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Polyacrylate anion exchangers in sorption of heavy metal ions with the biodegradable complexing agent

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ABSTRACT

The removal of Co(II) and Ni(II) from aqueous solutions in the presence of complexing agent on the polyacrylate anion exchangers with different basicity of functional groups Amberlite IRA 458, Amberlite IRA 958 and Amberlite IRA 67 was described. The complexing agent Baypure CX 100 is a new generation of chelators, undergoing biodegradation. It constitutes an alternative for the reagents of EDTA or NTA type. The studies were carried out by the static (batch) and the dynamic (column) methods. The influence of several parameters such as ratio of M(II)–L, pH, temperature were studied with respect to sorption equilibrium. Sorption isotherms were obtained and fitted using the Langmuir and Freundlich models. Kinetic curves were fitted using the pseudo first-order, the pseudo second-order as well as the intraparticle diffusion model equations to evaluate most effective one. Physicochemical properties of anion exchangers such as their structure, basicity of functional groups were also taken into account. Additionally, the obtained results were compared with those for the weakly acidic cation exchanger Purolite C-104.

1. Introduction

Nowadays because of their industrial importance chelating agents are produced and used in large quantities. Therefore the environmental fate of chelating agents receives considerable attention mainly for the reason that they are almost resistant to biodegradation (besides nitrilotriacetic acid, NTA) [1–6]. Their concentrations increase in aquatic systems to unacceptable levels i.e. for ethylenediaminetetraacetic acid (EDTA) 30–50 μg/L and for NTA less than 50 μg/L. In Central Europe EDTA has been classified to be one of the major organic pollutants. The available data suggest that EDTA, NTA, DTPA (ethylenetriaminepentaacetic acid) and their salts are not generally removed during the wastewater treatment. It has been estimated that wastewater effluents typically have 140–310 μg EDTA/L while NTA and its salts are substantially removed during the wastewater treatment. Because of not complying with the Organization for Economic Cooperation and Development (OECD) readily biodegradability criteria and increasing legislation such as OSPAR (The Convention for the Protection of the Marine Environment of the North-East Atlantic) there is a pressing requirement to replace them with biodegradable alternatives. Additional argument for this solution is the fact that in the environment conventional chelating agents have some undesired features such as the remobilization of radionuclides and toxic heavy metal ions from sediments and soils [7–9]. Therefore, the use of some easily biodegradable chelating agents, such as S,S-ethylenediaminedisuccinic acid (EDDS), tetrasodium salt of N-(1,2-dicarboxyethyl)-D,L-aspartic acid or iminodisuccinic acid (IDS) and poly(aspartic acid) (DS) has been proposed as an alternative to conventional complexing agents.

The synthetic sodium salt of N-(1,2-dicarboxyethyl)-D,L-aspartic acid, which goes by the product name Baypure CX 100, belongs to the group of aminopolycarboxylate chelating agents. Its structure is presented in Fig. 1. The products of Baypure brand, manufactured in a green process avoiding toxic chemicals by Lanxess (Germany), are new complexing and dispersing agents having a wide range of applications. It is worth mentioning that in June 2001 the Environmental Protection Agency (EPA) in the United States awarded the Bayer Company (currently Lanxess) with the Presidential Green Chemistry Award for Baypure CX 100. In June 2002 the Federation of German Industry (BDI) awarded the Lanxess with an environment prize. The first detergent based on Baypure CX 100 was also awarded the EU environmental flower ecolabel.

IDS is a medium-strong chelator that is able to replace EDTA when rather moderate chelating agents are sufficient for masking alkaline earth or heavy metal ions. As a substitute for EDTA it is used in a variety of applications, including detergent formulations, corrosion inhibitors, production of pulp and paper, textiles, ceramics, photochemical processes, and as trace nutrient fertilizers in agriculture. It can prevent the harmful effect of calcium and magnesium as well as heavy metal traces in cosmetic products such as shampoos, creams (including sun-care products) and soaps. It masks the

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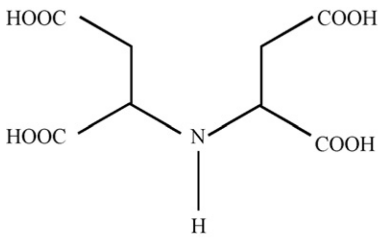

Fig. 1. The structure of IDS.

Table 1
The stability constants (log *K*) of metal ions with IDS [16].

M(II)/M(III)	IDS
Ca(II)	5.2
Cd(II)	8.4
Co(II)	10.5
Cr(III)	9.6
Cu(II)	13.1
Fe(II)	8.2
Fe(III)	15.2
Hg(II)	14.9
Mg(II)	6.1
Mn(II)	7.7
Ni(II)	12.2
Pb(II)	11.0
Zn(II)	10.8

heavy metal ions and, at the same time, enhances the effect of the surfactants. It is also effective as a bleaching agent stabilizer, water softener and deposit remover, with a superior ecological profile [10]. Baypure CX 100 comprises the following components: iminodisuccinic acid sodium salt > 32%, aspartic acid sodium salt < 7%, fumaric acid sodium salt < 3.5%, hydroxosuccinic acid < 0.9%, maleic acid sodium salt < 0.9%. This route yields a mixture of stereoisomers including of 25% S,S-IDS, 25% R,R-IDS, and 55% of the meso-form R,S-IDS, whereas the percentage of each IDS isomer in equilibrium at pH 8.5 is 55.5% R,S-IDS, 27.8% S,S-IDS, and 16.7% R,R-IDS [11,12]. Biodegradation tests according to the OECD standard 301F revealed ready biodegradability for all stereoisomers of IDS [13]. The IDS-degrading strain *Agrobacterium tumefaciens* BY6 can be isolated from the activated sludge. The strain is able to grow on each IDS isomer as well as on Fe(II), Mg(II) and Ca(II)–IDS complexes as the sole carbon, nitrogen, and energy source. In contrast, biodegradation and growth on Mn(II)–IDS are rather scant and very slow on Cu(II)–IDS (55 and 40% biodegradation after 28 days, respectively). During the test on IDS chelates, precipitation of the corresponding heavy metal hydroxide is observed, indicating liberation of free metal ions. These results correspond with the observations made during biodegradation tests with metal–IDS complexes [14,15]. It is worth mentioning that Baypure CX 100 is a pentadentate chelating ligand. The chelation involves the four carboxylate groups and the nitrogen atom. It forms an octahedral complex conditional upon occupation of the sixth coordination position by a water molecule. The reaction between the metal ion and the anion of IDS acid is reversible and occurs with the ratio 1:1:

$$M^{m+} + ids^{n-} \rightleftarrows [M(ids)]^{(n-m)-} \qquad (1)$$

where M^{m+} is the metal ion, ids^{n-} is the ionic form of N-(1,2-dicarboxyethyl)-D,L-aspartic acid.

