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Iminodisuccinic acid as a new complexing agent for removal of heavy metal ions from industrial effluents

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ABSTRACT

The sorption parameters of Cu(II), Co(II), Ni(II) as well as Fe(III) in the presence of a complexing agent of a new generation to the anion exchangers of different basicity of functional groups were investigated. A series of experiments were conducted to optimise the method for the their removal from industrial effluents. It was found that the sorption efficiency of strongly, medium as well as weakly basic anion exchangers varied depending on metal ions concentration, pH, contact time, agitation, temperature and properties of anion exchangers such as their form. From the determined breakthrough curves the distribution coefficients (D_g) and (D_v), the ion exchange capacities (C_w, C_t) and the time required for the moving the exchange zone (t_z) as well as the total time required for the formation of exchange zone (t_T) were calculated. The largest percentages of heavy metal complexes with IDS removal were found for the strongly basic anion exchanger (up to 98% for Cu(II), 82% for Fe(III), 67% for Ni(II) and 55% for Co(II)). Satisfactory results were also obtained for medium and weakly basic anion exchangers. Besides, a kinetic procedure was developed to study the kinetics of anion exchange. Two different kinetic behaviours were tested for the investigated systems.

1. Introduction

Industrial development has lead to a drastic increase of heavy metal concentrations in the environment. Except for heavy metal ions, synthetic organic metal-sequestering ligands such as aminopolycarboxylic acids (mainly ethylenediaminetetraacetic acid, EDTA and nitrilotriacetic acid, NTA) are also present in various wastewaters. Their presence is associated, among others, with their application in pulp and paper, textile, metallurgical, food, cosmetics, pharmaceutical and agricultural industries. The complexones such as EDTA, NTA, Quadrol (N,N,N′,N′-tetrakis(2-hydroxopropyl)-ethylenediamine) (Fig. 1) are extensively used in electroless copper plating in manufacture of printed circuit boards. Aminopolycarboxylates have also been reported as the most common substitutes for sodiumtriphosphate (STPP) in detergents. By forming complexes with calcium and magnesium ions they increase the cleaning action of soaps and detergents. They are also extensively used as stabilizing agents in food industry, in wastewater treatment plants they dissolve $CaCO_3$ scale deposit from hard water without the use of corrosive acids, they act as an anticoagulant for stored blood as well as in the decontamination of radioactive effluents from nuclear industry. Radioactive wastewaters contain both complexing agents (for example, EDTA concentration up to 30 mM) and radioactive metals like ^{60}Co, ^{239}Pu and ^{240}Pu. They are also used in the separation of rare earth elements from each other [1–5].

In the aminopolycarboxylates group, EDTA and DTPA have proven to be practically non-biodegradable in standard tests. The available data suggest that EDTA and its salts are not generally removed during wastewater treatment [6–8]. Under anaerobic conditions, no degradation could be found for any of the EDTA complexes and in the case of EDTA its degradation rate strongly depends on the type of microorganisms [9]. On the other hand, elimination of EDTA of up to 70–80% was found in wastewater treatment plants with facilities for chemical phosphate precipitation.

In the case of effluents containing heavy metal ions together with complexing agents, typical chemical precipitation methods in the presence of strong chelating agents such as EDTA, NTA, citrate, and tartarate may make the precipitation process ineffective, even when treating effluents of high metal concentration, because most metal ions are complexed with organic ligands over the entire pH range [9–11]. Therefore, more advanced techniques are required for the cleanup of such contaminants and retardation of heavy metal ions mobility.

Generally, the treatment methods can be grouped into three categories: chemical, physical and electrochemical. The chemical methods include substitution, reduction of the metal ion, oxidation of complexing agent and ion exchange. The physical methods include, among others, reverse osmosis. The electrochemical methods are, for example, electrowinning and electrochemical displacement. In the electrochemical reduction processes metal

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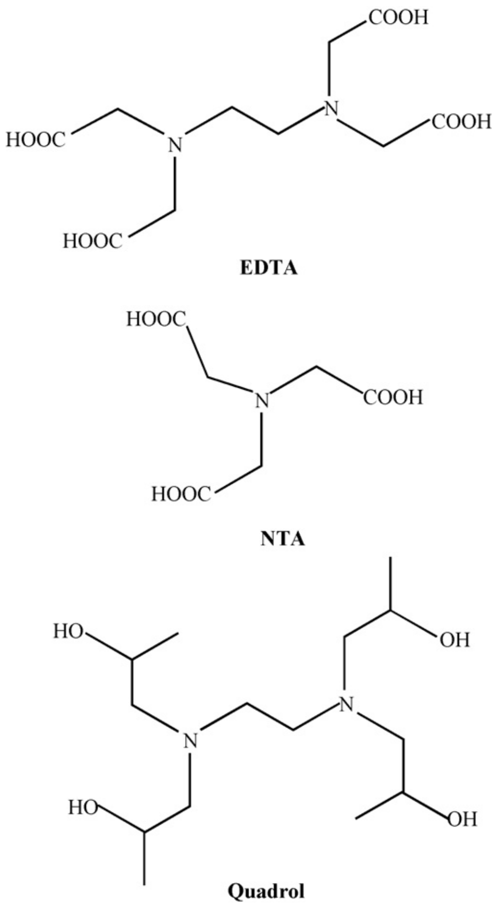
EDTA

NTA

Quadrol

Fig. 1. The structure of EDTA, NTA and Quadrol.

ions from the effluents are removed and then deposit as elemental metals on the cathodic plate to enable the complexing agent to be recovered for reuse from power plants. However, they are affected by several operating problems, e.g. membrane fouling and degradation [12,13]. One possible solution is carrying out biodegradation process resulting in the liberation of metal ions, having lower mobility under neutral conditions. To this end, studies on application of advanced oxidation processes (AOP) or advanced oxidation techniques (AOT) including some processes with such reactives like ozone, hydrogen peroxide, iron ions or UV irradiation as well as with such catalysts as TiO_2 are carried out [14–18]. Ozone has been found to degrade EDTA and the rate of destruction is influenced by coordination. It has been demonstrated that photocatalysis is a promising technology applicable for efficient removal of metal–EDTA complexes from, for example, radioactive wastewater containing Fe(III), Cu(II), Co(II) and Ni(II) [19,20]. Moreover, dissolved transition metal ions in aqueous solutions affect the rate and efficiency of photocatalytic oxidation of organic compounds. One of the recycling methods also investigated was the application of electrolysis in conjunction with a cation-exchange membrane for the recovery of metals in a solution of metal–EDTA complexes. With the current interest in remediation technologies, the electrolysis method has been extended for recycling of wastewater from soil washing [21].

Increasing concern about the direct or indirect potential effects of the presence of the above mentioned complexones in the environment, that is:

1. mobilization of contaminant metal ions adsorbed in sediments;
2. solubilization of radioactive metal ions and increase of their environmental mobility;
3. contribution to eutrophication water processes (e.g. the EDTA molecule contains approximately 10% of nitrogen that could eventually be available to the aquatic microbiota and redissolves calcium and ferrium phosphates, releasing phosphorous);
4. the ligand–metal complexes may significantly increase the bioavailability of extremely dangerous heavy metals, for example, Cu(II)–EDTA and Cd(II)–EDTA complexes which are more toxic than their respective free metals

cause, that these complexons are nowadays replaced by modern agents sufficiently biodegradable or eliminable. There is a number of alternative products on market which are claimed to be as effective as EDTA and NTA but most of them have also their restrictions. For example, organophosphonates were found to be not readily biodegradable. Others are readily biodegradable, such as citrates and gluconates, but do not have a sufficiently strong chelating power compared to NTA or EDTA. A series of new diethanolamine derivatives such as complexing agents have been designed by the Kemira Oyj Espoo Research Centre (Finland): N-bis[2-(carboxymethoxy)ethyl]glycine (BCA3), N-bis[2-(methyl-carboxymethoxy)ethyl]glycine (MBCA3), N-bis[2-(1,2-dicarboxyethoxy)ethyl]glycine (BCA5) and N-bis[2-(1,2-dicarboxyethoxy)ethyl] aspartic acid (BCA6). However, being of technical quality these new alternative complexing agents of low nitrogen content proved to be not readily biodegradable compounds. BCA6 was found to be the most sensitive to photodegradation, whereas BCA3 was quite photostable [22–24]. More recently, tetrasodium salt of L-asparaginic-N,N-diacetic acid (ASDA), 1,3-propylenediaminetetraacetic acid (1,3-PDTA), N-2(-hydroxyethyl)iminodiacetic acid (HEIDA), β-alaninediacetic acid (β-ADA) and methylglycinediacetic acid (MGDA) were introduced [25–29]. Particularly, MGDA is readily biodegradable in compliance with the OECD standards and is used for enhancing the cleaning efficiency of laundry and dishwashing detergents as well as industrial and all-purpose cleaners. Also such chelating agents as EGTA (ethylenedioxydiethylenediaminetetraacetic acid) and HEDTA (N-hydroxyethylethylenediaminetriacetic acid), EDDS (N,N′-ethylenediaminedisuccinic acid), IDS (N-(1,2-dicarboxyethyl)-D,L-aspartic acid also known as iminodisuccinic acid) and DS (polyaspartic acid) have also been proposed [30–37]. According to recent investigations, especially S,S′-EDDS is a viable replacement ligand in pulp and paper industry, in cosmetics, etc. and also IDS is comparable to EDTA. β-ADA is also a potential alternative. The structural formulae of the above-mentioned complexones are presented in Table 1

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The aim of this study was to explain the influence of chemical conditions on the ion exchange capacity and on the kinetics of copper(II), cobalt(II), nickel(II) and iron(III) in the presence of the complexing agent of a new generation that is sodium salt of N-(1,2-dicarboxyethyl)-D,L-aspartic, which has the commercial name Baypure CX 100. In the studies there was applied the ion exchange which is a method used in water treatment and wastewater purification. This method is suitable for removal of all contaminants in the ionic form also including heavy metal ions in the presence of complexing agents from different systems. The results obtained under different experimental conditions will be presented and discussed in this paper.

