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The biodegradable complexing agents as an alternative to chelators in sorption of heavy metal ions

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ABSTRACT

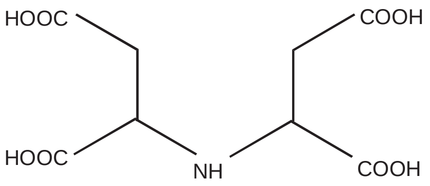
The aim of this study was to explain the influence of chemical conditions on the ion exchange capacity and the kinetics of heavy metal ions i.e. copper(II), zinc(II), cobalt(II) nickel(II), cadmium(II), lead(II) and iron(III) in the presence of complexing agents of a new generation. For investigations the following complexing agents were selected: sodium salt of *N*-(1,2-dicarboxyethyl)-D,L-aspartic acid, which has the commercial name Baypure CX 100 (IDS), glutamic diacetic acid (GLDA) also known as Dissolvine GL-38 and N,N′- ethylenediaminedisuccinic acid (EDDS) known as Enviomet^{TM} C140. In the studies an anion exchange was applied which is a method used in water treatment and wastewater purification. This method is suitable for removal of all contaminants in the ionic form 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.

***Keywords*:** Heavy metal ions; ion exchangers; biodegradable complexing agents

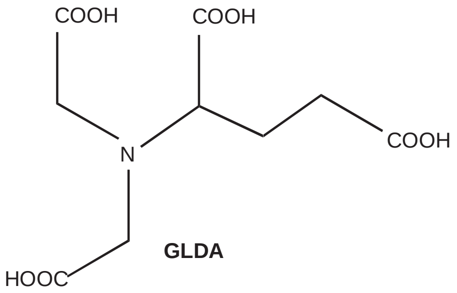
1. Introduction

The behaviour and effects of chelating agents in the environment have received considerable attention. Chelating agents belong predominantly to the two different groups— aminopolycarboxylates and polyphosphonates. Aminopolycarboxylates (APCs) such as ethylenediaminetetraacetate (EDTA), nitrilotriacetate (NTA) and diethylenetriaminepentaacetate (DTPA) are technically important chelating agents, which are used in large quantities for a wide variety of industrial applications [1–5]. Most of these complexing agents are resistant to the conventional biological and physicochemical methods for wastewater treatment and for the purification of drinking water.

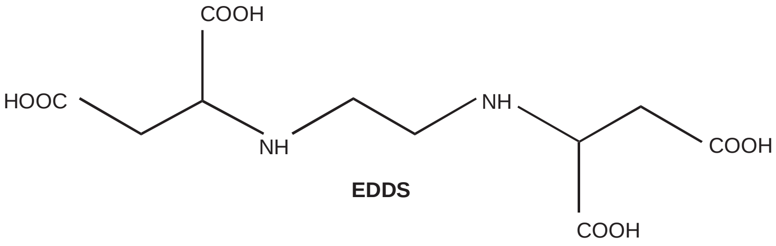
There are a number of alternative products to be as effective as EDTA and NTA but most of them also have some restrictions. For example, organophosphonates were found to be not readily biodegradable. Others are readily biodegradable, such as citrates and gluconates, but do not have a sufficiently strong chelating power compared to NTA or EDTA. 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 [5]. Also such chelating agents as EGTA (ethylenedioxydiethylenediaminetetraaceticacid)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. According to recent investigations, *S,S′*-EDDS is a viable replacement ligand in pulp and paper industry, in cosmetics etc. and also IDS is comparable to EDTA [6–18]. The structural formulae of the above-mentioned complexones are presented below:



IDS



GLDA



EDDS

Later considerable attention has been paid to the complexing agents of new generation. Characterized by much better biodegradability they constitute the alternative for traditional chelating agents. The end of the ’90s is the period of great interest in these agents. At present this interest is still growing, owing to better knowledge of their properties, effective methods of preparation as well as possibility of their modification.

This creates perspectives for their application broadening and popularisation. This may also be the result of general world trend and stricter legislation in the field of environmental protection with great emphasis on human health and thus the natural environment.

In the last decade ion exchange technology has found widespread application in the removal of heavy metals from industrial wastewaters. Commercial cation, anion and chelating ion exchange resins are effective in removing metal ions from a variety of aqueous sources. A number of investigators have studied the removal of inorganic metal ions Cu(II), Zn(II), Co(II), Ni(II), Pb(II), Cd(II) and Cr(III, VI) from aqueous solution using different resins [19–26]. For example, in the paper by Pehlivan and Altun [23] the removal of Pb(II), Cu(II), Zn(II), Cd(II) and Ni(II) from aqueous solution using Lewatit CNP 80 and Lewatit TP 207 was reported. Agrana and Sahu [22] studied the separation of Pb(II) from the binary mixture with Fe(III), Ca(II) and Ni(II) on Amberlite IRC 718.

Removal of metal ions in the form of negative complexes from waters and wastewaters on anion exchangers has also been intensively studied. Anion exchangers are characterized by high chemical and mechanical stability, high ion exchange capacity, and ion exchange rate. Recently the sorption of Cr(VI) on Lewatit MonoPlus MP 500 and Lewatit MonoPlus MP 64 was described [26].