The stability constants of heavy metal complexes with IDS are presented in Table 1 [16].

Taking into account new possible applications of biodegradable complexing agents, it seems advisable to study possibility of their removal from waters and wastewaters. In the presence of heavy metal ions they form complex compounds, which do not undergo biodegradation. Though removal of metal ions from the wastewaters is not complicated using typical chemical precipitation methods, the presence of complexing agents causes this process inefficient due to high stability of metal complexes. Application of active carbons was not effective either [17]. Thus in this case the most effective treatment method is ion exchange. It has been applied in water treatment and wastewaters purification for many years. For wastewaters containing complexing agents besides heavy metal ions, application of anion exchangers seems to be the most rational [18–22].

In the presented paper the possibility of removal of Co(II) and Ni(II) ions in the presence of Baypure CX 100 on the polyacrylate anion exchangers was studied. Polyacrylate anion exchangers with different basicity of functional groups Amberlite IRA 458, Amberlite IRA 958 and Amberlite IRA 67 were used. For comparison, the analogous sorption process on the polyacrylate cation exchanger with the carboxylic functional groups, Purolite C 104 was also carried out. The sorption kinetics was investigated and kinetic parameters were calculated using various kinetic models. Sorption isotherms were obtained and fitted using the Langmuir and Freundlich models.

2. Materials and methods

2.1. Resins and solutions

In the investigations the polyacrylate anion exchangers produced by Rohm and Haas and the polyacrylate cation exchanger produced by Purolite were used. The physicochemical properties and short specification of these resins are presented in Table 2. 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 resins were finally converted to the Cl^-, hydrated amine and H^+ forms, respectively.

The reagent-grade chemicals including chlorides of cobalt(II) and nickel(II) as well as the complexing agents Baypure CX 100 were used in the investigations. The stock solutions were prepared by dissolving the salt of metal ions in the sodium salt of the complexing agent. They were diluted as required to obtained standard solutions. The initial values of pH for individual complexes remained without pH adjustment were 7.9 for Co(II) and 7.8 for Ni(II). The other chemicals used were of analytical reagent grade (POCh S.A. Gliwice, Poland).

Table 2
Characteristics of ion exchangers used in the investigations.

Ion exchanger	Typical properties					
	Matrix	Active groups	Delivery form	Bead size (μm)	Total capacity (eq/dm^3)	Swelling (%)
Amberlite IRA 458	A-DVB (g)	$-N^+(CH_3)_3$	Cl^-	600–900	1.25	$Cl^- \rightarrow OH^-$ 20
Amberlite IRA 958	A-DVB (m)	$-N^+(CH_3)_3$	Cl^-	675–875	0.80	$Cl^- \rightarrow OH^-$ 20
Amberlite IRA 67	A-DVB (g)	$-N(CH_3)_2$	OH^-	550–750	1.60	$OH^- \rightarrow Cl^-$ 20
Purolite C 104	A-DVB (g)	$-COO^-$	H^+	100–1200	4.30	$H^+ \rightarrow Ca^{2+}$ 20

A-DVB: polyacrylic crosslinked with divinylbenzene; g: gel structure; m: macroporous structure.

2.2. Methodology

2.2.1. The batch experiments

The batch experiments were performed to obtain the amount of Co(II) and Ni(II) complexes with IDS sorbed by polyacrylate ion exchangers. Laboratory experiment was carried out in the conical 100 mL flasks dosed with a ground-in stopper. 50 mL proper aqueous phase containing 0.001 M of each metal and 0.5 g ion exchanger were put into a conical flask and shaken mechanically using the laboratory shaker (ELPHINE, type 357, Poland) for 1–240 min. After the pH of solution was stabilized and equilibrated, the ion exchanger was filtered. In order to determine metal(II) complexes concentrations atomic absorption spectrometer ContrAA (Analytic Jena AG, Germany) was used. The metal(II) complexes concentrations obtained in batch experiments were converted to the percentage of metal(II) removed i.e. recovery factor (%*R*) and the amount of metal(II) sorbed per unit mass of ion exchanger at the specific time and at the equilibrium (q_t, q_e).

The recovery factor was calculated from the equation:

$$\%R = \frac{c_0 - c_t}{c_0} \times 100\% \quad (2)$$

The resin phase concentrations of M(II) at the equilibrium, q_e (mg/g) and at the specific time, q_t (mg/g) were obtained according to:

$$q_e = \frac{(c_0 - c_e)\cdot V}{m} \quad (3)$$

$$q_t = \frac{(c_0 - c_t)\cdot V}{m} \quad (4)$$

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

2.2.2. The kinetic studies

The kinetic parameters for sorption of Co(II) and Ni(II) in the presence of IDS on the above-mentioned anion exchangers were determined using the pseudo first-order as well as the pseudo second-order models, which have a linear forms as [23]:

$$\log(q_1 - q) = \log(q_1) - \frac{k_1 t}{2.303} \quad (5)$$

$$\frac{t}{q} = \frac{t}{q_2} + \frac{1}{k_2 q_2^2} \quad (6)$$

where q_1, q_2 are the amount of metal complexes sorbed at equilibrium (mg/g), q the amount of metal complexes sorbed at time *t* (mg/g), k_1, k_2 is the equilibrium rate constant (1/min).

