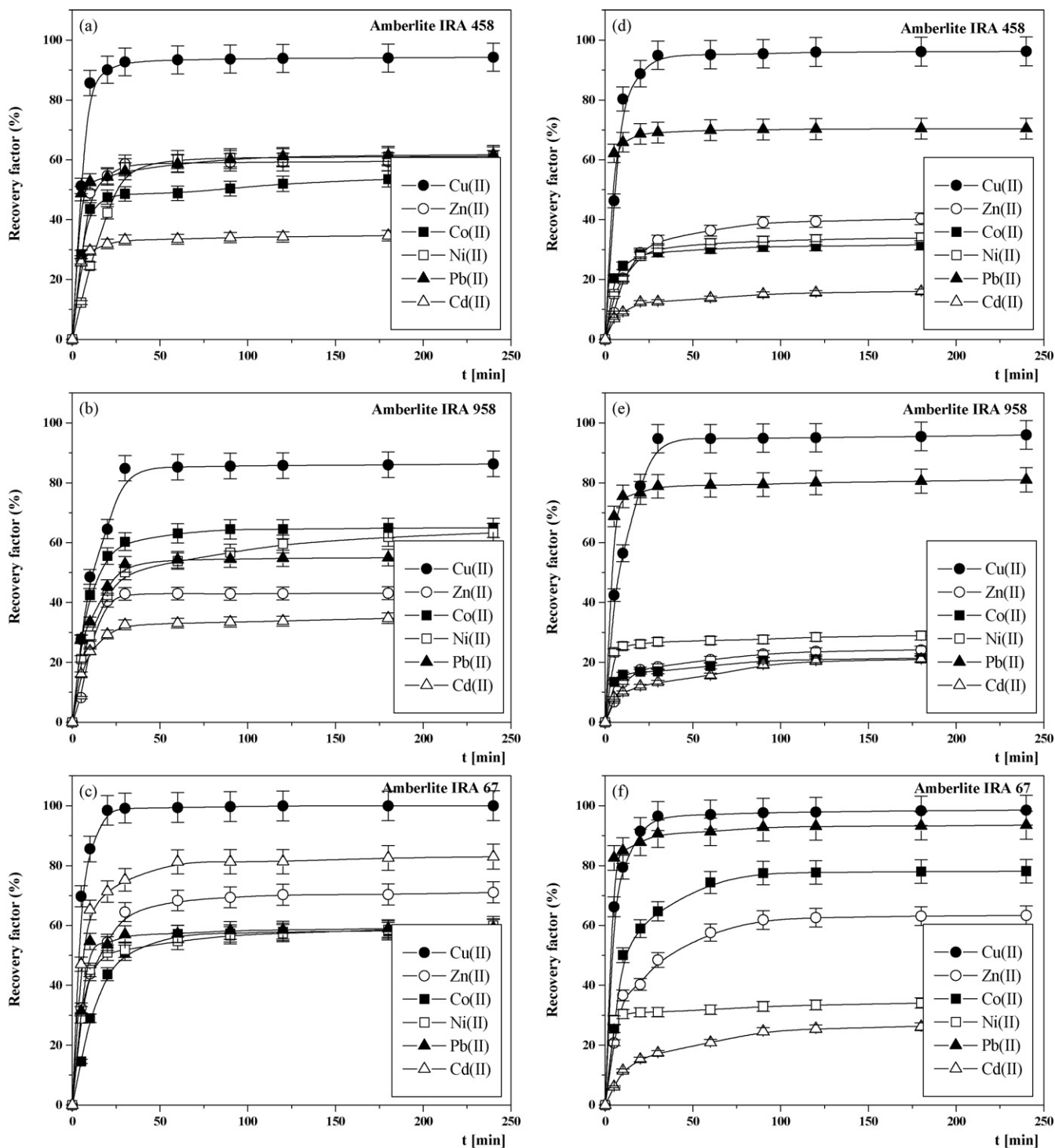
Fig. 2. Comparison of the recovery factor (%R) values for Cu(II), Zn(II), Co(II), Ni(II), Pb(II) and Cd(II) complexes with NTA (a–c) and IDA (d–f) on Amberlite IRA 458, Amberlite IRA 958 and Amberlite IRA 67.

exchangers with different basicity of the functional groups was investigated.