The aim of this work is to determine the influence of complexing agents of a new generation such as IDS, GLDA and EDDS in the removal of heavy metal ions from waters and wastewaters. Their influence on the effectiveness of sorption was tested for the monodisperse strongly basic polystyrene anion exchanger Lewatit MonoPlus M 500. The evaluation of different chemical conditions on the ion exchange capacity and on the kinetics of copper(II), zinc(II), cobalt(II) nickel(II), cadmium(II), lead(II) and iron(III) complexes permitted for optimalization of removal of heavy metal ions.

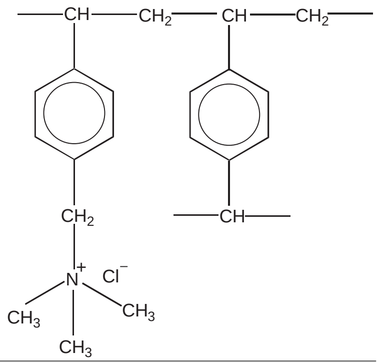
2. Materials and Methods

2.1. Resin

The monodisperse strongly basic polystyrene anion exchanger *Lewatit MonoPlus M 500* produced by the Lanxess, Germany was used in the investigations. Its brief characteristic is presented in Table 1 [27]. Prior to use it was washed with 1 M NaOH and 1 M HCl to remove organic and inorganic impurities and then washed several times with deionized water.

Table 1
Characteristic of the anion exchanger Lewatit MonoPlus M 500.

Lewatit MonoPlus M 500	
Matrix	PS-DVB
Structure	gel
Commercial form	Cl^-
Appearance	beige, opaque
Total capacity (Cl^- form)	1.3 eq/L
Bead size	0.62 mm ± 0.05
Max temp. range	60°C
Operating pH range	0–12



2.2. Chemicals

Copper(II) solution was prepared by dissolving copper(II) chloride in distilled water. Zinc(II), cobalt(II), nickel(II) and iron(III) solutions were prepared in an analogous. Cadmium(II) and lead(II) solutions were prepared by dissolving their nitrates in distilled water. They were further diluted to get the solutions of various known concentrations. Then the appropriate amount of IDS, GLDA or EDDS solutions were added in order to obtain M(II)/(III)-L = 1:1 complexes. The prepared solutions of complexed metal ions at initial concentration 1×10^{-3} M (i.e. 63.54 mg/L for Cu(II), 65.39 mg/L for Zn(II), 58.93 mg/L for Co(II), 58.69 mg/L for Ni(II), 55.84 mg/L for Fe(III), 112.411 mg/L for Cd(II) and 207.2 mg/L for Pb(II)). The initial pH values of the solutions were without adjustment (for M(II)-IDS complexes in the range 4.0–4.6; for M(II)-GLDA complexes in the range 8.5–9.5 and for M(II)-EDDS complexes in the range 8.0–8.5). All chemicals used were of analytical reagent grade.

2.3. Column studies

The breakthrough curves were determined using 10 mL of the swollen anion exchanger. The prepared solutions of complexed metal ions at initial concentration 1×10^{-3} M in the M(II)/(III):L = 1:1 system were passed continuously downwards through the resin beds keeping the flow rate at 0.6 mL/min. The effluent was collected in fractions in which the metal(II)/(III) content was determined. The mass (D_g) and volume (D_v) distribution coefficients as well as the working (C_w) and total (C_r) ion exchange capacities were calculated from the determined breakthrough curves according to equations 1–3 [28]:

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

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

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

where

$\overline{V}$ — 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),
c_0 — the initial concentration of M(II)/M(III) solution (mg/L).

The total ion exchange capacities (C_r) were calculated by integration along the curve.

2.4. Batch studies

The sorption of Cu(II), Zn(II), Co(II), Ni(II), Pb(II), Cd(II) and Fe(III) complexes with IDS, GLDA and EDDS on the above-mentioned anion exchanger was investigated by batch operation as a function of contact time and pH. The experiments were performed to determine the concentration of analyzed metals at the equilibrium (q_e) and at the specific time (q_t). The resin phase concentrations of M(II)/(III) complexes at the equilibrium, q_e (mg/g) and at the specific time, q_t (mg/g) were obtained according to:

$$q_e = \frac{(c_0 - c_e)V}{m} \tag{4}$$

$$q_t = \frac{(c_0 - c_t)V}{m} \quad (5)$$

where

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

In the case of equilibrium and kinetic experiments, 0.3 g of anion exchanger was added into 100 mL flasks and mixed in 30 mL solution of Cu(II), Zn(II), Co(II), Ni(II), Pb(II), Cd(II) and Fe(III) complexes with IDS, GLDA and EDDS in the M(II)/(III):L = 1:1 system, respectively. The initial concentration of each solution was 1×10^{-3} M. The flasks were shaken in a mechanical shaker Elpin type 357, (Elpi*N*-Plus, Poland) at the constant temperature of 25°C. The samples were collected at the defined time or at different time intervals. After completion of each batch of experiments the solution was filtered. The filtrate was analyzed by AAS method using ContrAA (Analytic Jena, Germany) to determine the amount of metal left after sorption. The experiments were conducted in the two parallel series. The reproducibility of the measurements was within 5%.