2.2.3. The sorption isotherms

Several equilibrium models have been developed to describe adsorption isotherm relationships. Sorption of metal complexes, q_e (mg/g), can be related to the equilibrium concentration of these complexes c_e (mg/L), by both the Freundlich isotherm model:

$$q_e = K_F c_e^{b_F} \quad (7)$$

and the Langmuir isotherm model:

$$q_e = \frac{q_0 b c_e}{1 + b c_e} \quad (8)$$

where $K_{F,}$ b_F are the Freundlich constant related to the sorption capacity; $q_{0,}$ b are the Langmuir constants.

The Langmuir constants represent the maximum sorption capacity for the solid phase loading and the energy constant related to the heat of sorption, respectively. The Freundlich constant b_F (also denoted as $1/n$) is related to the sorption intensity. The intercept and the slope of the linear plot of $\log q_e$ vs. $\log c_e$ provide the values of K_F and $1/n$, respectively. The constants q_0 and b can be also evaluated from the intercept and the slope of the linear plot of c_e/q_e vs. c_e, respectively [24,25].

2.2.4. The column experiments

In order to measure affinity of the above-mentioned metal complexes, the breakthrough curves were determined using 10 mL of the swollen anion exchanger in the appropriate form. The prepared solutions were passed continuously through the resin beds at the constant flow rate equal to 0.8 mL/cm^2 min. The effluent was collected in fractions in which the metal(II) complex content was determined by the AAS method.

2.2.5. FT-IR analysis

The FT-IR (Fourier transform infrared spectroscopy) spectrum of the Baypure CX 100 was recorded over the interval 400–4000 cm^{-1} by means of a Perkin-Elmer 1725 X. The samples were tabletted with KBr.

2.2.6. Microscopic studies

Scanning electron microscopy (SEM) was used to record the surfaces of Amberlite IRA 458, Amberlite IRA 958 and Amberlite IRA 67 samples before and after the sorption process. The samples were ground into powder and coated with a thin layer of palladium-gold alloy with a sputter coater (Polaron SC 7620). Subsequently, their surfaces were observed and photographed by SEM. The microscope of LEO1430VP trademark and EDX detector of Röntec trademark were used in this study.

3. Results and discussion

3.1. The FT-IR and SEM studies

In the spectroscopic studies FT-IR scans as well as SEM scans were recorded. The obtained spectrum of IDS (Fig. 2) possesses a broad band in the 3433 cm^{-1} region, corresponding to the O–H bond of an acid, a sharp peak at about 1573 cm^{-1}, corresponding to a C=O bond, and additional peaks in the 1313–1198 cm^{-1} region for stretching vibration of the C–O bond and in the 1404 cm^{-1} region for the O–H bond. IDS shows also peaks at 1132 cm^{-1} related to the deformation vibration of –OH group as well as at 794 and 649 cm^{-1} related to the stretching vibration of C–N bond of secondary amine.

Fig. 3a–f illustrates the SEM scans depicting different patterns of gel and macroporous polyacrylate anion exchanger surfaces as well as their changes after contacting with heavy metal ions in the

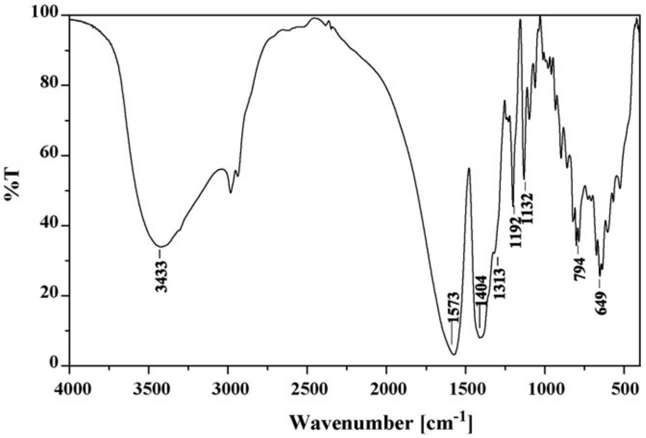

Fig. 2. FT-IR spectrum of IDS.