2. Materials and methods

2.1. Resins

The following medium and weakly basic anion exchangers Lewatit MonoPlus MP 64, Lewatit MP 62 produced by the Bayer

Table 1
Chelating agents of a new generation.

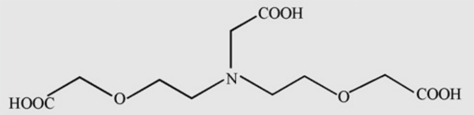
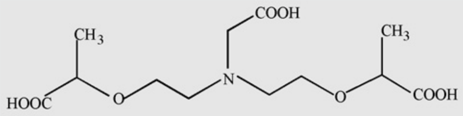
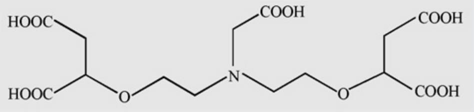
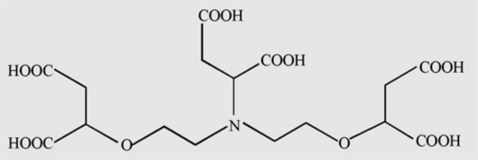
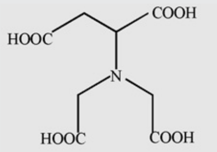
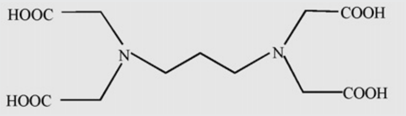
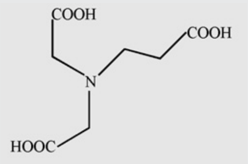
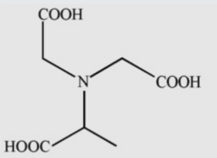
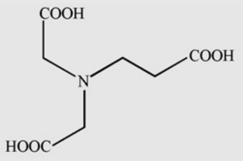
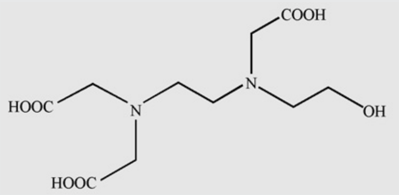
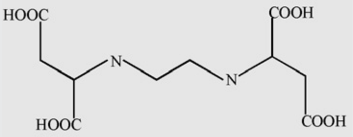
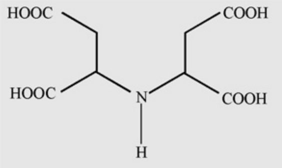
Chelator	Name	Structure	Manufacturer.
BCA3	N-bis[2-(carboxymethoxy)ethyl]glycine		Kemira Oyj Espoo, Finland
MBCA3	N-bis[2-(methylcarboxymethoxy)ethyl]glycine		Kemira Oyj Espoo, Finland
BCA5	N-bis[2-(1,2-dicarboxyethoxy)ethyl]glycine		Kemira Oyj Espoo, Finland
BCA6	N-bis[2-(1,2-dicarboxyethoxy)ethyl]aspartic acid		Kemira Oyj Espoo, Finland
ASDA	Asparaginic-N,N-diacetic acid		Mitsubishi Rayon
PDTA	Propylenediaminetetraacetic acid		Chemlex Chemicals, Inc.
β-ADA	β-Alaninediacetic acid		BASF
MGDA	Trisodium salt of methylglycinediacetic acid		BASF
HEIDA	N-2(2-hydroxyethyl)iminodiacetic acid		Dow Chemical Company
HEDTA	Hydroxyethylethylenediaminetriacetic acid		Dow Chemical Company

Table 1 (*Continued*)

Chelator	Name	Structure	Manufacturer.
EDDS	Ethylenediamine-N,N′-disuccinic acid		Innospec
IDS	Sodium salts of N-(1,2-dicarboxyethyl)-D,L-aspartic acid		Lanxess
			ADOB

AG, Germany as well as strongly basic anion exchanger Amberlite IRA 402 produced by the Rohm and Haas, France were used in the investigations. Short characteristic of these resins is 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 washed several times with deionized water.

2.2. Chemicals

In order to determine sorption capacity of resins towards copper(II), cobalt(II), nickel(II) and iron(III) in the presence of Baypure CX 100 (in this paper referred as IDS) they were reacted with appropriate solutions of these metals at pH without adjustment. For individual complexes the pH values were—6.75: Cu(II)–IDS = 1:1, 7.93: Co(II)–IDS = 1:1, 7.65: Ni(II)–IDS = 1:1, 4.89: Fe(III)–IDS = 1:1. The stock solution was further diluted to the required experimental concentration. The other chemicals used were of analytical grade.

2.3. Column studies

In order to measure affinity of the above-mentioned heavy metal complexes with IDS, the breakthrough curves were determined using 10 mL of the swollen anion exchanger in the appropriate form. The resins (in the commercial forms) were converted to acetate or iminodisuccinate forms obtained by contacting with an excess of 1 M CH_3COONH_4 at pH 7.0 or 0.1 M IDS at pH 7.5, respectively. Then the prepared solutions of complexed metal ions were passed continuously downwards through the resin beds keeping the flow rate at 0.8 mL/cm^2 min. The effluent was collected in fractions in which the metal(II)/(III) content was determined. The mass (D_g) and bed (D_v) distribution coefficients as well as the working (C_w) and total (C_r) ion exchange capacities of M(II) were calculated from the determined breakthrough curves according to Eqs. (1)–(3) [37]:

$$D_g = \frac{\overline{V} - (V_0 + V_i)}{m_j} \tag{1}$$

$$D_v = \frac{\overline{V} - (V_0 + V_i)}{V_j} \tag{2}$$

$$C_w = \frac{V_e \cdot c_0}{V_j} \tag{3}$$

where $\bar{V}$ the volume of effluent at $c = c_0/2$ (determined graphically) (mL), V_0 the dead volume in the column (liquid volume in the column between the bottom edge of ion exchanger bed and the outlet) (mL), V_i the void (interparticle) ion exchanger bed volume which amounts to ca. 0.4 of the bed volume (mL), m_j the dry ion exchanger mass (g), V_j the bed volume (mL), V_e the effluent volume to the break point (L), and c_0 the initial concentration of a solution of M(II)/M(III) (mg/L).

The total ion exchange capacities (C_r) were calculated by integration along the curve (the concentration of non-complexed copper(II) ions – sorbed on the cation exchanger Lewatit MonoPlus SP 112 (Fig. 6) was taken into account when calculating the working (C_w) and total (C_r) exchange capacities). The time required for the moving of the exchange zone (t_z) as well as the total time required for the formation of the exchange zone (t_T) were also calculated. These parameters are proportional to the volume of effluent (Eq. (4)) and to the total volume of effluent collected (Eq. (5)):

$$t_z = \frac{V_z}{U \cdot S} \tag{4}$$

$$t_T = \frac{V_T}{U \cdot S} \tag{5}$$

where U the flow rate (mL/min), S the total column cross-section area (cm^2). V_z the volume of effluent (mL), and V_T the total volume of effluent collected (mL).

The moving rate of the exchange zone (cm/s) is proportional to the height of the resin bed (cm):

$$v_{ex} = \frac{h_T}{t_T - t_F} \tag{6}$$

where t_F the time of exchange zone formation (related to the bed symmetry coefficient F) (s).

Table 2
Characteristics of ion exchangers used in the investigations.

Ion exchanger	Typical properties							
	Matrix	Active groups	Delivery form	Appearance	Bead size (μm)	Total capacity (eq/L)	pH range	Max. temp. range
Amberlite IRA 402	P-DVB (g)	$-N^+(CH_3)_3$	Cl^-	Beige, transparent	600–750	1.3	0–14	273–333
Lewatit MonoPlus MP 64	P-DVB (m)	$-{}^+N(CH_3)_3/-N(CH_3)_2$	Cl^-/OH^-	Beige, opaque	590 ± 50	1.3	0–7	273–313
Lewatit MP 62	P-DVB (m)	$-N(CH_3)_2$	OH^-	Beige, opaque	470 ± 60	1.7	0–8	273–313
Lewatit MonoPlus SP 112	P-DVB (m)	$-SO_3H$	H^+	Beige, opaque	660 ± 70	1.7	0–14	273–353

P-DVB: polystyrene cross-linked with divinylbenzene, g: gel structure; m: macroporous structure.