2. Materials and methods

2.1. Resins and solutions

In the investigations the polyacrylic anion exchangers produced by Rohm and Haas were used [20,21]. The physicochemical properties and short specification of these resins are listed in Table 1.

Prior to the use they were washed with 1 M NaOH and 1 M HCl (to remove organic and inorganic impurities) and then several times with deionized water. The resin was finally converted to the Cl⁻ or hydrated amine forms.

The reagent-grade chemicals including nitrates or chlorides of copper(II), zinc(II), cobalt(II), nickel(II), lead(II) and cadmium(II) as well as the complexing agents—EDTA, NTA, HEDTA and IDA (presented in Table 2) were used in the investigations. The stock solutions at the initial concentration 1×10^{-3} M were prepared by dissolving the salt of metal ions in the sodium salts of the respec-

tive complexing agents in the pH range 4.0–4.6. The initial values of pH for individual complexes remained without pH adjustment (for M(II)–EDTA complexes in the range 3.2–4.5; for M(II)–NTA complexes in the range 3.5–4.2; for M(II)–HEDTA complexes in the range 3.0–3.5; for M(II)–IDA complexes in the range 3.2–4.6) The other chemicals used were of analytical reagent grade (POCh S.A. Gliwice, Poland).

2.2. Methodology

2.2.1. Batch experiments

The batch experiments were performed to obtain the sorption data with different time intervals, concentration, pH values and metal:ligand ratio. The sorption of metal ions was investigated by taking 0.5 g of Amberlite IRA 458, Amberlite IRA 67 or Amberlite IRA 958 in 50 mL of solution at the desired concentration. The stoppered conical flasks were equilibrated for the desired time at room temperature using the laboratory shaker of ELPHINE type 357 produced in Poland. After the pH of solution was stabilized and equilibrated, the anion exchanger was filtered in order to determine the metal(II) ions bulk concentration by using Atomic Absorption Spectrometer ContrAA. Preliminary experiments showed that the sorption process is fast and removal rate is constant after 2 h. For pH dependence studies the pH adjustments were made by HCl/NaOH solutions. The concentrations of Cl^-/NO_3^- ions were not determined. The experiment was conducted in the three parallel series (reproducibility of the measurements was within 5%).

The metal ion concentrations obtained for batch experiments were converted to the percentage of metal ions removed (%R) and the amount of metal sorbed per unit weight of ion exchanger at the specific time and at the equilibrium (q_t, q_e). The recovery factor was calculated from the equation:

$$\%R = \frac{c_0 - c_t}{c_0} \times 100\% \tag{1}$$

The sorption capacity (q_t) at the specific time (t) was given by

$$q_t = \frac{(c_0 - c_t)V}{m} \tag{2}$$

where c_0 the initial concentration of M(II) in the aqueous phase (mg/L), c_t the concentration of M(II) in the aqueous phase at time t (mg/L), c_e the concentration of M(II) in the aqueous phase at equilibrium (mg/L), V the volume of the solution (L), and m the mass of the ion exchanger (g).

In the analogous way q_e was calculated.

2.2.2. Column experiments

In order to measure affinity of the above-mentioned metal ion complexes, the breakthrough curves were determined. 1 cm diameter columns joined to the feeder by means of the ground glass joint were used. 10 mL of the swollen anion exchanger in the appropriate form were packed to the columns. The prepared solutions were passed continuously downwards through the resin beds keeping the flow rate at 0.8 mL/(cm² min). The effluent was collected in fractions in which the metal(II) content was determined by the AAS method. From the determined breakthrough curves, the mass (D_g) and volume (D_v) distribution coefficients as well as column capacities were calculated according to the equations presented in [22].

3. Results and discussion

3.1. Adsorption studies

Besides removal of organic impurities in wastewater purification, polyacrylic ion exchangers are applied for removal of heavy
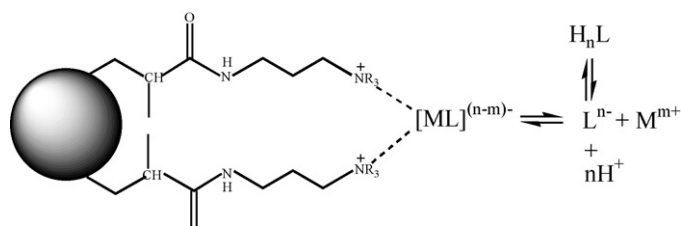

