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The effect of the novel complexing agent in removal of heavy metal ions from waters and waste waters

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ABSTRACT

The removal of Cu(II), Zn(II), Co(II), Ni(II), Pb(II) and Cd(II) from waters and industrial wastes in the presence of the novel chemical reagent *N*,*N*-bis(carboxymethyl)glutamic acid (GLDA) was investigated. The effect of surface properties on the sorption behaviour of studied complexes was investigated by FT-IR/PAS (Fourier transform-infrared photoacoustic spectroscopy) and SEM (scanning electron microscopy). The effects of contact time, concentration of the reagents and equilibrium pH of solution, temperature and presence of interfering ions on sorption of Cu(II), Zn(II), Co(II), Ni(II), Pb(II) and Cd(II) complexes with GLDA on the commercially available ion exchangers Lewatit MonoPlus MP 500, Amberlite IRA 958 and Diaion CR-20 were examined by batch and column techniques. It was found that pH of 9.0 was favourable for the sorption process, which followed the pseudo second-order equation. Of the sorption models used, the Dubinin–Radushkevich (D–R) model was found to be appropriate. The sorption was temperature-dependent as well as dependent on the presence of Ca(II), Mg(II), Cl^-, SO_4^{2-}, NO_3^- ions. The maximum sorption capacity ($q_{e,\mathrm{exp}}$) for Pb(II) complexes with GLDA on the polyacrylate anion exchanger Amberlite IRA 958 was found to be 99.80 mg/g. For the polystyrene anion exchanger Lewatit MonoPlus MP 500 the analogous value for Cu(II) complexes was as 81.62 mg/g. Therefore, it was found that GLDA is effective for the removal of Pb(II) and has the potential application for the purification of waters polluted by heavy metals. In the case of chelating Diaion CR-20, the decomposition of the sorbed complexes in the resin phase should be assumed.

1. Introduction

Heavy metal pollution is a problem associated with the areas of intensive industry. Industrial waste waters are main pollutants of waters. Hydrometallurgical, electroplating, tanning, artificial fertilizers and herbicides production as well as dyeing, textile, electrochemical, motor, energetic industries now are considered to be one of the largest sources of heavy metals in waste water. They contain heavy metals such as Cr(III,VI), As(III,V), Cd(II), Pb(II), Cu(II), Zn(II) and Hg(II), which are particularly dangerous for the environment and living organisms. Among various treatment techniques available, the most commonly used is ion exchange. Its main advantages are the recovery of valuable metals, selectivity, reduced sludge formation and the meeting of strict discharge specifications. For specific waste waters, when besides heavy metal ions they contain also complexing agents, the application of anion exchange is justified. In this case process of exchanging anions (heavy metal complexes with chelating agents) between a solution and an anion exchanger or a chelating ion exchanger is carried out. Another specific methods of treating this type of waste waters, for example from electroless copper rinse waters containing chelating agents were discussed in detail in paper [1]. Current chelate substances used in many fields of industry are based on aminopolycarboxylic acids (e.g. ethylenediaminetetraacetic acid EDTA) and also on phosphates (tripolyphosphates TPPs). However, as EDTA is not readily biodegradable and phosphates are known to cause eutrophication in natural waters. Therefore they are regarded to be as environmentally unfriendly [2–4]. In the group of different environmental concern of chelating agents, one should mention predominantly their stability as well as in the case of their high concentrations the ability to enhance the mobility and transport of the radionuclides such as uranium (as UO_2^{2+}), technetium (as TcO_4^-), radium (as Ra^{2+}) and also ^{90}Sr, ^{137}Cs, ^{239}Pu and ^{241}Am. The presence of complexing agents also enhances heavy metals mobility, for instance Zn(II), Cd(II), Ni(II), Cr(VI), Cu(II), Pb(II) and Fe(III) in soils [5–8].