The relation for estimation of zone formation time is as follows:

$$t_F = (1 - F)t_z \tag{7}$$

The bed symmetry coefficient (F) can be defined as the ratio of the time required for the exchange zone to move its own height down through the bed to the max time required for the exchange zone to move. If $F = 0$, the exchanger is essentially saturated with the ions being removed. One would expect that the time of formation of the zone at the top of the bed would be nearly equal to that required for the zone to descend by a distance equal to its own height. Conversely, if $F = 1.0$, if the exchanger within the zone at the steady state is essentially free of the ions being removed, the time of formation of the zone would be very short.

The height of the exchange zone can be determined by the relation:

$$h_{ex} = v_{ex} \cdot t_z \tag{8}$$

The quantities of metal complexes removed by the exchange zone from the breakthrough point to exhaustion of the bed were determined graphically from the obtained breakthrough curves.

2.4. Batch studies

The sorption of divalent metal ions Cu(II), Co(II), Ni(II) and trivalent ion Fe(III) in the presence of IDS on the above-mentioned anion exchangers was investigated by batch operation as a function of contact time, different metal–ligand ratios and pH. Batch experiments were performed to determine the recovery factors (%R) as well as the concentration of analyzed metals at the equilibrium (q_e) and at the specific time (q_t).

The recovery factors were calculated from the equation:

$$\%R = \frac{c_0 - c_t}{c_0} \cdot 100\% \tag{9}$$

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

$$q_e = \frac{(c_0 - c_e) \cdot V}{m} \tag{10}$$

$$q_t = \frac{(c_0 - c_t) \cdot V}{m} \tag{11}$$

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

The appropriate amounts of anion exchanger and a solution of known metal ion concentration were shaken in a mechanical shaker (ELPINE, type 357) at the constant temperature 25 °C. The experiments were conducted in the two parallel series. The reproducibility of the measurements was within 5%. The concentrations of chloride ions were not determined.

2.5. Analytical procedure

An atomic absorption spectrometer ContrAA, Analytic Jena was used for quantitative determination of the concentration of heavy metal ions(II)/(III).

3. Results and discussion

3.1. Complexation by IDS

Although the sorption of metal ions on ion exchangers of different types has been widely studied, scanty research was focused on the effect of biodegradable organic ligands such as iminodisuccinic acid on metal uptake. The complexing agent also known as N-(1,2-dicarboxyethyl)-D,L-aspartic acid is very promising taking into account its affect on the environment. For the four possible equilibrium states:

$$\mathrm{H_3ids^- + H^+ \rightleftarrows H_4ids} \tag{12}$$

$$\mathrm{H_2ids^{2-} + H^+ \rightleftarrows H_3ids^-} \tag{13}$$

$$\mathrm{Hids^{3-} + H^+ \rightleftarrows H_2ids^{2-}} \tag{14}$$

$$\mathrm{ids^{4-} + H^+ \rightleftarrows Hids^{3-}} \tag{15}$$

it was found that at around pH 7 this complexing agent is in the form of $\mathrm{Hids^{3-}}$, protonated or deprotonated with decreasing or increasing pH. IDS acts as a pentadentate N, O donor ligand forming chelates of octahedral structure with many metal ions. No bis or binuclear species were found. In the papers by Vasilev et al. [38,39] it was found that IDS forms weak complexes with alkaline earth metals and the moderately stable transition metals. Therefore in the presented paper the reaction of the complex formation:

$$\mathrm{M^{m+} + ids^{n-} \rightleftarrows [M(ids)]^{(n-m)-}} \tag{16}$$

was assumed to be the research basis.

The comparison of the stability constants of complexes (log K) of metal ions (M) and various ligands (L) was presented in [35]. In the paper by Hyvönen [40], it was found that in the dilute solutions of IDS more than 90% of metal ions are bound over a wide pH range. The speciation distributions of studied heavy metal ions as well as of iron(III) in the presence of IDS calculated using a 'NIST Critically Selected Stability Constants of Metal Complexes' the computer program by Motekaitis show that for Cu(II) the effective complexation region was at the pH values 3–12, Zn(II) 5–11 and Mn(II) 7–11. For Fe(III) the conditions are limited to the acidic region 3–6. The competitive hydrolysis of Fe(III) overcomes the complex formation between Fe(III) and IDS. The exemplary percentage distribution of copper(II) complexes with IDS as a function of pH is presented in Fig. 2a. As follows from Fig. 2b for low pH conditions (less than 3), the tendency for M(II)/M(III) ions to form complexes with IDS may be assumed as: Cu(II) > Fe(III) > Zn(II) > Mn(II), whereas for pH > 7 it can be as follows: Cu(II) > Zn(II) > Mn(II) > Fe(III).

3.2. Selection of anion exchangers

As follows from the previous studies strongly basic anion exchangers proved to be effective for the removal of metal ions in the presence of IDS. In this group, the anion exchangers, gel Lewatit MonoPlus M 500, Lewatit MonoPlus M 600 and macroporous Lewatit MonoPlus MP 500 were investigated [35]. In the presented studies attempts were made to investigate mainly medium and weakly basic anion exchangers. For comparison strongly basic Amberlite IRA 402 was also used.

Weakly basic anion exchangers have been extensively studied for many years. It is well known that they possess primary, secondary and/or tertiary amino groups. A mechanism of ion exchange involving dissociation reactions was first postulated by Helfferich [41] according to whom the free-base form of, e.g. a primary amino group in neutral and alkaline pH can be characterized by the dissociation equilibrium:

$$\mathrm{RNH_2 + H_2O \rightleftarrows RNH_3{}^+OH^-} \tag{17}$$

On the other hand, weakly basic anion exchangers bind the transition metal ions through the formation of coordinating bonds. As follows from the literature data, metal ions linking depends on the concentration and kind of heavy metal ion, the matrix flexibility of anion exchangers as well as the kind of functional groups. For

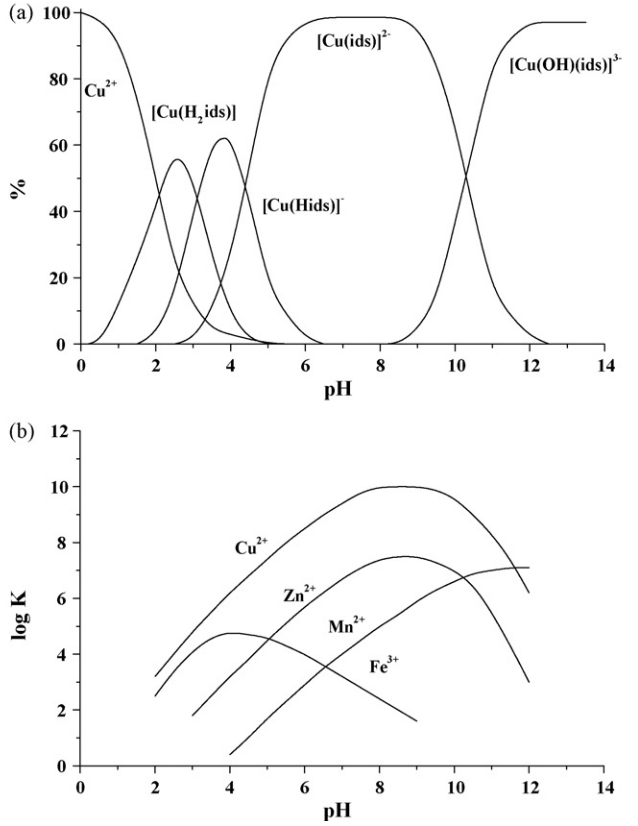


Fig. 2. (a) The percentage of individual forms of Cu(II) complexes with IDS. (b) The conditional stability constants for the M(ids)$^{n-m}$ complexes depending on the pH value.

anion exchangers with highly flexible functional groups, coordination by more than two nitrogen atoms is likely, whereas for those with poorly flexible groups that is primary amine groups coordination by only one nitrogen atom can be assumed [42,43]. In the presented paper this possibility was also taken into account due to possible decomposition of metal complexes with IDS.

3.3. Column studies results

Because majority of industrial and processing waters and wastewaters contain organic substances besides to heavy metals, it is very important to know the behaviour of heavy metals in the presence of organic ligands toward their sorption on anion exchangers. For this reason, the sorption of Cu(II), Co(II), Ni(II) and Fe(III) in the presence of IDS was studied on the medium and weakly basic anion exchangers Lewatit MonoPlus MP 64 and Lewatit MP 62 as well as on the strongly basic anion exchanger Amberlite IRA 402. The obtained breakthrough curves are presented in Fig. 3. The analogous breakthrough curves on Lewatit MonoPlus MP 64 and Lewatit MP 62 in the acetate and iminodisuccinate forms are presented in Figs. 4 and 5. To establish possible sorption of heavy metal ions unbound into complexes, strongly acidic cation exchanger was also used. The breakthrough curve for Cu(II) in the presence of IDS on Lewatit MonoPlus SP 112 is presented in Fig. 6. If the concentration of metal ion in the effluent from the column is plotted as a function of the total volume of effluent collected, a characteristic 'S' curve is obtained. Evidently, when the effluent metal concentration reaches 5% of its value in the influent, the exchange zone reaches the bottom of the bed. This point may be designated as the breakthrough point. As operation of the column is continued, the concentration of metal ion in the effluent rises until it reaches the value of the influent. At this point, the exchange zone has moved out of the bed, and the ion exchanger is exhausted. From the breakthrough curves the distribution coefficients as well as the ion exchange capacities towards M(II)/M(III) complexes with IDS were calculated. The obtained results are presented in Tables 3 and 4.