Fig. 3. The mechanism of sorption of metal ion in the presence of complexing agent on strongly basic polyacrylate anion exchanger.

metal ions from industrial wastewaters. For example, the strongly acidic cation exchanger with the polymethacrylic matrix Indion 652 has a maximum uptake value for copper(II), cobalt(II), nickel(II), cadmium(II) and zinc(II) ions compared to the commercially available chelating ion exchangers Lewatit TP-207, Purolite S-930 or Duolite C-467. Many scientific centres carry out the studies on sorption of arsenate as well as cyanide complexes of iron(II), nickel(II), zinc(II), copper(II), cobalt(II) and gold(I) on polyacrylate anion exchangers [23–29]. It was found that ion exchangers of the polyacrylate matrix exhibit higher affinity for cyanide complexes of copper(I) compared to analogous complexes of nickel(II). In the case of polystyrene ion exchangers, this effect is quite reverse. In such wastewater streams complexing agents occur predominantly in the form of metal complexes. The equilibrium speciation in a metal–ligand system is controlled by the concentrations of all metal ions and ligands and the stability constants of all complexes. In the case when other metal ions or ligands are added to the solution, a new equilibrium is attained. A common case is that, in addition to the complexation reaction when the 1:1 complexes of the ML type are formed (where M denotes metal ion and L ligand) when the ML_n (in the presence of excess of L) and M_nL (in the presence of excess of M) complexes occur. Complexes with more than one ligand may be formed if the coordination number of the metal ion is larger than that of donor atoms in the chelating agent and oppositely a complex with more than one nuclear atom may be formed if the coordination number of the metal ion is smaller than the number of donor atoms in ligand or as a result of steric hindrance. Determination of optimal conditions of metal complexes sorption requires not only knowledge of type of complexes being formed but also pH ranges in which these complexes occur. Though analysis of speciation diagrams of complexes of individual metal ions with complexing agents makes it possible to determine suitable pH ranges in which complexes occur in anion forms, complication may arise in the uptake of negative metal complexes by anion exchangers if the complexing anion possesses a high charge. These anions, if used in excess may also compete effectively with other anions present for the sites in the resin. For instance, the sorption of EDTA complexes of $[M(edta)]^{2-}$ and $[MH(edta)]^-$ types may be incom-
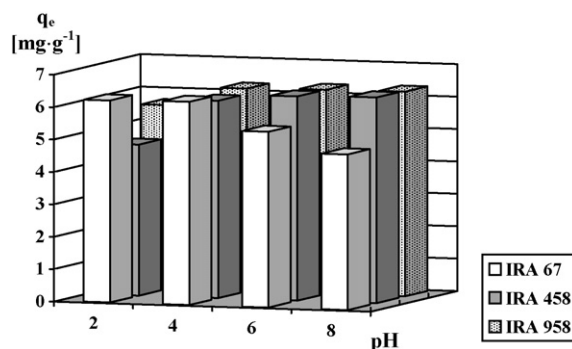

Fig. 4. Comparison of the recovery factors of Cu(II) complexes with EDTA on the polyacrylate anion exchangers depending on pH value.

Table 3
Kinetic parameters for heavy metal ions in the presence of EDTA on the polyacrylate anion exchangers.

Amberlite IRA 458

Metal ion	Cu(II)	Zn(II)	Co(II)	Ni(II)	Pb(II)	Cd(II)
Pseudo first-order						
q_1 (mg/g)	1.761	1.272	1.066	1.641	1.200	1.994
k_1 (1/min)	0.026	0.036	0.032	0.027	0.029	0.038
R^2	0.762	0.715	0.605	0.663	0.644	0.618
Pseudo second-order						
q_2 (mg/g)	6.116	6.329	5.534	5.664	20.533	11.223
k_2 (g/mg min)	0.122	0.190	0.113	0.145	0.186	0.288
h (mg/g min)	4.552	7.627	3.610	4.492	7.874	36.364
R^2	0.998	0.999	0.999	0.999	0.998	0.999
Intraparticle diffusion						
k_i (mg/g min)	0.168	0.173	0.162	0.230	0.253	0.186
R^2	0.768	0.358	0.448	0.526	0.446	0.558