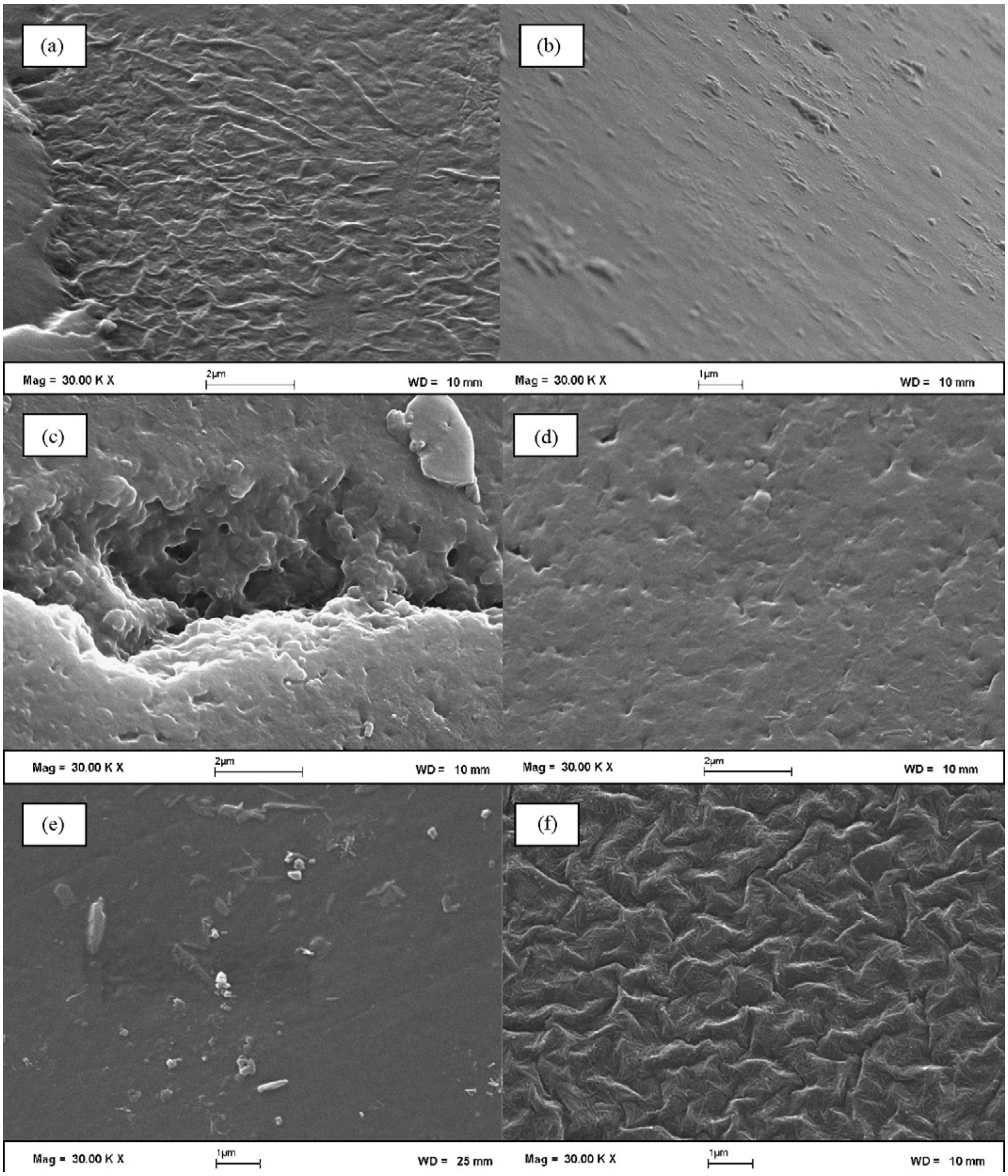

Fig. 3. SEM scans of the polyacrylate anion exchangers before and after being contacted with heavy metal ions in the presence of IDS: Amberlite IRA 458 (a and b), Amberlite IRA 958 (c and d) and Amberlite IRA 67 (e and f).

presence of IDS. It is noticed that after the sorption process their surface was dense in comparison with the ones not being in contact with metal complexes. The most visible changes there are in the case of Amberlite IRA 67.

3.2. *The effect of the phase contact time and kinetic studies*

A series of contact time experiments for sorption of Co(II) and Ni(II) in the presence of IDS was carried out at the initial concentration 0.001 M. Fig. 4 shows the obtained results for M(II)–IDS complexes sorption on Amberlite IRA 458, Amberlite IRA 958 and Ambrelite IRA 67. It was found that the values of recovery factors (%*R*) of Co(II) and Ni(II) in the presence of IDS on the anion exchangers Amberlite IRA 458, Amberlite IRA 958 and Amberlite IRA 67 increase and achieved the constant value at the time about 60 min. From the obtained results it is also evident that the sorption process proceeded in two distinct phases. Initially the sorption rates were very fast. The recovery factors (%*R*) for these metal ions at 10 min were: 89.1 for Co(II), 91.5 for Ni(II) on Amberlite IRA 458; 79.3 for Co(II), 78.4 for Ni(II) on Amberlite IRA 958; 68.9 for Co(II), 75.8 for Ni(II) on Amberlite IRA 67. After that period of time, the sorption rate becomes slower, therefore these values change insignificantly and the sorption equilibration is attained. The fast-phase sorption may be explained by high concentration of accessible functional groups, which take part in the ion exchange process. Probably it is connected with the size of complexes undergoing sorption and their stability. The stability constant for nickel(II) complexes with IDS is higher than for cobalt(II) ($\log K = 12.2$ for Ni(II) and $\log K = 10.5$ for Co(II)) [16].

Prediction of batch sorption kinetics is necessary for design of industrial sorption column. The most commonly used kinetic expressions to explain the solid/liquid sorption processes known in literature are the pseudo first-order kinetic and the pseudo second-order kinetic models [25]. The intraparticle diffusion model was also used to predict the sorption kinetics. In the presented studies they were used for evaluation of Co(II) and Ni(II) sorption in the presence of IDS. The obtained data are presented in Table 3. The R^2 values for the pseudo second-order kinetic model (about

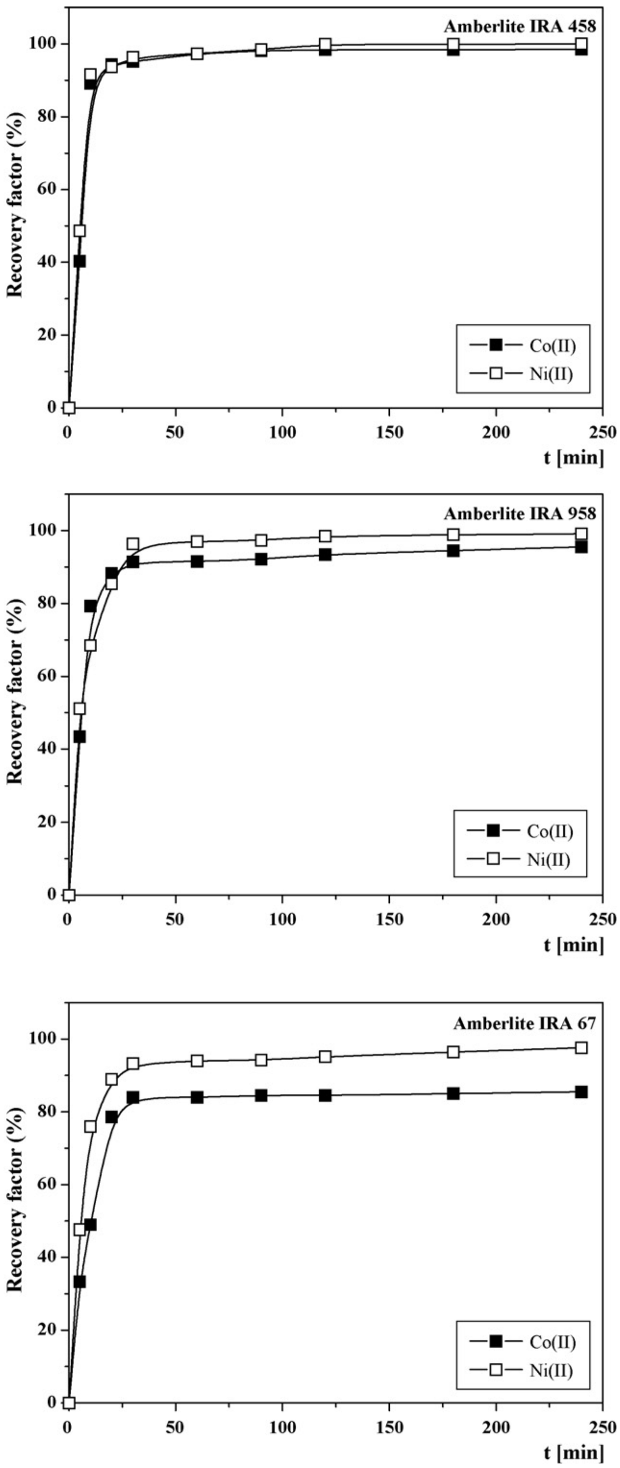

Fig. 4. Comparison of the recovery factor (%R) values for Co(II) and Ni(II) in the presence of IDS on Amberlite IRA 458, Amberlite IRA 958 and Amberlite IRA 67.