Adsorption isotherm studies were carried out using the batch equilibrium technique. Initial concentrations of the studied solutions were prepared in the range 0.5×10^{-4} M – 2×10^{-2} M. A series of 100 mL flasks containing 0.3 g anion exchanger samples and 30 mL solutions of Cu(II) complexes with IDS, GLDA and EDDS were mixed until equilibrium were obtained. The adsorption equilibrium data were fitted into the Langmuir and Freundlich models, which were represented as [29,30]:

$$q_e = \frac{q_0 K_L c_e}{1 + K_L c_e} \quad (6)$$

$$q_e = K_F c_e^{\frac{1}{n}} \quad (7)$$

where

q_e — the equilibrium M(II)/(III) complexes concentration on the anion exchanger, (mg/g),
c_e — the equilibrium M(II)/(III) complexes concentration in solution (mg/ L),
q_0 — the monolayer capacity of anion exchanger (mg/g),
K_L — the Langmuir adsorption constant (L/mg) related to the free energy of adsorption.
K_F — the Freundlich constant related to the adsorption capacity (mg/g),
$1/n$ — the Freundlich constant related to the surface heterogeneity.

2.5. Desorption process

Regeneration of the strongly basic anion exchanger Lewatit MonoPlus M 500 was tested using 1 M HCl solution. The saturated anion exchanger with Cu(II) complexes with IDS, GLDA or EDDS (0.5 g) was put in flasks in contact with 50 mL of regeneration agent. The flasks were shaken at constant temperature of 25°C. The anion exchanger was separated and the liquid was analysed in order to determine the concentration of Cu(II).

3. Results and discussion

3.1. Complexes with IDS, GLDA and EDDS

For the four possible equilibrium states of IDS: $H_3ids^- + H^+ \rightleftarrows H_4ids$; $H_2ids^{2-} + H^+ \rightleftarrows H_3ids^-$; $Hids^{3-} + H^+ \rightleftarrows H_2ids^{2-}$ and $ids^{4-} + H^+ \rightleftarrows Hids^{3-}$ it was found that at around pH 7 this complexing agent is in the form of $Hids^{3-}$ protonated or deprotonated with decreasing or increasing pH. The aqueous complexation of IDS is characterized by the formation of 1:1 metal to ligand complexes, weak complexes with alkaline earth metals and the moderately stable transition metal monocomplexes $[Ni(ids)]^{2-}$, $[Co(ids)]^{2-}$ and $[Cd(ids)]^{2-}$ [12–15]. In the case of GLDA the following reactions: $H_3glda^- + H^+ \rightleftarrows H_4glda$; $H_2glda^{2-} + H^+ \rightleftarrows H_3glda^-$; $Hglda^{3-} + H^+ \rightleftarrows H_2glda^{2-}$ and $glda^{4-} + H^+ \rightleftarrows Hglda^{3-}$ are possible whereas for EDDS they can be as follows: $H_3edds^- + H^+ \rightleftarrows H_4edds$; $H_2edds^{2-} + H^+ \rightleftarrows H_3edds^-$; $Hedds^{3-} + H^+ \rightleftarrows H_2edds^{2-}$ and $edds^{4-} + H^+ \rightleftarrows Hedds^{3-}$ [16–18].

Therefore in this paper the reaction of the complex formation:

Table 2
The stability constants of M(II)-L=1:1 complexes with IDS, GLDA and EDDS [10,11,15].

M(II)	IDS	GLDA	EDDS
Ba(II)	2.1	3.5	3.0
Ca(II)	5.2	5.9	4.6
Cd(II)	8.4	9.1	16.4
Co(II)	10.5	10.0	13.6
Cu(II)	13.1	13.1	18.4
Fe(III)	15.2	11.7	22.0
Mg(II)	6.1	5.2	6.0
Ni(II)	12.2	10.9	16.7
Zn(II)	10.8	10.0	13.4
Pb(II)	11.0	10.5	12.7

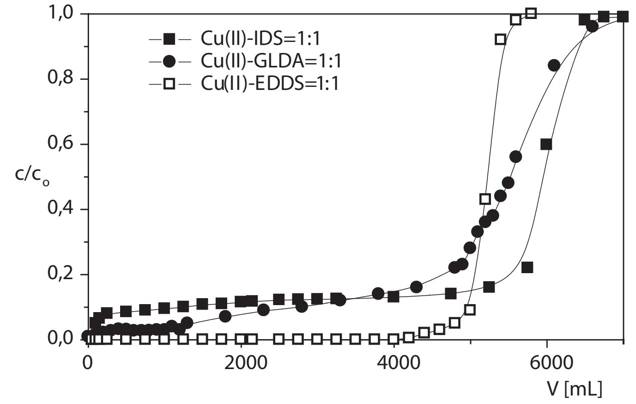


Fig. 1. The breakthrough curves of Cu(II) complexes with IDS, GLDA and EDDS on Lewatit MonoPlus M 500 (c_0 1 × 10^{-3} M, swollen anion exchanger dose 10 mL, flow rate 0.6 mL/min).

$$M^{m+} + L^{4-} \rightleftarrows [ML]^{(4-m)-} \quad (8)$$

was taken into account, where L = ids, glda, edds. The comparison of stability constants of M(II)-L = 1:1 complexes is presented in Table 2.