Amberlite IRA 958

Metal ion	Cu(II)	Zn(II)	Co(II)	Ni(II)	Pb(II)	Cd(II)
Pseudo first-order						
q_1 (mg g^{-1})	1.472	1.656	1.007	1.8074	1.120	1.359
k_1 (min^{-1})	0.058	0.029	0.027	0.023	0.030	0.043
R^2	0.776	0.521	0.631	0.592	0.612	0.726
Pseudo second-order						
q_2 (mg g^{-1})	6.601	6.455	5.633	5.792	20.746	11.274
k_2 (g g^{-1} min^{-1})	0.488	0.205	0.756	0.138	0.118	0.237
h (mg g^{-1} min^{-1})	6.329	8.569	8.876	4.496	51.020	30.211
R^2	0.999	0.998	0.999	0.999	0.999	0.998
Intraparticle diffusion						
k_i (mg g^{-1} min^{-1})	0.252	0.172	0.076	0.165	0.428	0.195
R^2	0.602	0.608	0.465	0.490	0.661	0.493

Amberlite IRA 67

Metal ion	Cu(II)	Zn(II)	Co(II)	Ni(II)	Pb(II)	Cd(II)
Pseudo first-order						
q_1 (mg g^{-1})	1.456	1.682	1.246	1.562	1.432	1.423
k_1 (min^{-1})	0.023	0.032	0.046	0.038	0.051	0.048
R^2	0.729	0.763	0.758	0.742	0.768	0.755
Pseudo second-order						
q_2 (mg g^{-1})	6.145	6.231	5.332	5.723	20.201	11.042
k_2 (g g^{-1} min^{-1})	0.090	0.193	0.024	0.144	0.187	0.217
h (mg g^{-1} min^{-1})	3.627	7.315	7.031	7.231	48.310	32.331
R^2	0.999	0.999	0.998	0.999	0.999	0.999
Intraparticle diffusion						
k_i (mg g^{-1} min^{-1})	0.253	0.163	0.178	0.145	0.365	0.197
R^2	0.622	0.566	0.752	0.793	0.656	0.638

plete in the presence of edta^{4-} or Hedta^{3-}, although the sorption of the latter two species is actually weaker than expected. A large excess of the complexing agent in this case is an important factor affecting the sorption process and therefore should be also taken into consideration. The other important factors are the side reactions in which M and L take part, i.e. neutralization, precipitation and redox reactions. It should be noted that metal hydroxide usually precipitates soon after the formation of polynuclear complexes has begun.

Taking the above into account it was stated that the values of recovery factors ($\%R$) of metal ions on the anion exchangers Amberlite IRA 458, Amberlite IRA 958 and Amberlite IRA 67 increase and reach the plateau at the time of about 2 h. The exemplary values of the recovery factors of the studied complexes with different complexing agents determined on these anion exchangers are presented in Figs. 1 and 2. As follows from the comparison of the obtained results in the case of sorption of Cu(II), Zn(II), Co(II), Ni(II), Pb(II) and Cd(II) complexes with EDTA (Fig. 1a–c), the recovery factors assume the values in the range 80–100% and are slightly differenti-

ated for all the anion exchangers in the investigations. For all studied heavy metal ions adsorption occurred very rapidly—the equilibrium state was attained at the anion exchanger/solution phase contact time of about 30 min. For Amberlite IRA 458 almost 100% values of the recovery factors ($\%R$) for the heavy metal complexes of Cu(II), Zn(II), Co(II), Ni(II), Pb(II) and Cd(II) with EDTA were found. For the analogous complexes with HEDTA, NTA and IDA these values (besides Cu(II)) are lower. For example, the percentage reduction in the sorption capacity of Amberlite IRA 458 for the above-mentioned complexes with HEDTA is about 20% and it is the lowest for Ni(II) ions. For the analogous complexes with NTA and IDA, those values are equal to 47% and 63%, respectively and they are the lowest for Cd(II) ions (Figs. 1d–f and 2a–f).

In the case of Cu(II), Zn(II), Co(II), Ni(II), Pb(II) and Cd(II) ions sorption in the presence of HEDTA, the obtained recovery factors are higher for Cu(II), Zn(II) than for Cd(II) and Ni(II) (Fig. 1d–f). The affinity series for the studied anion exchangers can be as follows: Amberlite IRA 458 Cu(II) > Zn(II) > Co(II) > Pb(II) > Cd(II) > Ni(II); Amberlite IRA 958 Cu(II) > Co(II) > Zn(II) > Pb(II) > Cd(II) > Ni(II) and Amberlite IRA 67 Cu(II) > Pb(II) > Co(II) > Zn(II) > Ni(II) > Cd(II).