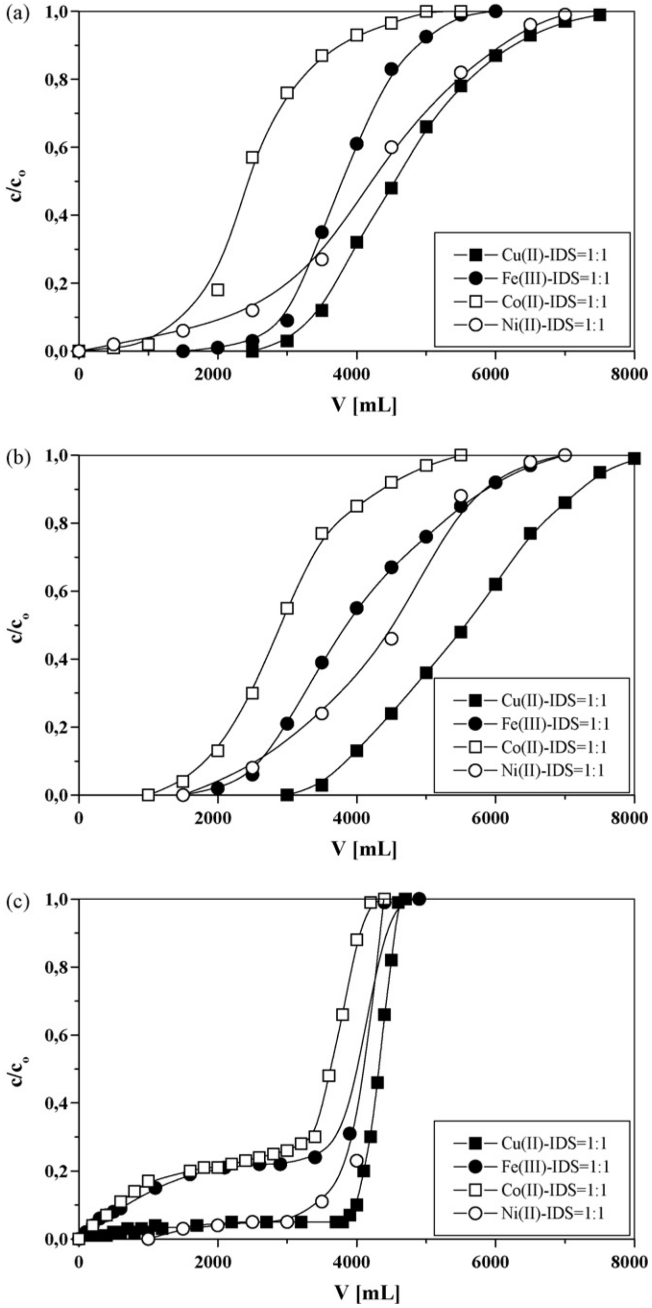


Fig. 3. The breakthrough curves of Cu(II), Co(II), Ni(II) and Fe(III) in the presence of IDS on (a) Amberlit IRA 402, (b) Lewatit MonoPlus MP 64, and (c) Lewatit MP 62.

As follows from the determined breakthrough curves and comparison of calculated sorption parameters, the macroporous medium and weakly basic anion exchangers Lewatit MonoPlus MP 64 and Lewatit MP 62 were more effective for sorption of the above mentioned complexes (Fig. 3, Tables 3 and 4) than the gel strongly basic anion exchanger Amberlite IRA 402. For this anion exchanger, for example, the D_g values obtained from the breakthrough curves for Cu(II), Ni(II), Co(II) and Fe(III) were 1183, 1134, 996, 1090, respectively and were lower than those for Lewatit MonoPlus MP 64 (1949, 1808, 1047, 1630) and Lewatit MP 62 (1935, 1573, 1012, 1344). In the case of the cation exchanger

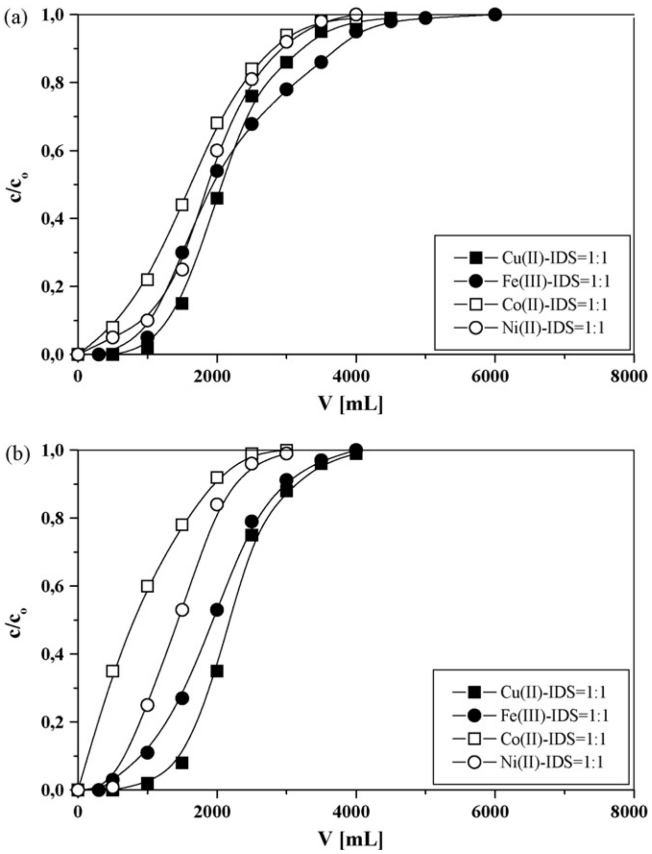


Fig. 4. The breakthrough curves of Cu(II), Co(II), Ni(II) and Fe(III) in the presence of IDS on Lewatit MonoPlus MP 64 in the (a) Ac and (b) IDS forms.

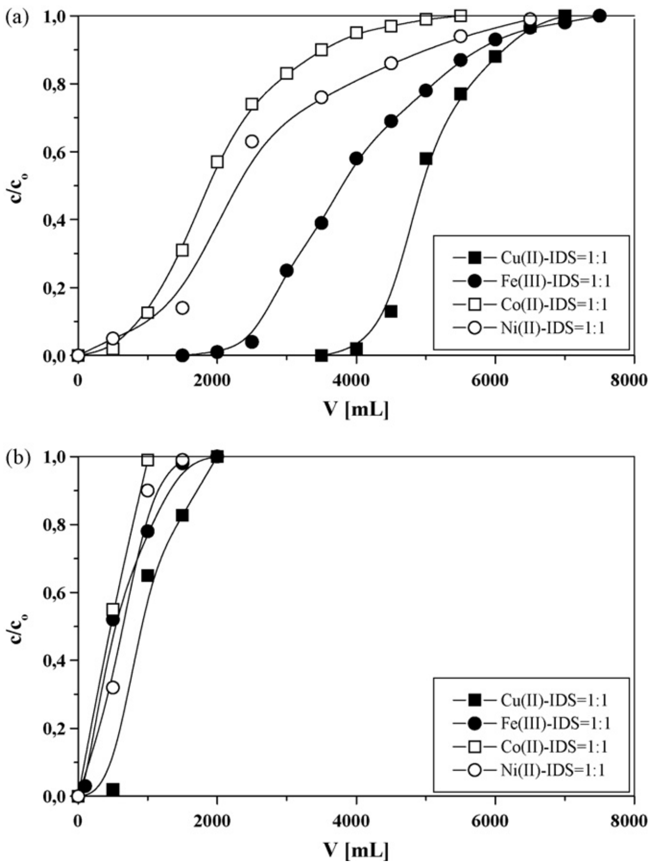


Fig. 5. The breakthrough curves of Cu(II), Co(II), Ni(II) and Fe(III) in the presence of IDS on Lewatit MP 62 in the (a) Ac and (b) IDS forms.

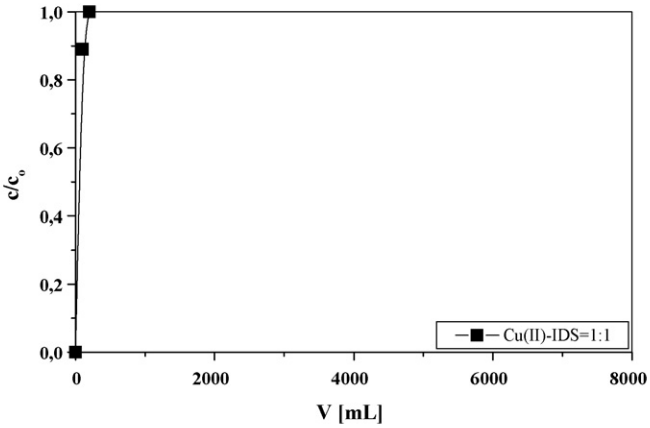


Fig. 6. The breakthrough curves of Cu(II) in the presence of IDS on Lewatit MonoPlus SP 112.

Lewatit MonoPlus SP 112 in the H$^+$ form complexes decomposition does not occur in the ion exchanger phase (Fig. 6), as sorption of Cu(II) cations was not observed.