3.2. Sorption of M(II) complexes with IDS, GLDA and EDDS—the dynamic method

Assuming that the Cu(II) complexes 1:1 are formed, the anion exchange reactions for Lewatit MonoPlus M 500 can be written as:

$$2R–N^+ (CH_3)_3\, Cl^- + [Cu(ids)]^{2-} \rightleftarrows [R–N^+ (CH_3)_3]_2\, [Cu(ids)]^{2-} + 2Cl^- \quad (9)$$

$$2R–N^+ (CH_3)_3\, Cl^- + [Cu(glda)]^{2-} \rightleftarrows [R–N^+ (CH_3)_3]_2\, [Cu(glda)]2^- + 2Cl^- \quad (10)$$

$$2R–N^+ (CH_3)_3\, Cl^- + [Cu(edds)]^{2-} \rightleftarrows [R–N + (CH_3)_3]_2\, [Cu(edds)]^{2-} + 2Cl^- \quad (11)$$

where R—the anion exchanger skeleton (PS-DVB).

From the research results presented in Fig. 1 and Table 3, the mass (D_g) and volume (D_v) distribution

Table 3
The mass (D_g) and volume (D_v) distribution coefficients as well as working (C_w) and total (C_r) ion exchange capacities for Cu(II) complexes with IDS, GLDA and EDDS on Lewatit MonoPlus M 500.

Cu(II)	IDS	GLDA	EDDS
D_g	1827.50	1654.09	1567.57
D_v	595.12	549.59	520.84
C_w	0.0009	0.0006	0.0254
C_r	0.0336	0.0323	0.0330