In the case of heavy metal complexes with NTA the values of the recovery factors are lower but more differentiated (Fig. 2a–c), therefore the affinity series of these complexes can be arranged as follows: Amberlite IRA 458: Cu(II) > Ni(II) = Pb(II) = Zn(II) > Co(II) > Cd(II); Amberlite IRA 958 Cu(II) > Co(II) > Ni(II) > Pb(II) > Zn(II) > Cd(II) and Amberlite IRA 67 Cu(II) > Cd(II) > Zn(II) > Pb(II) > Co(II) > Ni(II). It is worth mentioning that the weakly basic anion exchanger Amberlite IRA 67, contrary to the strongly basic anion exchangers Amberlite IRA 458 and Amberlite IRA 958 has the highest affinity for Cd(II) in the presence of NTA.

For the above-mentioned complexes with IDA, the recovery factors are also higher for Amberlite IRA 67 than for Amberlite IRA 458 and Amberlite IRA 958. But for these strongly basic anion exchangers, except for Cu(II) and Pb(II) they are only in the range 12–40%.
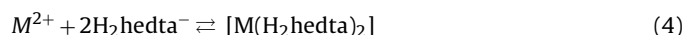
3.2. Effect of pH values

It is well known that the toxicity of heavy metals is a function of free metal ion concentration rather than the total metal concentration. The most important factor controlling the soluble/insoluble phase distribution, besides the nature of species, is the pH value. Because of the fact that the capacities of the polyacrylate anion exchangers like Amberlite for metal ions complexed with aminopolycarboxylic acids depend on the pH value, the following types of complexes should take part in the sorption process:

pH 3.2–4.5 EDTA in the form of edta^{4-}

$$M^{2+} + \text{edta}^{4-} \rightleftarrows [\text{M(edta)}]^{2-} \tag{3}$$

pH 3.5–4.2 HEDTA in the form of H$_2$hedta$^-$

$$M^{2+} + 2H_2\text{hedta}^- \rightleftarrows [\text{M(H}_2\text{hedta})_2] \tag{4}$$

pH 2.9–3.2 NTA in the form of nta^{3-} $M^{2+} + \text{nta}^{3-} \rightleftarrows [\text{M(nta)}]^-$ (5)

pH 2.9–3.2 IDA in the form of ida^{2-} $M^{2+} + \text{ida}^{2-} \rightleftarrows [\text{M(ida)}]$.   (6)