In the nearest future it may be reasonable and even necessary to find alternative and apply more biodegradable chelating agents of a new generation [9–12]. Therefore *S*,*S*′-ethylenediamine disuccinic acid (EDDS) [13], *N*-(1,2-dicarboxyethyl)-D,L-aspartic acid also known as iminodisuccinic acid (IDS) [14,15], polyaspartic acid (DS) [16], methyleneglycinediacetic acid (MGDA) [17], *N*,*N*-bis(carboxymethyl)glutamic acid

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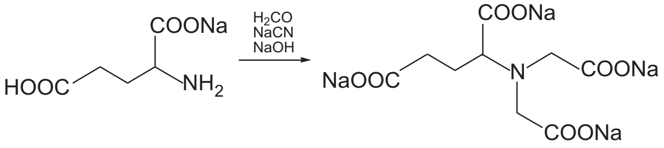
Nomenclature

MP 500	Lewatit MonoPlus MP 500
IRA 958	Amberlite IRA 958
CR 20	Diaion CR 20
b_T	the Temkin constant related to the heat of sorption [J/mol]
C	the intercept which reflects the boundary layer effect
c_e	the equilibrium concentration of M(II)[mg/L]
c_t	the concentration of M(II) in the aqueous phase at time t [mg/L]
C_w	the working ion exchange capacity [g/mL]
C_r	the total ion exchange capacity [g/mL]
c_0	the initial concentration of M(II) solution [mg/L]
D_g	the mass distribution coefficient [–]
D_v	the bed distribution coefficient [–]
ΔG°	the change in Gibbs free energy of sorption [kJ/mol]
ΔH°	the change in enthalpy of sorption [kJ/mol]
h	the initial sorption rate [mg/g min]
K_d	the distribution coefficient [L/g]
K_F	the constant of Freundlich isotherm [mg/g(L/mg)$^{1/n}$]
K_L	the Langmuir constant related to the free energy of sorption [L/mg]
K_T	the Temkin isotherm constant [L/g]
k_1	the rate constant of pseudo first-order sorption [L/min]
k_2	the rate constant of pseudo second-order sorption [g/m min]
k_i	rate parameter of intraparticle diffusion model [mg/g min$^{-1/2}$]
m	the mass of the ion exchanger [g]
$1/n$	the Freundlich constant related to the surface heterogeneity [–]
q_e	the amount of M(II) sorbed at equilibrium [mg/g]
q_t	the amount of M(II) sorbed at time t [mg/g]
q_0	the Langmuir monolayer sorption capacity [mg/g]
R	the gas constant [kJ/mol K]
R_L	the Hall parameter [–]
S (%)	the sorption percent [%]
ΔS°	the change in entropy of sorption [J/mol K]
T	the temperature [K]
V	the volume of the solution [L]
V_i	the void (interparticle) ion exchanger bed volume which amounts to ca. 0.4 of the bed volume [mL]
V_j	the bed volume [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]
$\overline{V}$	the volume of effluent at $c = c_0/2$ (determined graphically) [mL]
X_m	the D–R sorption capacity [mg/g]
β	the constant related to the sorption energy [mol^2/J]
ε	the Polanyi potential given by: $\varepsilon = RT\ \ln\left(1+\frac{1}{c_e}\right)$

(GLDA) [18,19], L-asparaginic-*N*,*N*-diacetic acid (ASDA) [20,21], 1,3-propylenediaminetetraacetic acid (1,3-PDTA) [22], *N*-2(-hydroxyethyl)iminodiacetic acid (HEIDA) [23], β-alaninediacetic acid (β-ADA) [24,25], ethylenedioxydiethylenediaminetetraacetic acid (EGTA) [26,27] were proposed. Their structures were presented in paper [28].

According to the recent investigations, especially easily biodegradable S,S′-EDDS is a viable replacement ligand in bleaching applications [13,29]. It has been proposed as a safe and environmentally friendly replacement for EDTA in soil extraction and for enhancement of phytoremediation. Also IDS is comparable to EDTA. Iminodisuccinic acid is produced in the process, which does not generate any off-gases and harmful effluents. The other significant product of the Lanxess firm is DS. Besides the complexing properties used, among others, in thickening of sugar beet juice in raw sugar production, DS being an environmentally friendly dispersing agent found application in filler slurries in the production process of roofing tiles, wall paints with good light reflection and coating compositions. MGDA is also readily biodegradable in compliance with the Organization for Economic Co-operation and Development (OECD) standards and is used for enhancing the cleaning efficiency of laundry and dishwashing detergents as well as industrial and all-purpose cleaners. ASDA was proposed for remediation of soil polluted by heavy metals, especially Cu(II) and Pb(II) whereas PDTA is used primarily in the photo-processing industry. HEIDA and ADA are also a potential alternative. They are used when relatively weak chelating agents are indispensable. However, EGTA owing to preferential binding of Ca(II) ions with significantly greater affinity than the other divalent cations is used to functionalize polymeric membranes used in removal of heavy metal ions and in medical applications [30].