Based on the obtained results, the studied anion exchangers can be arranged in the order: Lewatit MonoPlus MP 64 > Lewatit MP 62 > Amberlite IRA 402. For Lewatit MonoPlus MP 64 and Lewatit MP 62 the affinity series of metal complexes in the 0.001 M M(II)/M(III)-0.001 M IDS system was found to be as follows: Cu(II) > Ni(II) > Fe(III) > Co(II). The analogous affinity series was found also for Amberlite IRA 402. The highest affinity is exhibited by both Cu(II) and Ni(II) complexes with IDS, which creates possibility of their selective separation from Co(II) and Fe(III) ones.

The results show significant effects of the form of the anion exchangers under investigation on effectiveness of individual metal complexes with IDS sorption. The chloride/free base form of Lewatit MonoPlus MP 64 and free base form of Lewatit MP 62 seem to be the most effective. However, in the case of Amberlite IRA 402 for chloride form, the first fractions of the purified solution should be redirected on the column for their further purification, as complexes of smaller affinity for the anion exchanger presumably of the [M(H_2ids)] or [M(Hids)]$^-$ type are formed in the first stage of the process (as indicated by the shape of the obtained breakthrough curves). The distribution coefficients for the acetate and iminodisuccinate forms of Lewatit MonoPlus MP 64 and Lewatit MP 62 are lower compared to those for the commercial forms. In the case of iminodisuccinate form, complete sorption of Cu(II), Co(II), Ni(II) and Fe(III) complexes is found. Taking into account applicability of the anion exchangers in question in the sorption process, they can be arranged as follows:

> Lewatit MonoPlus MP 64 in the chloride/free base form ≈ Lewatit MP 62 in the free base form > Lewatit MonoPlus MP 62 in the acetate form > Lewatit MonoPlus MP 64 in the acetate form > Lewatit MonoPlus MP 64 in the IDS form > Lewatit MP 62 in the IDS form.

As follows from the sorption parameters presented in Table 4 for the M(II)/M(III)–IDS complexes on Lewatit MonoPlus MP 64 and Lewatit MP 62 the moving rates of the exchange zone (v_{ex}) are almost similar to Amberlite IRA 402 with simultaneous increase of the height of the exchange zone (h_{ex}). Also, the times of the exchange zones formation (t_F) as well as their moving to the points

Table 3
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 Cu(II), Co(II), Ni(II) and Fe(III) complexes with IDS on Lewatit MonoPlus MP 64 and Lewatit MP 62.

M(II)–IDS system	D_g	D_v	C_w	C_r
Lewatit MonoPlus MP 64				
Cu(II)–IDS = 1:1	1949.09	454.06	0.0159	0.0297
Cu(II)–IDS = 1:2	671.35	156.40	0.0025	0.0095
Co(II)–IDS = 1:1	1047.95	244.13	0.0027	0.0153
Ni(II)–IDS = 1:1	1808.98	421.42	0.0029	0.0243
Fe(III)–IDS = 1:1	1630.24	379.78	0.0084	0.0214
Lewatit MonoPlus MP 64 in the Ac form				
Cu(II)–IDS = 1:1	939.05	218.76	0.0029	0.0138
Co(II)–IDS = 1:1	700.91	163.28	0.0028	0.0098
Ni(II)–IDS = 1:1	799.89	186.34	0.0029	0.0053
Fe(II)–IDS = 1:1	829.46	193.23	0.0017	0.0109
Lewatit MonoPlus MP 64 in the IDS form				
Cu(II)–IDS = 1:1	883.45	205.81	0.0031	0.0137
Co(II)–IDS = 1:1	339.67	79.13	0.0024	0.0055
Ni(II)–IDS = 1:1	610.89	142.31	0.0026	0.0086
Fe(III)–IDS = 1:1	830.74	193.53	0.0050	0.0122
Lewatit MP 62				
Cu(II)–IDS = 1:1	1935.34	555.56	0.0203	0.0352
Cu(II)–IDS = 1:2	903.68	259.41	0.0057	0.0183
Co(II)–IDS = 1:1	1012.18	290.56	0.0059	0.0176
Ni(II)–IDS = 1:1	1573.42	451.67	0.0088	0.0256
Fe(III)–IDS = 1:1	1344.96	386.08	0.0078	0.0226
Lewatit MP 62 in the Ac form				
Cu(II)–IDS = 1:1	1722.59	494.49	0.0222	0.0321
Co(II)–IDS = 1:1	654.36	187.84	0.0024	0.0121
Ni(II)–IDS = 1:1	795.19	228.27	0.0018	0.0155
Fe(III)–IDS = 1:1	1320.91	379.18	0.0084	0.0224
Lewatit MP 62 in the IDS form				
Cu(II)–IDS = 1:1	317.40	91.11	0.0025	0.0064
Co(II)–IDS = 1:1	161.05	46.23	0.0018	0.0028
Ni(II)–IDS = 1:1	217.24	62.36	0.0023	0.0038
Fe(III)–IDS = 1:1	180.90	51.93	0.0003	0.0035

of the bed exhaustion (t_T) are also the highest for the above anion exchanger. However, relative sorption capacity in the exchange zone is the largest for Amberlite IRA 402, as indicated by the value of the bed symmetry coefficient larger than 0.6. In the case of the anion exchangers Lewatit MonoPlus MP 64 and Lewatit MP 62 the bed symmetry coefficients are slightly lower than those on Amberlite IRA 402 (values in the range 0.29–0.52), with significant increase in the height of the exchange zone for them (reaching even 100% in some cases, e.g. for the Co(II)–IDS complexes). The total sorption capacity of the resin (C_t) is the largest for the Cu(II)–IDS complexes (Table 3). The moving rates (v_{ex}) of the exchange zone are larger for copper(II) and nickel(II) than cobalt(II) and iron(III).

Table 4
The sorption parameters (t_z, t_T, t_F, v_{ex}, h_{ex}, F) for Cu(II), Co(II), Ni(II) and Fe(III) complexes with IDS on Lewatit MonoPlus MP 64, Lewatit MP 62 and Amberlite IRA 402.

M(II)–IDS system	t_z	t_T	t_F	v_{ex}	h_{ex}	F
Lewatit Mono Plus MP 64						
Cu(II)–IDS = 1:1	4918	7747	3493	0.0050	14.73	0.290
Co(II)–IDS = 1:1	4535	5164	2193	0.0023	19.44	0.517
Ni(II)–IDS = 1:1	6484	7230	2640	0.0038	17.99	0.593
Fe(III)–IDS = 1:1	4451	6197	2720	0.0037	16.31	0.389
Lewatit MP 62						
Cu(II)–IDS = 1:1	5195	8780	3647	0.0045	12.9	0.298
Co(II)–IDS = 1:1	4467	5681	2855	0.0035	20.1	0.361
Ni(II)–IDS = 1:1	5451	7119	3228	0.0037	17.3	0.408
Fe(III)–IDS = 1:1	5554	6245	3531	0.0034	19.1	0.364
Amberlite IRA 402						
Cu(II)–IDS = 1:1	4597	4855	544	0.0038	13.58	0.882
Co(II)–IDS = 1:1	3851	4545	918	0.0035	10.01	0.678
Ni(II)–IDS = 1:1	3467	4648	1160	0.0037	12.66	0.666
Fe(III)–IDS = 1:1	2867	4028	386	0.0035	10.03	0.865

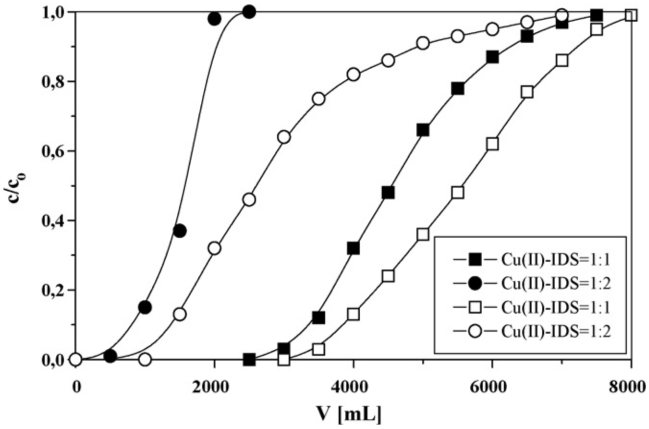


Fig. 7. The breakthrough curves of Cu(II) in the presence of IDS on Lewatit MonoPlus MP 64 (close points) and Lewatit MP 62 (open points).

It is interesting to note that the sorption of metal complexes with IDS on anion exchangers increases with the increasing cations tendency to form anionic complexes. Moreover, according to the literature data [39] the stability constants of Cu(II) complexes ($\log\beta$) of $[CuH_2(ids)]$, $[CuH(ids)]^-$ and $[Cu(ids)]^{2-}$ types in the M(II)–L = 1:1 system are as follows: 5.09, 6.7, 12.74 while in the M(II)–L = 1:2 system are: 5.19, 6.63, 12.43 [38]. Therefore, taking into account the effect of the equivalents ratio, the affinity for the studied anion exchangers Lewatit MonoPlus MP 64 and Lewatit MP 62 for the Cu(II)–IDS = 1:2 system is lower than in the case of Cu(II)–IDS = 1:1 complexes (Fig. 7).