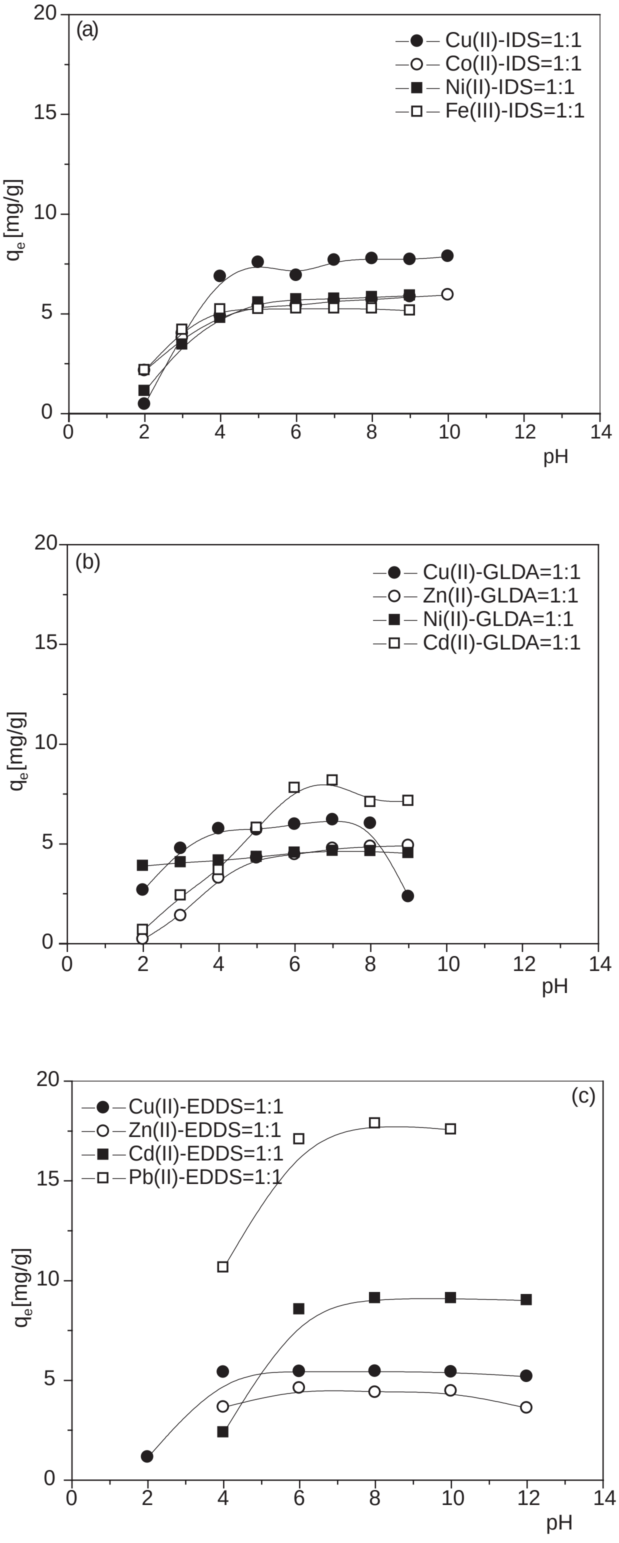


Fig. 2a–c. Comparison of the of the resin phase concentrations of M(II)/(III) complexes with IDS—(a) GLDA—(b) and EDDS—(c) on Lewatit MonoPlus M 500 depending on the pH value of the solution (c_0 1 × 10^{-3} M, anion exchanger dose 10 g/L, shaking time 3 h, shaking speed 180 rpm, temperature 25°C).

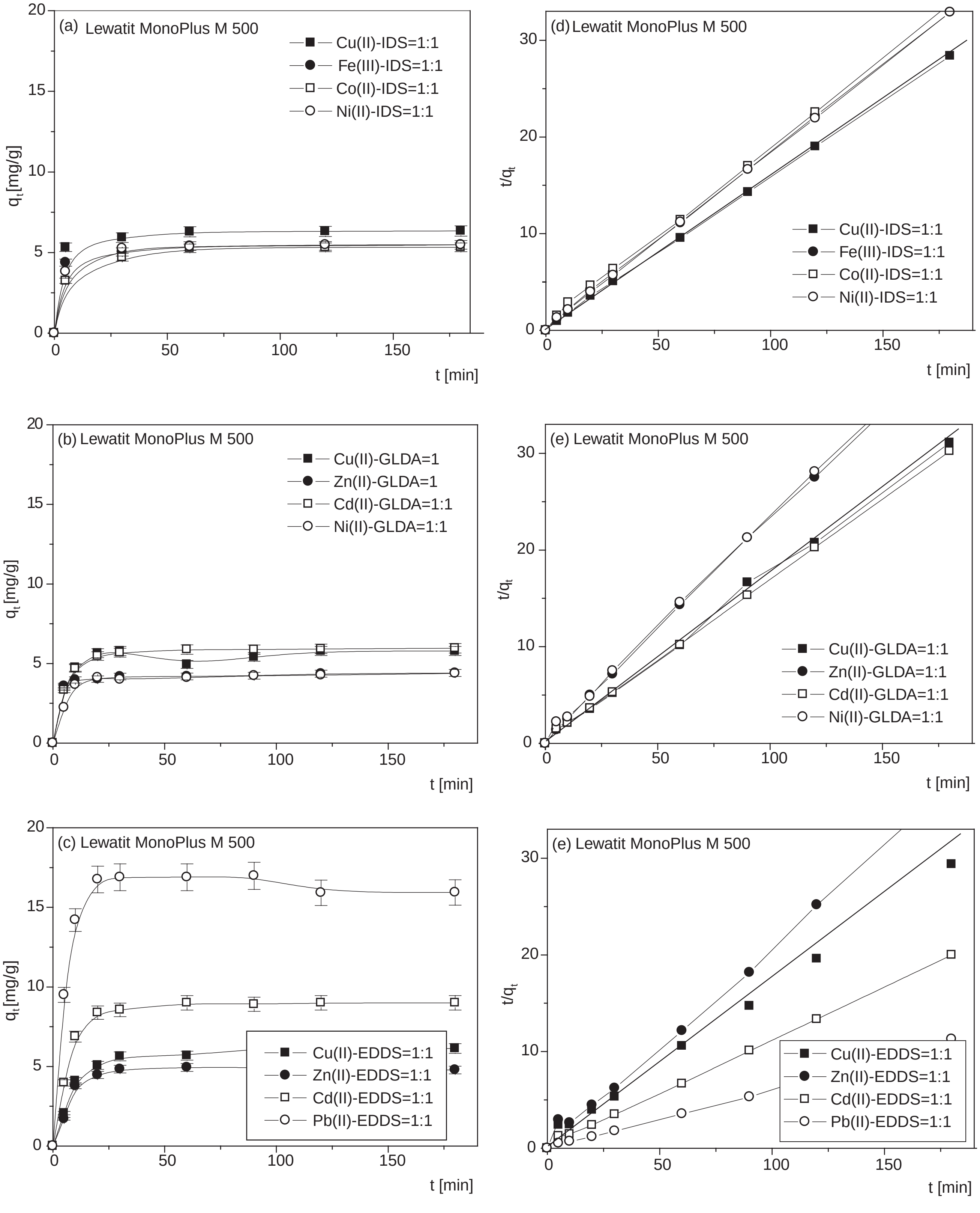


Fig. 3a–f. Comparison of the sorption capacities (a-c) and the pseudo second order linear kinetic plots (d-f) for the M(II)/(III) complexes with IDS, GLDA and EDDS on Lewatit MonoPlus M 500 depending on the phase contact time (c_0 1×10^{-3} M, anion exchanger dose 10 g/L, shaking time from 5 to 180 min, shaking speed 180 rpm, temperature 25°C).

coefficients as well as the working ion exchange capacities (C_w) and the total ion exchange capacities (C_r) of Cu(II) complexes with IDS, GLDA and EDDS for the strongly basic anion exchanger Lewatit MonoPlus M 500 depend on the structure of complexes formed.