Generally, the scheme of sorption is presented in Fig. 3. At pH about 2, where the dominant species are non-complexed metal ions, their removal is insignificant. Then with the increasing pH values, neutral, one or two negative complexes should be sorbed. In the preliminary experiments it was established that the recovery factors of Fe(III) complexes are lower (values below 30%) which confirms that the complexes of [M(edta)]$^-$ type exhibit lower affinity for polyacrylate anion exchangers in comparison to that of
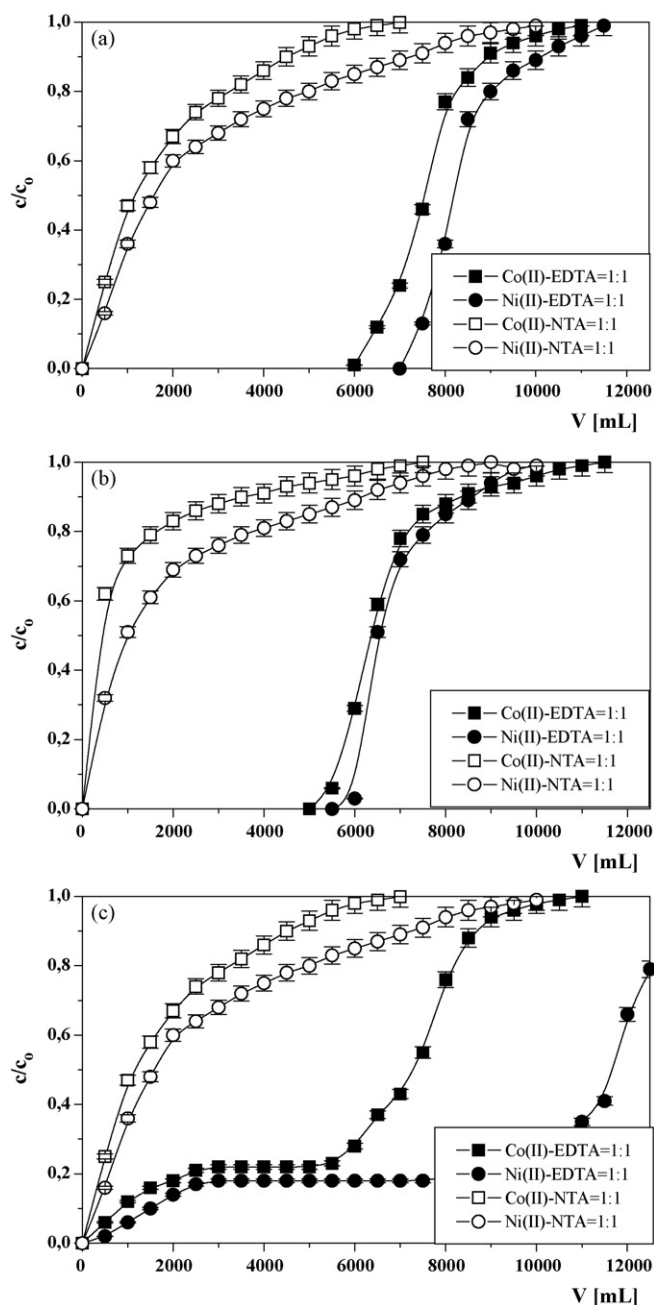
Fig. 5. The breakthrough curves of Co(II) and Ni(II) in the presence of EDTA and NTA on Amberlite IRA 458 (a), Amberlite IRA 958 (b) and Amberlite IRA 67 (c).

[M(edta)]$^{2-}$ type. It was also confirmed by the obtained results of heavy metal ions sorption in the presence of HEDTA and IDA where the complexes undergoing sorption have lower recovery factors than those with EDTA and NTA. Therefore the type of formed complexes (depending on pH values) seems to be a decisive factor for sorption effectiveness.

Taking the above statements into consideration, there were carried out the studies of sorption of Cu(II), Zn(II), Co(II), Ni(II), Pb(II) and Cd(II) complexes with EDTA on the polyacrylate anion exchangers in the pH range from 2.0 to 8.0. The exemplary results for the Cu(II) complexes with EDTA are presented in Fig. 4. With the increasing pH of the solution, the amount of sorbed complexes on the anion exchangers Amberlite IRA 458 and Amberlite IRA 958 increase and reach the plateau at pH above 5. The reverse tendency was observed in the case of Amberlite IRA 67. The recovery factors

as well as the amount of sorbed complexes are high in the range of pH from 2 to 6 and then gradually decrease. Such behaviour of weakly basic anion exchangers is in agreement with the literature data as the ion exchangers of this type achieve complete ion exchange capacity in acidic solutions.

3.3. Kinetic studies

The prediction of kinetics is necessary for designing sorption systems because the nature of sorption process depends on physical or chemical characteristics of the ion exchanger and also on the system conditions. In order to investigate the mechanism of sorption, the rate constants of chemical sorption and intraparticle diffusion for the studied heavy metal ions in the presence of a complexing agent were determined using the equations of the pseudo first-order system, pseudo second-order and intraparticle diffusion models, respectively. The appropriate equations, based on which the calculations were made, were presented in the paper by Kumar and Sivanesan [30]. The exemplary values of rate parameters for heavy metal complexes with EDTA are presented in Table 3. As follows from the presented data, the rate parameters are well fitted by the pseudo second-order kinetic model (the correlation coefficients in the range 0.998–0.999). As shown by many other authors, this model describes very well sorption of metal ions, dyes, herbicides, oil, and organic substances from aqueous solutions [31–35]. At the initial concentration 1×10^{-3} M, the equilibrium capacities of the studied ion exchangers for Cu(II), Zn(II), Co(II), Ni(II), Pb(II) and Cd(II) in the presence of EDTA are the highest for Pb(II) and Cd(II). Therefore the order of sorption for polyacrylate anion exchangers Amberlite IRA 458, Amberlite IRA 958 as well as Amberlite IRA 67 can be as follows: Pb(II) > Cd(II) > Zn(II) > Cu(II) > Ni(II) > Co(II).