One of the most important ways of minimizing costs of ion exchange process is to obtain the regeneration effluent at the highest concentration possible. As proved previously, in this paper sodium chloride was the most effective and cheap regenerating agent used. Regeneration of the anion exchangers by means of 1 M NaCl is quick and almost complete as follows from the mass balance. In the case of Cu(II)–IDS complexes 98% desorption was achieved. The slightly lower values were obtained for Co(II)–IDS, Ni(II)–IDS and Fe(III)–IDS (95%, 94% and 91%).

3.4. Effect of agitation in batch experiments

In the preliminary studies the effect of the agitation speed was examined. The obtained results show that the sorption process can be constant for agitation speed in excess of 180 rpm. Therefore 180 rpm was used in batch experiments.

3.5. Effect of contact time

Sorption of metal–ligand complexes by ion exchangers consists of three steps: the charge species migrate to the surface of anion exchangers. Then attraction or repulsion (depending on the ion exchanger matrix charge and the type of functional groups) takes places. If there are metal–ligand complexes of the same charge as the ion exchange matrix with attached functional groups, limited mass transport will occur across the surface of ion exchange particle. Furthermore, surface reactions may occur if the complex has any interacting groups, which can associate with the surface functional groups of the ion exchanger. The second step consists of diffusion of the complexed molecules through the pores of the ion exchanger to the functional groups and finally, the sorption reaction takes place. The variety of rate determining mechanisms namely: film diffusion, particle diffusion and chemical reaction may be involved depending on the metal ion under consider-

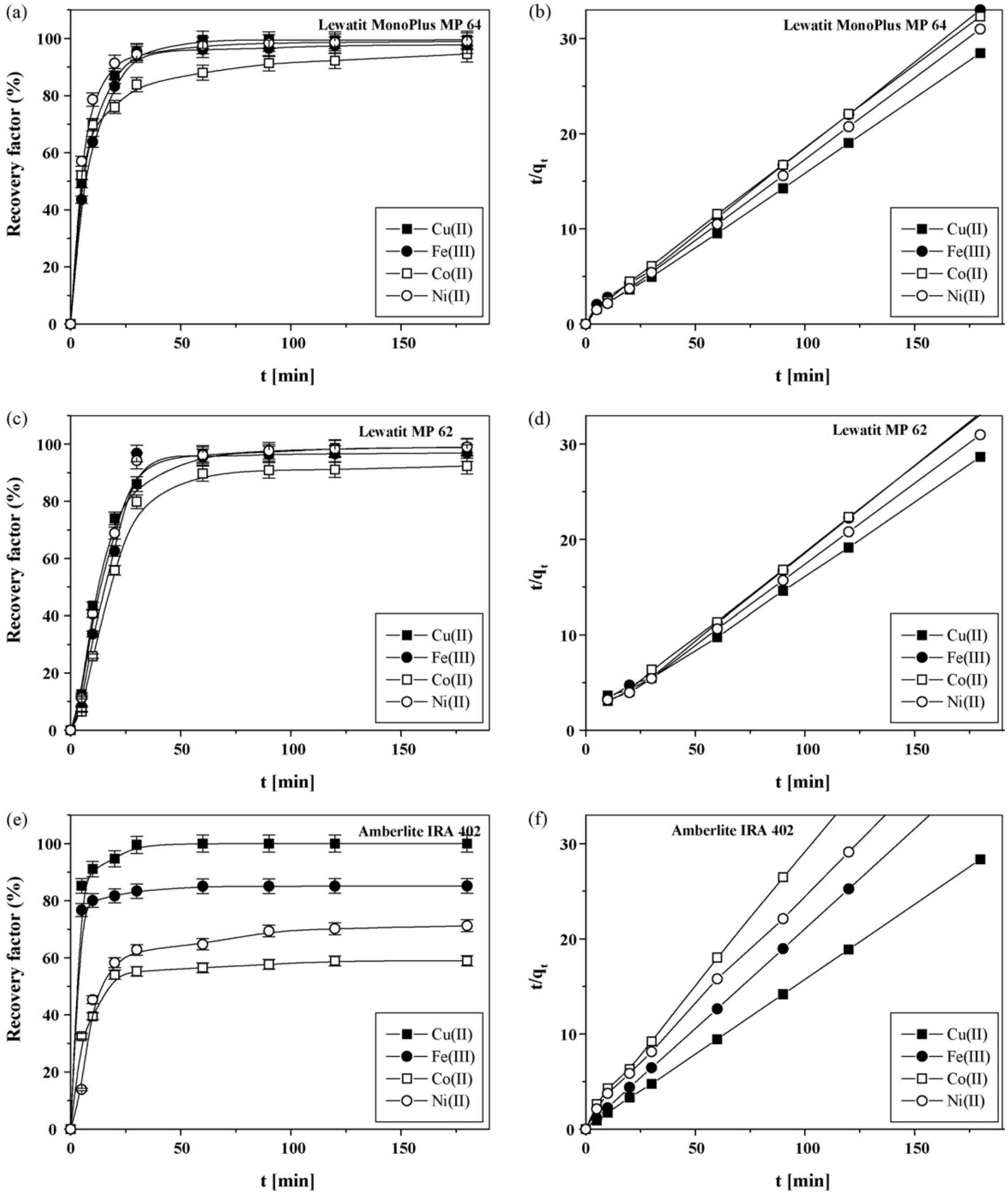


Fig. 8. Comparison of the recovery factor (%*R*) values and the pseudo-second-order kinetics for Cu(II), Co(II), Ni(II) and Fe(III) complexes with IDS on (a and b) Lewatit MonoPlus MP 64, (c and d) Lewatit MP 62 and (e and f) Amberlite IRA 402, depending on the phase contact time (0.5 g of the anion exchanger, initial concentration 1×10^{-3} M).

ation, resin form and the hydrodynamic conditions employed. Other factors affecting this process are the rate of change of complex formation or destruction in solution phase and the competition for soluble ligands or exchange sites among various metal ions.

The obtained results depending on the phase contact time for the 0.001 M M(II)/M(III)–0.001 M IDS system confirmed the research carried out by means of the dynamic method. The values of recovery factors (%*R*) of the studied heavy metal complexes with IDS determined for Amberlite IRA 402, Lewatit MonoPlus MP 64 and Lewatit MP 62 are presented in Fig. 8. As shown, the rate of sorption of studied complexes by the anion exchangers was quite rapid. The metal complexes removal in the first 30 min was in the range of 83–95% in the case of Lewatit MonoPlus MP 64, 86–96% and 55–99% in the case of Lewatit MP 62 and Amberlite IRA 402, respectively. Equilibria were reached within 2 h. At equilibrium, for Lewatit MonoPlus MP 64 99.4% of the Cu(II) complexes, 98.6% of the Ni(II) complexes, 97.6% of the Fe(III) complexes and 92.2% of the cobalt(II) complexes were removed from the solution.

The rate constants for sorption of the above-mentioned complexes on Lewatit MonoPlus MP 64, Lewatit MP 62 and Amberlite IRA 402 were determined using the pseudo-first-order as well as the pseudo-second-order models, which have linear forms as [43,44]:

$$\log(q_e - q) = \log(q_e) - \frac{k_1 t}{2.303} \qquad (18)$$

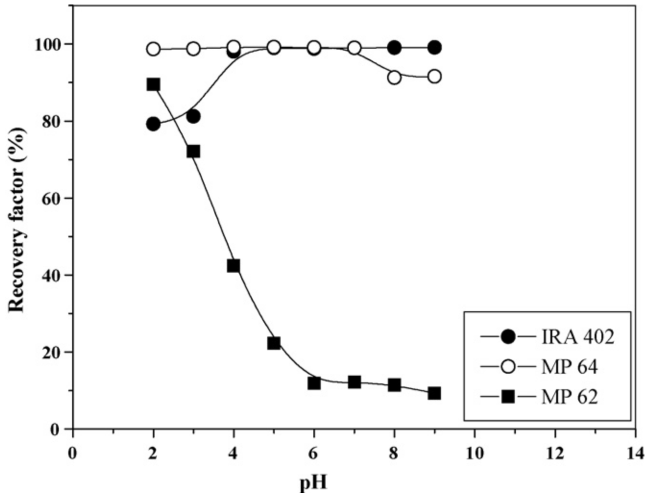


Fig. 9. Comparison of the recovery factor (%*R*) values for Cu(II) complexes with IDS on Amberlite IRA 402, Lewatit MonoPlus MP 64 and Lewatit MP 62 depending on the pH value of the solution.

$$\frac{t}{q} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2} \tag{19}$$

where q_e the amount of metal complexes sorbed at equilibrium (mg/g), q the amount of metal complexes sorbed at time t (mg/g), and k_1, k_2 the equilibrium rate constant (min^{-1}).

The initial adsorption rate (h) is equal to $k_1 q_e$ and $k_2 q_e^2$ (mg/g min) for pseudo-first- and the pseudo-second-order models, respectively. Fig. 8(b, d and f) shows that the data are well described by the pseudo-second-order equation (R^2 values were in the range 0.979–1.000). For Lewatit MonoPlus MP 64 the q_e values obtained were 6.45 for Cu(II)–IDS, 5.88 for Ni(II)–IDS, 5.64 for Fe(III)–IDS and 5.58 for Co(II)–IDS whereas for Lewatit MP 62 they were slightly higher that is 6.88, 6.43, 6.54 and 5.23, respectively. The k_2 values obtained by regression were for the above-mentioned complexes 0.0562, 0.0554, 0.0534, 0.0479 for Lewatit MonoPlus MP 64 and 0.0117, 0.0100, 0.089, 0.057 for Lewatit MP 62, respectively. These values indicate that the sorption of copper was the most rapid.