0.999–1.000) were closer to that than the pseudo fist-order kinetic model (0.876–0.910) indicating better agreement. Additionally, for the pseudo fist-order kinetic model all intercepts of the straight line plots of $\log(q_1 - q)$ vs. t do not give values equal to $\log(q_1)$ or even reasonably close values. The reaction is therefore not likely to be the pseudo fist-order kinetic reaction.

It is worth mentioning that studied metal ions can be desorbed from the anion exchangers with 1 M NaCl (these data are not presented). All cobalt(II) complexes with IDS (100%) are desorbed, whereas only 93% of nickel(II) recovery from the resin phase was achieved.

Table 3
Kinetic parameters of Co(II) and Ni(II) ions in the presence of IDS on polyacrylate anion exchangers.

Metal complex	Co(II)–IDS = 1 : 1	Ni(II)–IDS = 1 : 1
Amberlite IRA 458		
Pseudo first-order		
q_1 (mg/g)	2.492	1.787
k_1 (1/min)	0.048	0.051
R^2	0.7433	0.8220
Pseudo second-order		
q_2 (mg/g)	5.624	5.889
k_2 (g/mg min)	0.357	0.326
h (mg/g min)	12.136	11.325
R^2	1.0000	1.0000
Intraparticle diffusion		
k_i (mg/g min)	0.149	0.118
R^2	0.698	0.679
Amberlite IRA 958		
Pseudo first-order		
q_1 (mg/g)	2.987	1.387
k_1 (1/min)	0.014	0.038
R^2	0.9274	0.718
Pseudo second-order		
q_2 (mg/g)	5.840	5.844
k_2 (g/mg min)	0.198	0.216
h (mg/g min)	6.321	7.391
R^2	0.9999	1.0000
Intraparticle diffusion		
k_i (mg/g min)	0.142	0.154
R^2	0.6791	0.6371
Amberlite IRA 67		
Pseudo first-order		
q_1 (mg/g)	2.042	1.416
k_1 (1/min)	0.029	0.023
R^2	0.4787	0.5921
Pseudo second-order		
q_2 (mg/g)	5.261	5.733
k_2 (g/mg min)	0.182	0.189
h (mg/g min)	5.061	6.222
R^2	0.9999	0.9999
Intraparticle diffusion		
k_i (mg/g min)	0.128	0.135
R^2	0.6496	0.6818

3.3. *The sorption isotherm studies*

The influence of metal ion concentration on effectiveness of sorption process provides an indication of the sorption capacity of the applied ion exchanger. The studies were carried out at constant concentration of the ion exchanger and various initial concentrations of Co(II) and Ni(II). The results indicate that increases in the initial metal ion concentration result in increases in metal sorption (Fig. 5). It was found that Co(II) and Ni(II) sorption in the presence of IDS was well represented by the Langmuir isotherm model (Fig. 6). The correlation coefficients of the linear plot of c_e/q_e vs. c_e obtained from them were high, ranging from 0.897 to 0.999. However, the calculated equilibrium capacities q_0 according to the Langmuir isotherm model are in good agreement with the values of experimental capacities $q_{e,\mathrm{exp}}$. These values for sorption of Co(II) and Ni(II) on Amberlite IRA 458, Amberlite IRA 958 and Amberlite IRA 67 are presented in Table 4. The highest amount of metal ions adsorbed per unit mass of anion exchanger (mg/g) are for the Ni(II) complexes on Amberlite IRA 458 and Amberlite IRA 958 and the smallest for Amberlite IRA 67. In the case of Co(II) complexes