3.4. The column studies

The breakthrough curves for Co(II) and Ni(II) in the presence of EDTA and NTA on Amberlite IRA 458, Amberlite IRA 958 and Amberlite IRA 67 from single metal ion solutions of a concentration 1×10^{-3} M are shown in Fig. 5. Typical 'S' shaped curves were obtained in the experiments except for the results for the Co(II) and Ni(II) complexes with EDTA on Amberlite IRA 67. In this case the concentration of the solution leaving the column reaches approximately 12 mg/L and changes very slowly, which indicates that in this case different type complexes undergo sorption. The mass (D_g) and volume (D_v) distribution coefficients were determined form the breakthrough curves (Table 4). Thus it was shown that the nickel(II)

Table 4
The mass (D_g) and volume (D_v) distribution coefficients as well as the working (C_w) and total (C_r) ion exchange capacities (g/mL) for the Co(II) and Ni(II) complexes with EDTA and NTA on the polyacrylate anion exchangers.

M(II)–NTA system	D_g	D_v	C_w	C_r
Amberlite IRA 458				
Co(II)–EDTA = 1:1	2014.06	756.48	0.0035	0.0450
Ni(II)–EDTA = 1:1	2188.92	822.16	0.0041	0.0495
Co(II)–NTA = 1:1	306.37	115.07	0.0010	0.0105
Ni(II)–NTA = 1:1	422.77	158.79	0.0011	0.0157
Amberlite IRA 958				
Co(II)–EDTA = 1:1	1953.53	633.14	0.0295	0.0393
Ni(II)–EDTA = 1:1	2018.22	654.10	0.0323	0.0405
Co(II)–NTA = 1:1	135.14	43.80	0.0002	0.0066
Ni(II)–NTA = 1:1	326.41	105.79	0.0002	0.0119
Amberlite IRA 67				
Co(II)–EDTA = 1:1	1977.09	727.77	0.00019	0.0362
Ni(II)–EDTA = 1:1	3166.48	1165.58	0.00021	0.0379
Co(II)–NTA = 1:1	320.74	118.07	0.00011	0.0098
Ni(II)–NTA = 1:1	438.70	161.49	0.00015	0.0123

complexes with EDTA and NTA exhibit larger affinity for the studied anion exchanger than the corresponding cobalt(II) complexes. The determined working (C_w) and total (C_r) ion exchange capacities for the above-mentioned metal complexes with EDTA and NTA indicate that the strongly basic anion exchangers achieve larger effective sorption capacity towards the Co(II) and Ni(II) complexes than the weakly basic anion exchanger Amberlite IRA 67.

4. Conclusions

The obtained data indicate that the sorption of heavy metal complexes with aminopolycarboxylic acids on the polyacrylate anion exchangers is effective and provides the advantage of simultaneous removal of these metals and organic ligands. As follows from the studies, the polyacrylate anion exchangers exhibit large affinity for the heavy metal complexes with EDTA. Anion exchangers affinity for heavy metal complexes depends on physicochemical properties of polyacrylic anion exchangers as well as on the structure and charge of formed complexes as well as their stability. Owing to the advantageous properties of polyacrylate anion exchangers as well as the research results, the anion exchangers Amberlite IRA 458 and Amberlite IRA 958 can be applied in removal of heavy metal ions in the presence of complexing agents from aqueous solutions as well as in purification of wastewaters at pH range from 4 to 8. Amberlite IRA 67 can be applied in their removal at pH from 2 to 6.

The kinetics of sorption of heavy metal ions in the presence of EDTA on the polyacrylate anion exchangers was studied on the basis of the pseudo first- and pseudo second-order rate mechanism. The kinetics of Cu(II), Zn(II), Co(II), Ni(II), Pb(II) and Cd(II) sorption on Amberlite IRA 458, Amberlite IRA 958 and Amberlite IRA 67 follows the pseudo second-order rate expression. A pseudo second-order model has been developed to predict the rate constant of sorption and the equilibrium capacity.

Based on the determined the mass (D_g) and volume (D_v) distribution coefficients of Co(II) and Ni(II) complexes with EDTA or NTA it was found that nickel(II) exhibit larger affinity for the studied anion exchanger than the corresponding cobalt(II).

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