3.6. Effect of pH and temperature

As mentioned earlier in the sorption process on anion exchangers the negative complexed ions take part. Their structure, charge as well as concentration affect the sorption process. Occurrences of individual, negative forms of metal complexes and free ligands depend on pH value of the solution. Thus determination of pH ranges in which heavy metals occur in the form of anion complexes allows for preliminary determination of sorption system in which removal of heavy metal complexes can take place. Additionally, the pH of the solution determines the degree of ionization of the functional groups especially in the case of weakly basic anion exchangers.

The exemplary data for experiments to establish the pH effect on sorption of Cu(II) in the presence of IDS are given in Fig. 9. For the medium basic anion exchanger Lewatit MonoPlus MP 64 the obtained data indicate that in the sorption process of Cu(II)–IDS complexes quaternary ammonium groups take part. In contact with an alkaline solution, the tertiary amine groups become dissociated and the quaternary ammonium salts are the only ionic groups. This type of resin can be considered to be strongly basic resin with a low ionic density (number of ionic group per unit volume). In the case of Amberlite IRA 402 sorption increases with the increasing pH, reaching a saturation value at around pH 5.0. At all studied pH values, i.e. 2.0–9.0 Amberlite IRA 402 exhibits higher sorption values for Cu(II) complexes than for the other heavy metal ions, i.e. Co(II) and Ni(II) in the presence of IDS. At low pH values only weakly basic Lewatit MP 62 possesses higher sorption capacity for these species, which is in agreement with the nature of the anion exchanger of this type.

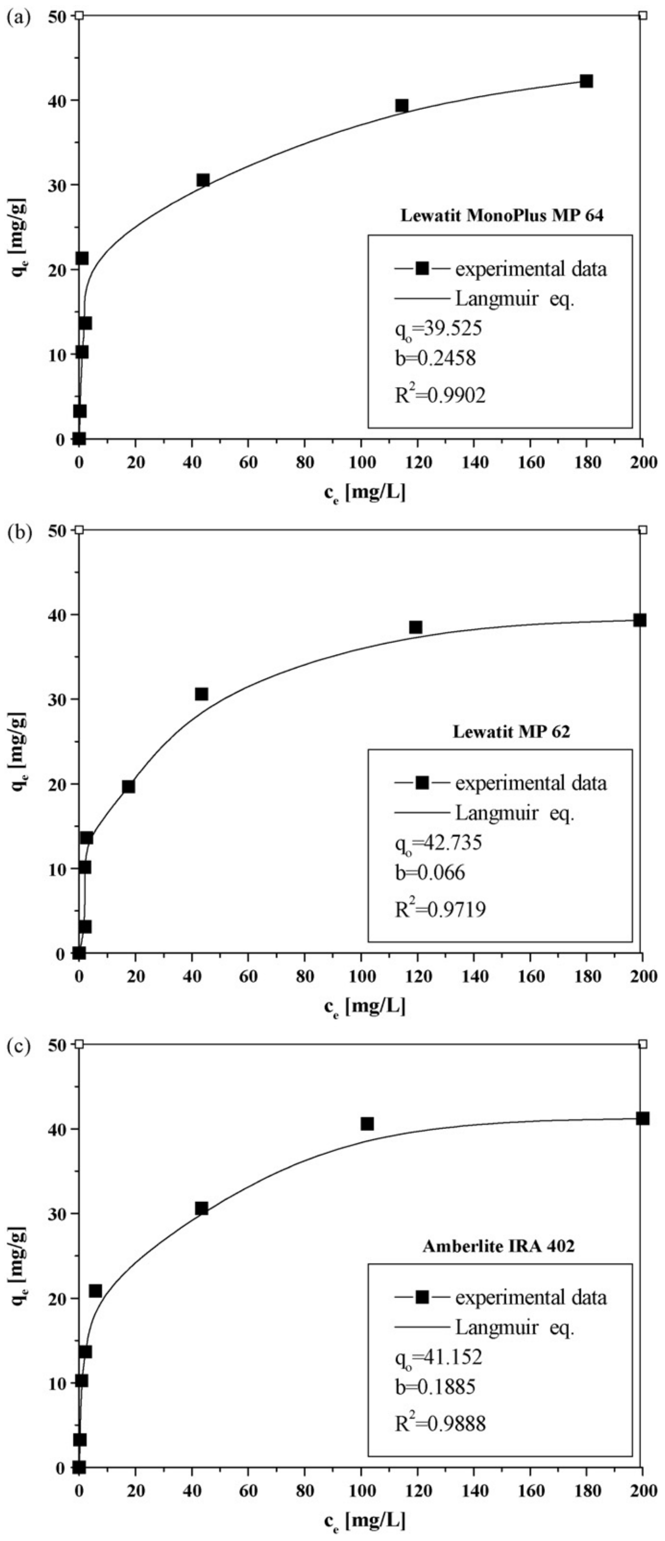


Fig. 10. The Langmuir sorption isotherms of Cu(II) in the presence of IDS on (a) Lewatit MonoPlus MP 64, (b) Lewatit MP 62, and (c) Amberlite IRA 402.

As follows from the effect of temperature, no significant improvement of the sorption process was observed under the effect of temperature increase from 25 °C to 55 °C (data not presented).

3.7. Effect of Cu(II) complex with IDS concentration—sorption isotherm

The heavy metal complexes sorption capacities of the studied anion exchangers were determined under non-competitive conditions (i.e. sorption from single metal ions-solutions) at constant pH values (Fig. 10). The medium basic anion exchanger Lewatit MonoPlus MP 64 possesses comparable affinity for the studied complexes with strongly basic anion exchanger Amberlite IRA 402, maybe due to the ionic density effect. The experimental data were fitted to the Langmuir and Freundlich isotherms. The well-known Langmuir equation was represented as

$$\frac{1}{q_e} = \frac{1}{bq_0c_e} + \frac{1}{q_0} \tag{20}$$

where q_e the equilibrium M(II)/(III) ions concentration on the ion exchanger (mg/g), c_e the equilibrium M(II)/(III) ions concentration in solution (mg/L), q_0 the monolayer capacity of ion exchanger (mg/g), and b the Langmuir adsorption constant (L/g) related to the free energy of adsorption.

The values of q_0 and b were calculated from the slope and the intercept of the linear plots c_e/q_e versus c_e. On the other hand, the Freundlich equation was represented as

$$q_e = K_F c_e^{bF} \tag{21}$$

where K_F and $b_F = 1/n$ are the Freundlich constants corresponding to the adsorption capacity and the adsorption intensity.

The plot of $\ln q_e$ versus $\ln c_e$ was employed to generate the intercept K_F and the slope $1/n$. The isotherm constants as well as the regression coefficients indicate that those values are also high for weakly basic Lewatit MP 62 (Fig. 10). Low values of R^2 for the Freundlich isotherm indicate the inadequacy of this model to explain the sorption process. Taking into account the values of the Langmuir constants (q_0), the anion exchangers can be arranged as follows:

Lewatit MonoPlus MP 62 > Amberlite IRA 402 > Lewatit MonoPlus MP 64

4. Conclusions

1. In the presented paper the polystyrene anion exchangers with different basicity of functional groups were assessed in terms of their applicability for removal heavy metal ions(II) and iron(III) in the presence of the readily biodegradable complexing agent N-(1,2-dicarboxyethyl)-D,L-aspartic acid (IDS). As the traditional complexing agents do not comply with ready-biodegrability criteria and with increasing legislation there is a pressing requirement to replace them with biodegradable alternatives. IDS satisfies these conditions, additionally is an effective complexing agent which can be applied in removal of heavy metal ions.
2. In general, resin basicity has a significant impact on sorption equilibria. The medium and weakly basic anion exchangers Lewatit MonoPlus MP 64 and Lewatit MP 62 were found to have a good total capacity toward all considered metal ions. Satisfactory results were also obtained using the strongly basic anion exchanger Amberlite IRA 402. For this anion exchanger, the results are comparable with those obtained for Lewatit MonoPlus M 500 [35].
3. Equilibrium sorption data were well fitted by the Langmuir model. The maximum sorption capacity was obtained for Lewatit MonoPlus MP 64.
4. For all anion exchangers applied the pseudo-second-order equation gives the best fit to the equilibrium data. For Lewatit MonoPlus MP 64 the q_e values obtained were 6.45 mg/g for Cu(II)–IDS, 5.88 mg/g for Ni(II)–IDS, 5.64 mg/g for Fe(III)–IDS and 5.58 for Co(II)–IDS.
5. The sorption process depends on the pH of the solution of M(II)/(III)–IDS complexes.
6. The anion exchange process seems to be the most suitable for removal of such contamination because of its simplicity, effectiveness, recovery and relatively low cost.