The values of distribution coefficients obtained from the breakthrough curves are the highest for IDS. In the case of GLDA and EDDS they are similar.

3.3. Sorption of M(II)/(III) complexes with IDS, GLDA and EDDS—the batch method

Most metal ions are soluble in water within certain pH ranges and are quite insoluble besides the appropriate pH range. Even within the optimum pH ranges for solubility most metal ions are soluble to only a limited extent. In the presence of complexing agents, they are capable of maintaining in solution. Formed metal complexes are generally hydrophilic compounds but this does not exclude adsorption and different adsorption properties between the chelate species. It was observed that the efficiency of removal of selected heavy metal complexes increases with pH in all cases. Figure 2a shows the variation of the resin phase concentrations of M(II)/(III) at the equilibrium in the presence of IDS as a function of pH for Lewatit MonoPlus M 500. For comparison, the values obtained for the GLDA and EDDS complexes are also included (Figs. 2b–c). For Lewatit MonoPlus M 500 maximum sorption was observed for EDDS complexes in the pH range 6–12. The sorption for IDS is higher than that observed for GLDA. The sorption capacities were from 3.19 mg/g at the pH value 4.0 to 6.93 mg/g at pH 8.0 for IDS; from 3.19 mg/g at the pH value 4.0 to 6.93 mg/g at pH 8.0 for GLDA and from 3.19 mg/g at the pH value 4.0 to 6.93 mg/g at pH 8.0 for EDDS, respectively.

In Figs. 3a–c the contact time curves for sorption of M(II)/M(III) complexes with IDS, GLDA and EDDS on Lewatit MonoPlus M 500 are presented.

For Cu(II), Zn(II), Co(II), Ni(II), Fe(III), Cd(II) and Pb(II) in the single metal ion systems for the initial concentration 1×10^{-3} M, the time to reach an equilibrium state was about 20 min. At lower initial metal ion concentrations the variation of the unadsorbed M(II)/(III) complexes concentration in the solution was negligible after 60 min of contact time. In the case of IDS the percentages of sorption of Cu(II), Fe(III), Co(II) and Ni(II) complexes were about 99%, 97%, 90% and 93%, respectively. The residual concentrations of metal complexes were found to be as follows: 0.14 mg/L for Cu(II), 1.13 mg/L for Fe(III), 5.73 mg/L for Co(II) and 3.99 mg/L for Ni(II). In the case of Cu(II), Zn(II), Cd(II) and Ni(II) complexes with GLDA and Cu(II), Zn(II), Cd(II) and Pb(II) complexes with EDDS these values were as follows: 91%, 67%, 52%, 75% and 96%, 73%, 80% and 74%, respectively.

For the kinetic data, kinetic analysis was also performed with the aid of a pseudo second order equation. The value of the rate constant k_2 were calculated using the formula,

$$\frac{dq}{dt} = k_2(q_e - q_t)^2 \tag{12}$$

where q_e and q_t — the removal amount of M(II)/(III) ions per unit mass of the anion exchanger at equilibrium and time.

Figs. 3d–f show a plot of the linearized form of the pseudo second order model according to the equation:

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 {q_e}^2} \tag{13}$$

for the sorption of M(II)/(III) complexes with IDS, GLDA and EDDS on Lewatit MonoPlus M 500 for the contact times in the range 1–180 min. In addition to the pseudo second order rate equation, the intraparticle diffusion model was commonly used for examining the steps involved during adsorption. It can be expressed as:

$$q_t = k_i t^{0.5} \tag{14}$$

where k_i — the diffusion coefficient (mg/g min$^{0.5}$).

The rate of sorption was assumed to be proportional to the difference between the capacity at equilibrium and the capacity at any time. The obtained results show that the pseudo first-order model did not adequately describe the sorption results of M(II)/(III) complexes with IDS, GLDA and EDDS on Lewatit MonoPlus M 500 because the correlation coefficients (R^2) between the predicted and the experimental values are ranged between 0.675 and 0.955 (data not presented). As evident from the data presented in Table 4, the R^2 values for the pseudo second-order kinetic model were closer than the pseudo first-order kinetic model indicating better agreement. The R^2 for the pseudo second-order model of the abovementioned ions ranged between 0.9992 and 0.9996, 0.9993 and 0.9997 and 0.9973 and 0.9999 for IDS, GLDA and EDDS, respectively.

To optimize the design of an adsorption system for the adsorption of adsorbates, it is important to establish the most appropriate isotherm model. Various isotherm equations like those of Langmuir, Freundlich, and Redlich-Peterson have been used to this aim. In this paper, the adsorption parameters for Cu(II) complexes with IDS, GLDA and EDDS obtained from the fitting of Langmuir isotherm models with the experimental data are listed in Table 5. They describe the mono-component

Table 4
Kinetic parameters for M(II)/(III) complexes with IDS, GLDA and EDDS on Lewatit MonoPlus M 500.