In response to these concerns, a novel readily biodegradable chelating agent, tetrasodium of *N*,*N*-bis(carboxymethyl)glutamic acid (also denoted as Dissolvine GL-38) that is manufactured principally from the flavour enhancer monosodium glutamate (MSG) by the fermentation of readily available corn sugars was proposed [31]:



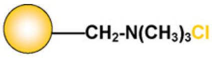
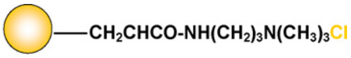
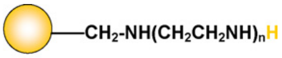
L-sodium Glutamate L-GLDA-Na$_4$

In contrast to the manufacture of EDTA whose carbon content is fossil based, the carbon source of GLDA is primarily biobased. Therefore GLDA is the only chelating agent with ‘green’ carbon atoms.

However, taking into account the fact that though complexing agents of a new generation are environmentally friendly, combined with heavy metal ions such as copper(II), lead(II), cadmium(II), zinc(II), nickel(II) or mercury(II) only a few of them are biodegradable so it is necessary to get to know the ways of effective removal of this type of combinations from waters and waste waters. Literature lacks the data about their application in heavy metal ions removal. Studies of the above-mentioned problem seem to be advisable as removal of toxic heavy metals is essential.

This paper is a continuation of sorption studies of heavy metal complexes with aminopolycarboxylic complexing agents of a new generation on ion exchangers and sorbents of different types. Here the report of study of the sorption of Cu(II), Zn(II), Co(II), Ni(II), Pb(II) and Cd(II) ions with GLDA (Dissolvine GL-38) on the macroporous polystyrene and polyacrylate anion exchangers as well as the chelating ion exchanger is presented. The influence of the phase contact time, concentrations of the reagents, pH of solutions, temperature and the presence of interfering ions on the ion exchange removal of heavy metal ions from waters and waste waters was studied. As a rule, the sorption process on the ion exchangers should not only be used for separation of heavy metal ions from contaminated effluents but also concentrate metal solutions which can be applied economically as a source of heavy metals or have relatively low volumes to be stored or dumped in an economically and environmentally convenient way.

Table 1
Structure of the applied ion exchangers.

 $-CH_2-N(CH_3)_3Cl$	 $-CH_2CHCO-NH(CH_2)_3N(CH_3)_3Cl$	 $-CH_2-NH(CH_2CH_2NH)_nH$
PST-DVB **Strongly basic resin type 1 (SBA1)** **Lewatit MonoPlus MP 500**	**A-DVB** **Strongly basic resin (SBA)** **Amberlite IRA 958**	**PST-DVB** **Chelating ion exchange resin** **Diaion CR-20**

2. Materials and methods

2.1. Chemicals and instruments

The resin *Lewatit MonoPlus MP 500* is a polystyrene, strongly basic, monodisperse, macroporus anion exchanger of type 1 obtained from Lanxess (Leverkusen, Germany). This resin is ideal for all demineralization applications as well as special applications, i.e. complexed heavy metal recovery and oxoanions. Its total ion exchange capacity is 1.1 eq/L, the particle size 0.63 mm ± 0.05 mm, the thermal stability to 313 K.

The resin *Amberlite IRA 958* is a polyacrylate, strongly basic, macroporous anion exchanger of type 1 obtained from Rohm and Haas (Chauny, France). It is used for removal of organic compounds. Its total ion exchange capacity is 0.8 eq/L, the particle size 0.675–0.875 mm, the thermal stability to 363 K.

The resin *Diaion CR 20* is a commercially available chelating ion exchanger obtained from Mitsubishi Chemical Industries Ltd. (Tokyo, Japan). It has polyamine groups as chelating ligands bonded to a highly porous crosslinked polystyrene matrix. Diaion CR-20 shows large affinity for transition metal ions, but does not adsorb alkali, alkaline earths, and Sn(II), Zr(IV), Th(IV), Al(III) and Fe(II) ions. Its total ion exchange capacity is >0.8 eq/L, the particle size 0.3–0.55 mm, the thermal stability to 373 K.

The chemical structure of the above resins is presented in Table 1. Prior to the use they were contacted with 1 M NaOH and 1 M HCl to remove organic and inorganic impurities and to convert the ion exchange sites to the desired forms. Then they were washed several times with demineralized water.