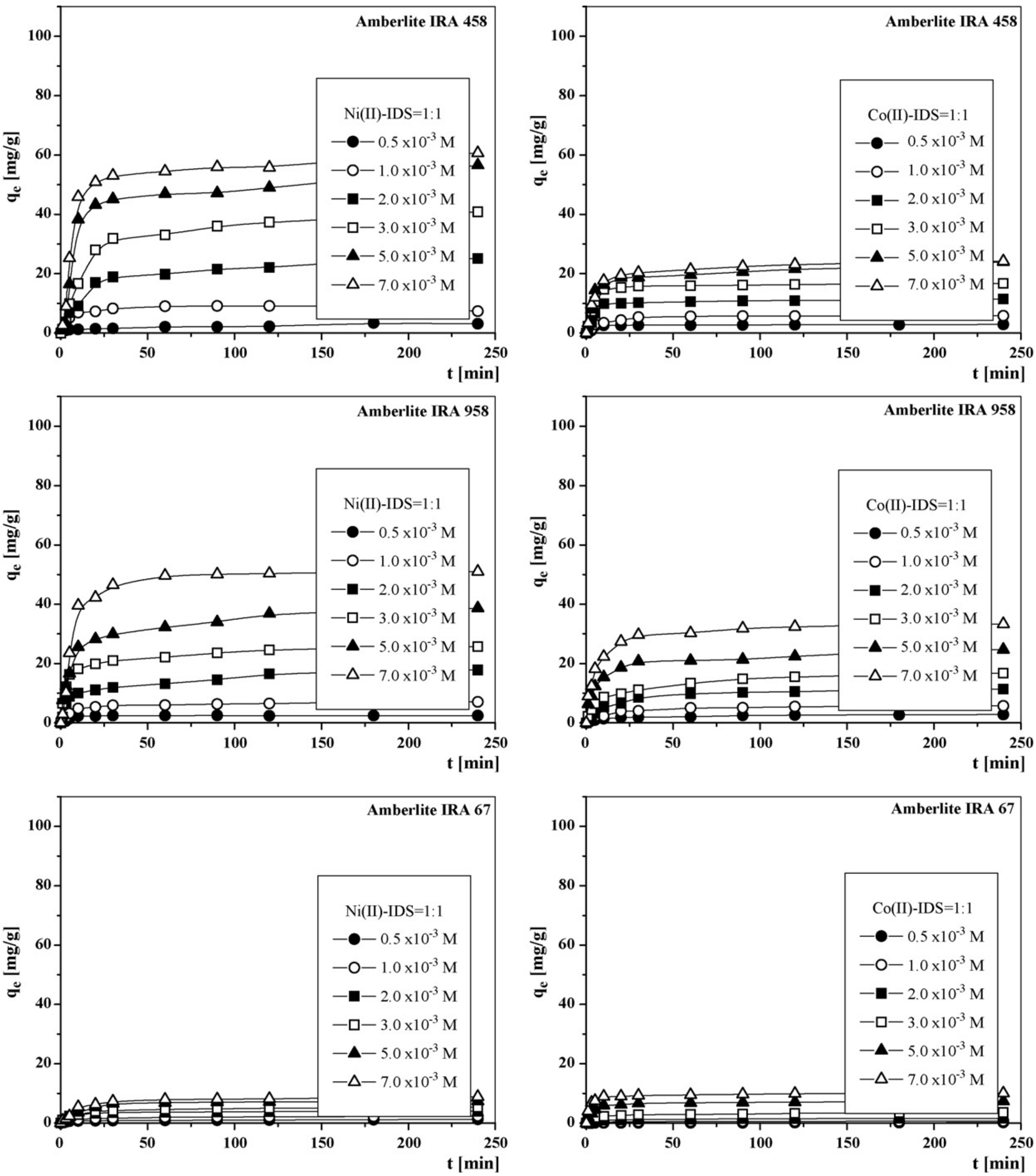

Fig. 5. The effect of Co(II) and Ni(II) concentrations in the presence of IDS on the sorption capacity on Amberlite IRA 458, Amberlite IRA 958 and Amberlite IRA 67.

Table 4
The Langmuir and Freundlich isotherm constants for the sorption of Co(II) and Ni(II) in the presence of IDS on the polyacrylate anion exchangers in the one-component system.

M(II)	Anion exchanger	$q_{e,\text{exp}}$	Langmuir constants			Freundlich constants		
			q_0	b	R^2	K_F	n	R^2
Ni(II)	Amberlite IRA 458	60.65	65.238	0.010	0.9602	8.226	0.921	0.7477
Ni(II)	Amberlite IRA 958	51.00	53.158	0.083	0.9760	7.352	1.123	0.8315
Ni(II)	Amberlite IRA 67	12.45	13.193	0.0032	0.9802	6.924	1.505	0.9837
Co(II)	Amberlite IRA 458	23.96	25.641	0.253	0.9994	5.551	2.333	0.8789
Co(II)	Amberlite IRA 958	33.33	34.722	0.112	0.9744	6.091	2.525	0.9234
Co(II)	Amberlite IRA 67	14.16	15.522	0.002	0.8967	4.662	1.982	0.7531

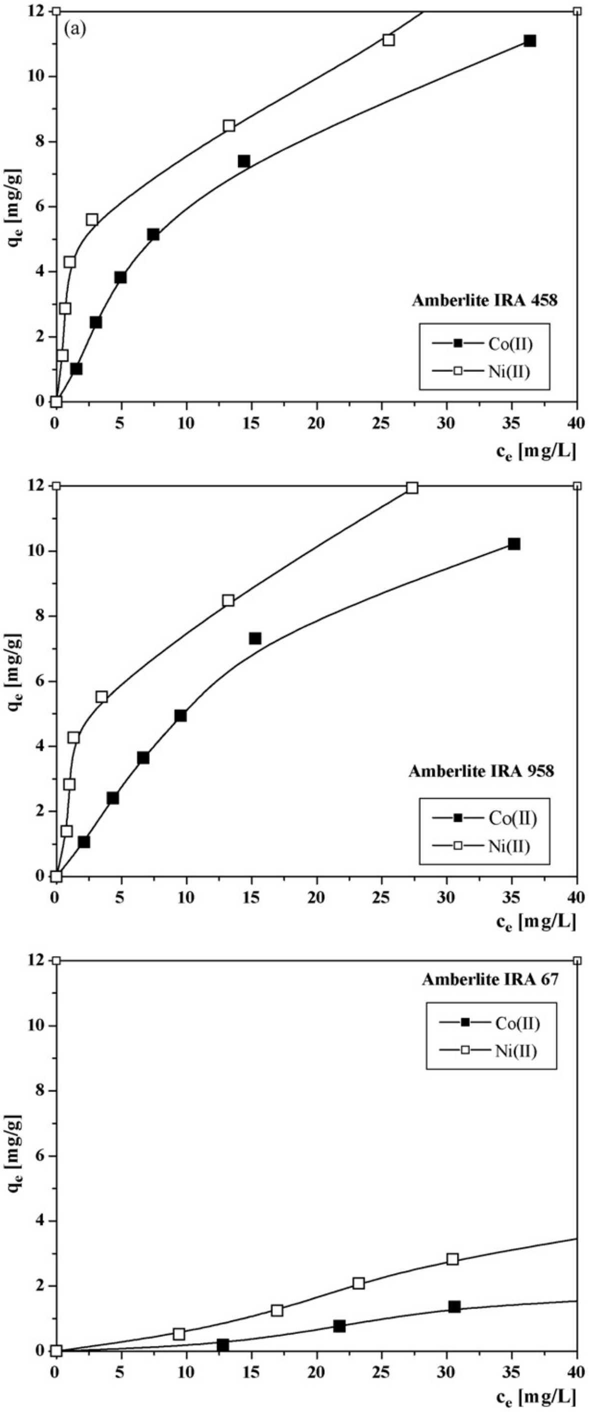

Fig. 6. The Langmuir sorption isotherms of Co(II) and Ni(II) in the presence of IDS on Amberlite IRA 458, Amberlite IRA 958 and Amberlite IRA 67.

these values are significantly lower. The other constants of the two models for the considered metal ions are also presented in Table 4.