Metal ion	*Cu(II)-IDS*	*Fe(III)-IDS*	*Co(II)-IDS*	*Ni(II)-IDS*
		Pseudo second-order		
q_2 [mg/g]	6.385	5.509	5.444	5.515
k_2 [g/mg min]	0.114	0.104	0.053	0.119
h [mg/g min]	4.655	3.171	1.591	3.624
R^2	0.9998	0.9998	0.9998	0.9992
		Intraparticle diffusion		
k_i [mg/g min]	0.313	0.278	0.325	0.288
R^2	0.4578	0.4898	0.6781	0.5143
Metal ion	*Cu(II)-GLDA*	*Zn(II)-GLDA*	*Ni(II)-GLDA*	*Cd(II)-GLDA*
		Pseudo second-order		
q_2 [mg/g]	5.800	4.409	6.027	4.403
k_2 [g/mg min]	0.065	0.144	0.079	0.085
h [mg/g min]	2.211	2.795	2.874	1.658
R^2	0.9996	0.9996	0.9997	0.9993
		Intraparticle diffusion		
k_i [mg/g min]	0.305	0.210	0.343	0.246
R^2	0.505	0.4386	0.5810	0.5627
Metal ion	*Cu(II)-EDDS*	*Zn(II)-EDDS*	*Cd(II)-EDDS*	*Pb(II)-EDDS*
		Pseudo second-order		
q_2 [mg/g]	6.329	4.879	9.166	16.103
k_2 [g/mg min]	0.032	0.088		0.482
h [mg/g min]	1.295	2.133	3.593	1.250
R^2	0.9979	0.9973	0.9991	0.9999
		Intraparticle diffusion		
k_i [mg/g min]	0.411	0.305	0.553	0.872
R^2	0.7011	0.5799	0.6050	0.4605

equilibrium characteristics of sorption of Cu(II) complexes with IDS, GLDA and EDDS on Lewatit MonoPlus M 500. The analogous dates obtained on base of the Freundlich model are also presented in this table. The experimental equilibrium sorption data were obtained by varying the concentrations of Cu(II) in the presence of the above-mentioned chelators on Lewatit MonoPlus M 500 (Fig. 4).

Table 5
Isotherm parameter values for the removal of Cu(II) complexes with IDS, GLDA and EDDS on Lewatit MonoPlus M 500.

	Langmuir constants		
System	q_o	K_L	R^2
Cu(II)-IDS	82.644	0.022	0.9950
Cu(II)-GLDA	88.495	0.026	0.9750
Cu(II)-EDDS	95.238	0.024	0.9939
	Freundlich constants		
System	K_F	n	R^2
Cu(II)-IDS	6.198	2.326	0.9377
Cu(II)-GLDA	3.272	1.655	0.9739
Cu(II)-EDDS	7.556	2.246	0.8894

The obtained values of R^2 suggest that the Langmuir isotherm provides a good model of the sorption system. The sorption capacity for Cu(II)-EDDS is higher than those for Cu(II)-GLDA and Cu(II)-IDS, but the sorption constant, K_L, for Cu(II)-GLDA is higher than those for Cu(II)-EDDS and Cu(II)-IDS. The calculated sorption capacities (q_0) were 95.24 mg/g for Cu(II)-EDDS, 88.49 mg/g for Cu(II)-GLDA and 82.64 mg/g for Cu(II)-IDS, respectively and they are with agreement with the obtained experimental capacities ($q_{e,exp}$) 96.82 mg/g for Cu(II)-EDDS, 85.55 mg/g for Cu(II)-GLDA and 80.33 mg/g for Cu(II)-IDS. The sorption capacity order has been found for the Cu(II)-IDS, Cu(II)-GLDA and Cu(II)-EDDS complexes sorption on Lewatit MonoPlus M 500 as: EDDS > GLDA > IDS.