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References

[1] M. Fuerhacker, G. Lorbeer, R. Haberl, Emission factors and sources of ethylenediaminetetraacetic acid in waste water—a case study, Chemosphere 52 (2003) 253–257.
[2] M. Sillanpää, J. Rämö, Adsorption of metal–ethylenediaminetetraacetic acid chelates onto lake sediment, Chemosphere 45 (2001) 881–885.
[3] O. Gyliene, T. Vengris, A. Stončius, O. Nivinskiene, Decontamination of solutions containing EDTA using metallic iron, J. Hazard. Mater. 159 (2008) 446–451.
[4] R.S. Juang, S.H. Lin, T.Y. Wang, Removal of metal ions from the complexed solutions in fixed bed using a strong-acid ion exchange resin, Chemosphere 53 (2003) 1221–1228.
[5] S.I. Amer, Simplified removal of chelated metals, Metal Finishing 102 (2004) 36–40.
[6] Ch. Kim, S.K. Ong, Recycling of lead-contaminated EDTA wastewater, J. Hazard. Mater. 69 (1999) 273–286.
[7] M.D. Tucker, L.L. Barton, B.M. Thomson, B.M. Wagener, A. Aragon, Treatment of waste containing EDTA by chemical oxidation, Waste Manage. 19 (1999) 477–482.
[8] C. Kim, S.K. Ong, Recycling of lead-contaminated EDTA wastewater, J. Hazard. Mater. 69 (1999) 273–286.
[9] R.M. Spearot, J.V. Peck, Recovery process of complex copper-bearing rinse waters, Environ. Prog. 3 (1984) 123–128.
[10] R.T. Belly, J.J. Lauff, C.T. Goodhue, Degradation of ethylenediaminetetraacetic acid by microbial population from an aerated lagoon, Appl. Microbiol. 29 (1975) 787–794.
[11] O. Tunay, I. Kabdasli, R. Tasli, Pretreatment of complexed metal wastewaters, Water Sci. Technol. 29 (1994) 265–274.
[12] F.Ch. Chang, S.-L. Lo, Ch.-H. Ko, Recovery of copper and chelating agents from sludge extracting solutions, Sep. Purif. Technol. 53 (2007) 49–56.
[13] C.P. Huang, M.C. Hsu, P. Miller, Recovery of EDTA from power plant boiler chemical cleaning wastewater, J. Environ. Eng. 126 (2000) 919–924.
[14] J.K. Yang, A.P. Davis, Competitive adsorption of Cu(II)–EDTA and Cd(II)–EDTA onto TiO_2, J. Colloid Int. Sci. 216 (1999) 77–85.
[15] S.J. Kim, H.G. Lee, S.J. Kim, J.K. Lee, E.G. Lee, Photoredox properties of ultrafine rutile TiO_2 acicular power in aqueous 4-chlorophenol, Cu–EDTA and Pb–EDTA solutions, Appl. Catal. A: Gen. 242 (2003) 89–99.
[16] E.H. Park, J. Jung, H.H. Chung, Simultaneous oxidation of EDTA and reduction of metal ions in mixed Cu(II)/Fe(III)–EDTA system by TiO_2 photocatalysis, Chemosphere 64 (2006) 432–436.
[17] N.K. Vel Leitner, I. Guilbault, B. Legube, Reaktivity of OH^- and e_{aq}^- from electron beam irradiation of aqueous solutions of EDTA and aminopolycarboxylic acids, Radiat. Phys. Chem. 67 (2003) 41–49.
[18] T.H. Madden, A.K. Datye, M. Fulton, M.R. Prairie, S.A. Majumadar, B.M. Stange, Oxidation of metal–EDTA complexes by TiO_2 photocatalysis, Environ. Sci. Technol. 31 (1997) 3475–3481.
[19] J.K. Yang, S.M. Lee, EDTA effect on the removal of Cu(II) onto TiO_2, Colloid Int. Sci. 282 (2005) 5–10.
[20] P.M. Nirel, P.E. Pardo, J.C. Landry, R. Revaclier, Method for EDTA speciation determination: application to sewage treatment plant effluents, Water Res. 32 (1998) 3615–3620.
[21] O. Gylienė, O. Nivinskienė, I. Razmutė, Copper(II)–EDTA sorption onto chitosan and its regeneration applying electrolysis, J. Hazard. Mater. 137 (2006) 1430.
[22] S. Metsärinne, P. Peltonen, R. Aksela, T. Tuhkanen, Photodegradation of new amino acid derivatives suitable for chelating agents in pulp bleaching applications, Chemosphere 56 (2004) 1077–1084.
[23] S. Metsärinne, E. Ronkainen, R. Aksela, T. Tuhkanen, M. Sillanpää, Determination of novel complexing agents in pulp and paper mill effluents and in lake water by liquid chromatography, J. Chromatogr. 1094 (2005) 56–59.
[24] S. Metsärinne, E. Ronkainen, T. Tuhkanen, R. Aksela, M. Sillanpää, Biodegradation of novel amino acid derivatives suitable for complexing agents in pulp bleaching applications, Sci. Total Environ. 377 (2007) 45–51.
[25] G. Xueyi, K. Inoue, Elution of copper from vermiculite with environmentally benign reagents, Hydrometallurgy 70 (2003) 9–21.
[26] L. Nitschke, A. Wilka, C. Cammerer, G. Lind, G. Metzner, Biodegradation and aquatic of β-alaninediacetic acid (β-ADA), Chemosphere 34 (1997) 807–815.

[27] M. Borowiec, J. Skut, K. Hoffman, J. Hoffman, Life cycle assessment of chelating compounds use in liquid fertilizers by biodegradation test, Proc. ECOpole 1 (2007) 91–95 (in Polish).

[28] M. Borowiec, J. Skut, K. Hoffman, J. Hoffman, Biodegradation as a process of the life cycle assessment of chelating compounds use in liquid fertilizers, Ecol. Chem. Eng. 14 (2007) 1095–1101.

[29] C. Gabriel, C.P. Raptopoulou, A. Terzis, N. Lalioti, A. Salifoglou, Synthesis, structural, spectroscopic and magnetic susceptibility studies of a soluble Cr(III)–heida (2-hydroxyethyliminodiacetic acid) complex. Relevance to aqueous chromium(III)–heida speciation, Inorg. Chim. Acta 360 (2007) 513–522.

[30] P. Ager, W.D. Marshall, An approach to complexant recycling in softwood pulping, Can. J. Anal. Sci. Spectrosc. 46 (2001) 162–169.

[31] P.C. Vandevivere, H. Saveyn, W. Verstraete, T.C.J. Feijtel, D.R. Schowanek, Biodegradation of metal-[*S*,*S*]-EDDS complexes, Env. Sci. Technol. 35 (2001) 1765–1770.

[32] A. Polettini, R. Pomi, E. Rolle, D. Ceremigna, L. De Propris, M. Gabellini, A. Tornato, A kinetic study of chelant-assisted remediation of contaminated dredged sediment, J. Hazard. Mater. 137 (2006) 1458–1465.

[33] P.W. Jones, D.R. Williams, Chemical speciation simulation used to assess the efficiency of environment-friendly EDTA alternatives for use in the pulp and paper industry, Inorg. Chim. Acta 339 (2002) 41–50.

[34] S. Tandy, A. Ammann, R. Schulin, B. Nowack, Biodegradation and speciation of residual SS-ethylenediaminedisuccinic acid (EDDS) in soil solution left after soil washing, Environ. Pollut. 142 (2006) 191–199.

[35] D. Kołodyńska, H. Hubicka, Z. Hubicki, Studies of application of monodisperse anion exchangers in sorption of heavy metal complexes with IDS, Desalination 239 (2009) 216–228.

[36] D. Kołodyńska, Z. Hubicki, M. Gęca, Polyaspartic acid as a new complexing agent in removal of heavy metal ions on polystyrene anion exchangers, Ind. Eng. Chem. Res. 47 (2008) 6221–6227.

[37] D. Kołodyńska, H. Hubicka, Z. Hubicki, Sorption of heavy metal ions from aqueous solutions in the presence of EDTA on monodisperse anion exchangers, Desalination 227 (2008) 150–166.

[38] V.P. Vasilev, A.V. Katrovtseva, I.P. Gorelov, N.V. Tukumova, Stability of complexes of Ni(II) with iminodisuccinic acid, Zh. Neorg. Khim. 41 (1996) 1320–1323 (in Russian).

[39] V.P. Vasilev, A.V. Katrovtseva, S.A. Bychkova, N.V. Tukumova, Stability of complexes of Co(II) and Cu(II) with iminodisuccinic acid, Zh. Neorg. Khim. 43 (1998) 808–809 (in Russian).

[40] H. Hyvönen, M. Orama, H. Saarinen, R. Aksela, Studies on biodegradable chelating ligands: complexation of iminodisuccinic acid (ISA) with Cu(II), Zn(II), Mn(II) and Fe(III) ions in aqueous solution, Green Chem. 5 (2003) 410–414.

[41] F.G. Helfferich, Ion Exchange, Dover Publications Inc., New York, 1995.

[42] Ch-Ch Wang, Ch-Ch Wang, Adsorption characteristics of metal complexes by chelated copolymers with amio group, React. Funct. Polym. 66 (2006) 343–356.

[43] C. Stöhr, J. Horst, W.H. Höll, Application of the surface complex formation model to ion exchange equilibria. Part V. Adsorption of heavy metal salts onto weakly basic anion exchangers, React. Funct. Polym. 49 (2001) 117–132.

[44] K.V. Kumar, S. Sivanesan, Selection of optimum sorption kinetics: comparison of linear and non linear method, J. Hazard. Mater. 134 (2006) 277–279.