The polyacrylate anion exchangers, according to their applicability for sorption of Co(II) and Ni(II) complexes in the presence of IDS in the 1:1 system can be put in the order:

Co(II): Amberlite IRA 958 > Amberlite IRA 458 > Amberlite IRA 67,
Ni(II): Amberlite IRA 458 > Amberlite IRA 958 > Amberlite IRA 67.

In the case of sorption of Co(II) and Ni(II) on the weakly acidic cation exchanger Purolite C 104 (these data are not presented) the obtained sorption capacities are lower in comparison to those on the anion exchangers. For Co(II) and Ni(II) $q_{e,\mathrm{exp}}$ are as follows 4.57 and 2.11 mg/g, respectively. Slight sorption of Co(II) and Ni(II) ions in the presence of IDS on the cation exchanger Purolite C 104, can be connected with the fact that in the ion exchange phase during the sorption process they decompose.

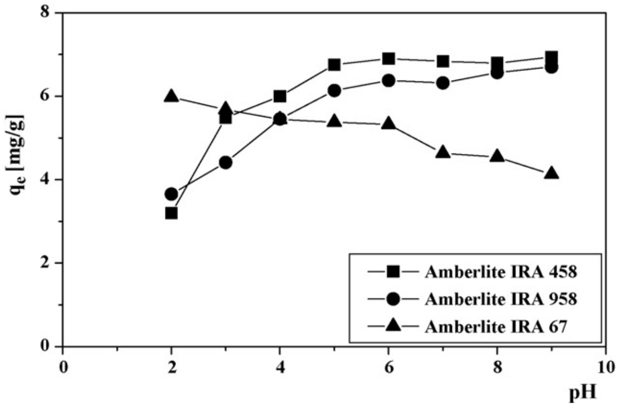

Fig. 7. The influence of the pH value on the effectiveness of sorption of Ni(II) complexes in the presence of IDS on the studied ion exchangers.

Cobalt(II) and nickel(II) ions in the presence of IDS were also selected to study metal sorption on polyacrylate anion exchangers in the two-component system (in analogous conditions as in one component system). When the Langmuir isotherm model was applied to the data in the two-component system, the highest correlation coefficients, which give the best fit between the experimental and predicted data were obtained only for the equilibrium of Ni(II) whereas for Co(II), the Langmuir model resulted in a large deviation. The calculated equilibrium capacities q_0 on Amberlite IRA 458, Amberlite IRA 958 and Amberlite IRA 67 according to the Langmuir isotherm model are as follows: for Ni(II) 16.72, 13.22, 10.03 mg/g and for Co(II) 12.51, 9.01, 3.33 mg/g, respectively. The study indicated the presence of sorption competition between these two metal ions but the same order was observed when these metals were sorbed individually. The obtained sorption behaviour of Co(II) and Ni(II) is likely due to their similar physicochemical properties, such as electronegativity (Pauling electronegativity for Co(II) 1.88 and for Ni(II) 1.91), charge (2+), covalent radius (for Co(II) 116 pm and for Ni(II) 115 pm) and the same type of formed complexes (octahedral) [26]. In the group of factors, which play a significant role in sorption are also stability and size of formed complexes.

3.4. The effect of the pH values

As follows from the spatial diagrams known in literature in strong acidic solutions heavy metal ions occur in the form of aqua-complexes [27–30]. With the increasing pH of the solution, there is a narrow range of pH in which heavy metal ions form neutral complexes and in the solution of pH ~ 4 formation of anion (one- or two-negative) complexes is observed. Taking into consideration a series of metal complexes affinity for anion exchangers as a rule two-negative complexes exhibit higher affinity compared with one-negative ones [31]. However, in the studies on heavy metal ions sorption on anion exchangers in the presence of various kinds of complexing agents, all anion forms of complexes should be treated as potentially competitive. Besides metal cations, which in the presence of aminopolycarboxylic acids form negative complexes, simple inorganic anions as well as organic ligands which did not enter complexes with metals and which are charged negatively must be taken into consideration.

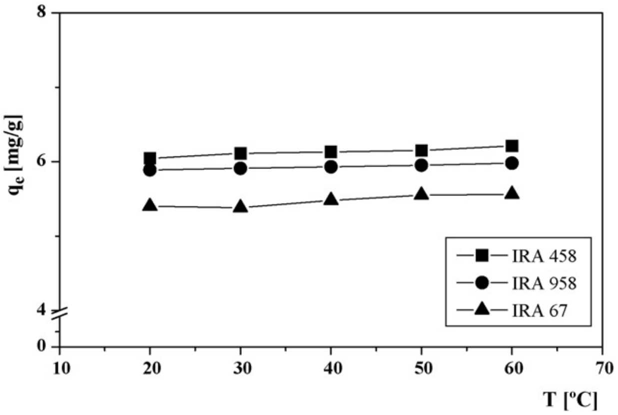

Fig. 8. The influence of the temperature on the effectiveness of sorption of Ni(II) complexes in the presence of IDS on the studied anion exchangers.

Fig. 7 shows the relationship between the initial pH of Ni(II) complexes with IDS and the sorption capacity for polyacrylate anion exchangers. The increase in sorption capacity in the range from 3.19 to 6.93 mg/g and from 3.65 to 6.70 mg/g with the increasing pH values from 2 to 9 was observed only for the strongly basic polyacrylate anion exchangers Amberlite IRA 458 and Amberlite IRA 958, respectively. For the weakly basic anion exchanger Amberlite IRA 67 these values decrease with the increasing pH values.

3.5. *The effect of temperature*

The temperature dependence of heavy metal sorption in the presence of IDS was studied on strongly and weakly basic anion exchangers. Fig. 8 shows the effect of temperature on the sorption of Ni(II) on Amberlite IRA 458, Amberlite IRA 958 and Amberlite IRA 67 as a function of contact time. The equilibrium sorption capacities q_e slightly increased with the increasing Ni(II) solution temperature from 20 to 60 °C which indicate increasing of complexing species mobility.