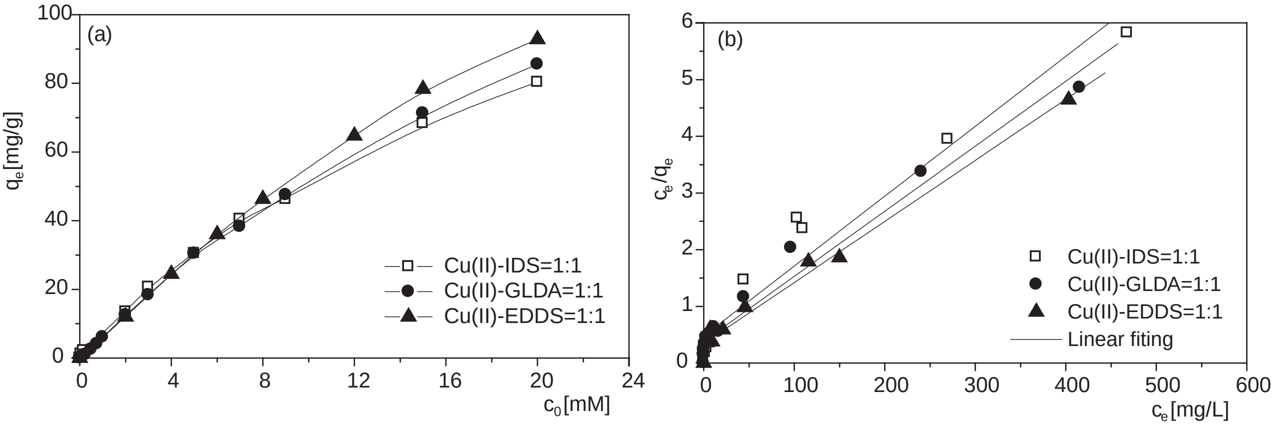


Fig. 4. The Langmuir sorption isotherms (a) and their linear forms (b) of Cu(II) complexes with of IDS, GLDA and EDDS on Lewatit MonoPlus M 500 (c_0 0.5 × 10^{-4}–2 × 10^{-2} M, anion exchanger dose 10 g/L, shaking time 3 h, shaking speed 180 rpm, temperature 25°C).

3.4. Desorption process

The desorption efficiency of Cu(II) complexes with IDS, GLDA and EDDS from Lewatit MonoPlus M 500 obtained using with 1 M HCl are shown in Fig. 5. The obtained results reveal that the desorption efficiency was equal to 92 %, 99 % and 96 %, respectively. These curves show a steep rise initially, followed by a negligible concentration of copper(II) in the effluent. The amount of Cu(II) sorbed on this anion exchanger decrease from 6.38 mg/g to 0.51 mg/g in the case of the Cu(II)-IDS complexes, from 5.80 mg/g to 0.06 mg/ g in the case of the Cu(II)-GLDA complexes and from 6.13 mg/g to 0.24 mg/g in the case of the Cu(II)-EDDS complexes. In these three cases the removal of the most part of copper(II) from the anion exchanger and consequently its regeneration was achieved with 30 minutes. The regeneration of Lewatit MonoPlus M 500 using 1 M HCI solution for the removal of copper(II) and the conversion into chloride form enables almost 100% recovery of the sorptive capacity.

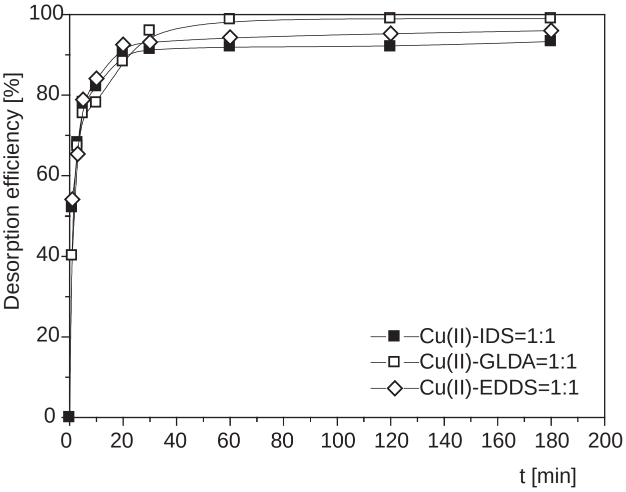


Fig. 5. The desorption efficiency of the Cu(II)-IDS, GLDA and EDDS complexes from Lewatit MonoPlus M 500 using 1M HCl (anion exchanger dose 10 g/L, shaking time from 1 to 180 min, shaking speed 180 rpm, temperature 25°C).

4. Conclusion

Summing up, it can be stated that the sodium salts of IDS, EDDS and GLDA can be of great significance in purification of wastewaters from heavy metal ions. The obtained results demonstrate the possibility of removal of anionic complexes from wastewaters using the strongly basic polystyrene anion exchanger Lewatit MonoPlus M 500. As it is reasonable and even necessary to find alternative more biodegradable chelating agents than the traditional ones of the EDTA types, IDS, GLDA and EDDS can be very promising in the future to this aim.

In this paper the sorption of some heavy metal complexes with such readily biodegradable complexing agents from aqueous solutions on Lewatit MonoPlus M 500 was studied as a function of pH, contact time and concentration of metal solutions. It was proved that pH and initial concentration of heavy metal(II)/(III) complexes influence on the effectiveness of their sorption. The batch equilibrium was relatively fast and reached equilibrium after about 60 min of the contact. The ion exchange process, which is pH dependent showed the maximum removal of heavy metal ions in the pH range 4.0-8.0. The experimental data have been analyzed using the Langmuir and the Freundlich isotherm models. Under the optimized conditions, the percentage of metal complexes removal by Lewatit MonoPlus M 500 adsorption was over 95%. The sorption of studied metal ions in the presence of IDS, EDDS and GLDA on Lewatit MonoPlus M 500 followed the pseudo second order reversible kinetics. The regeneration of Lewatit MonoPlus M 500 using 1 M HCI solution for the removal of copper(II) and the conversion into chloride form enables almost 100% recovery of the sorptive capacity.

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