3.6. *The column studies*

The breakthrough curves of Co(II) and Ni(II) complexes with IDS with different molar ratios on Amberlite IRA 458, Amberlite IRA 958 and Amberlite IRA 67 are presented in Fig. 9. As follows from the presented data, the breakthrough curves of the complexes with IDS in the M(II)–L = 1:1 and M(II)–L = 1:2 systems on the strongly basic polyacrylate anion exchangers are apparently similar to the classical breakthrough curves. The shape of the curves for Co(II) complexes with IDS (Co(II):IDS = 1:1) on Amberlite IRA 67 suggests possible formation of more than one type of complex. Additionally, as evident from the SEM scans, in the case of Amberlite IRA 67 in the sorption process the polymer chain shrinks because the fraction of free hydrophilic functional groups decreases. Thus the metal ions, such as Co(II) or Ni(II) are difficult to diffuse into.

As follows from the breakthrough curves, mainly Ni(II) complexes with IDS in the M(II)–L = 1:1 system exhibit higher affinity for both gel and macroporous polyacrylate anion exchangers than for the corresponding Co(II) complexes. The greatest differentiation in affinity of the Co(II) and Ni(II) pair was found on the anion exchangers Amberlite IRA 458 and Amberlite IRA 958. As it was mentioned earlier as a rule two-negative complexes exhibit higher affinity compared with one-negative ones for anion exchangers. However, this relationship was not confirmed in the case of heavy metal complexes with IDS (complexes of the molar ratio M(II)–L = 1:2 exhibit smaller affinity for those of the molar ratio 1:1). Thus in this case their size can be decisive for sorption effectiveness. To large complexes are excluded from the ion exchanger phase during the process due to the sieve effect.

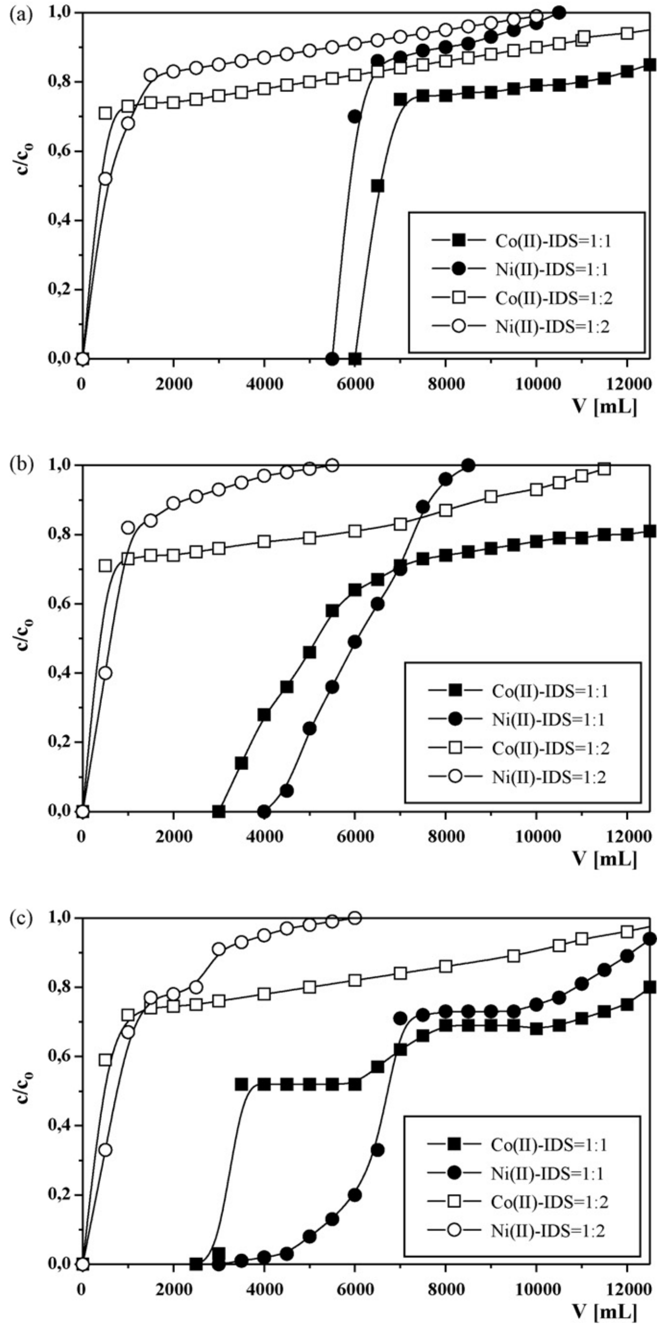

Fig. 9. The breakthrough curves of Co(II) and Ni(II) in the presence of IDS with different molar ratios on Amberlite IRA 458 (a), Amberlite IRA 958 (b) and Amberlite IRA 67 (c).

4. Conclusions

The method presented sodium salt of N-(1,2-dicarboxyethyl)-D,L-aspartic acid can be of great significance in purification of wastewaters from heavy metal ions using polyacrylate anion exchangers. Phase contact time, pH, and initial metal concentration influence the effectiveness of heavy metal complexes sorption on anion exchangers Amberlite IRA 458, Amberlite IRA 958 and Amberlite IRA 67. Batch equilibrium was relatively fast and it reached equilibrium after about 60 min of contact. The ion exchange process, which is pH dependent showed maximum removal of Ni(II) in the pH range 4.0–8.0 only for the strongly basic anion exchangers Amberlite IRA 458 and Amberlite IRA 958. The sorption capacities were from 3.19 mg/g at the pH value 4.0–6.93 mg/g at pH 8.0. For the weakly basic Amberlite IRA 67 this tendency is reverse. It was shown that temperature slightly affects sorption efficiency. The equilibrium related to the ion exchange capacity and the amount of the ion exchanger was obtained by using the plots of the Langmuir adsorption isotherm. It was observed that the maximum capacities were in good agreement with the experimental data. The sorption of studied metal ions in the presence of IDS on the polyacrylate anion exchangers followed the pseudo second-order reversible kinetics. The intraparticle diffusion represented the rate-limiting step.

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