The metal–chelate solutions of Cu(II), Zn(II), Co(II), Ni(II), Pb(II) and Cd(II) were prepared by adding equimolar amounts of respective metal salts to the Dissolvine GL-38 (GLDA) solutions with a concentration of 1.0×10^{-3} mol/L in the M(II)–GLDA = 1:1 system. GLDA (38% solution) was obtained from Akzo Nobel Functional Chemicals (Amersfoort, The Netherlands). The percentage of individual forms of GLDA depending on the pH value is presented in Fig. 1. In the research the obtained solutions were used without pH adjustment which were as follows: Cu(II) – 8.74, Zn(II) – 9.17, Co(II) – 8.54, Ni(II) – 9.02, Pb(II) – 9.30 and Cd(II) – 9.35. The other chemicals used were of analytical grade.

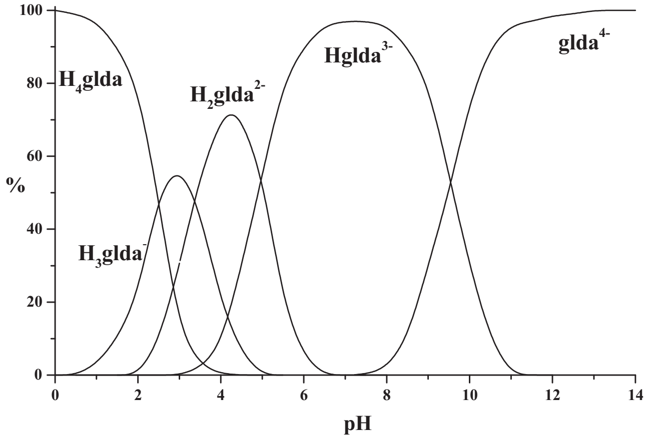


Fig. 1. The percentage of individual forms of GLDA depending on the pH value [18].

The laboratory shaker Elpin type 357 (Elpin-Plus, Lubawa, Poland) was used for the agitation. The pH values were measured with a Radiometer PHM 84 pH meter (Copenhagen, Denmark) with the glass REF 451 and calomel pHG 201-8 electrodes. The concentrations of heavy metals were measured by the AAS method using a ContrAA (Analytic Jena, Jena, Germany) spectrometer. FT-IR/PAS scans were made by Bio-Rad Excalibur 3000 MX spectrometer (Bio-Rad Laboratories BV, Veenendaal, The Netherlands) equipped with the photoacoustic detector MTEC 300. The SEM analysis of ion exchangers was studied by the scanning electron microscope LEO1430VP (Carl Zeiss, Jena, Germany) with the EDX detector (Röntec, GmbH).

2.2. Batch experiments

In the batch experiments, 50-mL of solutions of Cu(II), Zn(II), Co(II), Ni(II), Pb(II) and Cd(II) complexes with GLDA were agitated with selected ion exchangers (0.5 g) in conical 100 mL flasks at different time intervals at room temperature. The precision of the volume measurements was 0.1%. The experiments were conducted in the two parallel series with the reproducibility ±5%. The obtained results were presented as the mean value. Based on the obtained results, the sorption percent S (%), the metal complexes concentration (q_t, mg/g) and the distribution coefficient (K_d, L/g) were calculated by the mass balance equations:

$$S\,(\%) = \frac{(c_0 - c_t)}{c_0} \times 100 \tag{1}$$

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

$$K_d = \frac{(c_0 - c_t)}{c_t} \times \frac{V}{m} \tag{3}$$

In order to investigate the effect of pH, 50 mL of 1.0×10^{-3} mol/L complexed with the GLDA metal solutions of Cu(II), Zn(II), Co(II), Ni(II), Pb(II) and Cd(II) and 0.5 g of Lewatit MonoPlus MP 500, Amberlite IRA 958 and Diaion CR-20 were used. Experiments were performed in the pH range 2–12. As for the temperature, the investigations were conducted for Cu(II) complexes with GLDA in the temperature range 293–313 K.

2.2.1. Sorption isotherm studies

Sorption isotherm studies were carried out using the batch equilibrium technique. The initial concentrations of the studied solutions were prepared in the range 7.5×10^{-4} to 2.5×10^{-2} mol/L. 0.5 g of the ion exchanger sample and 50 mL of the studied solutions were contacted in 100 mL flasks for 3 h.

2.2.2. Kinetic studies

During the kinetic studies 0.5 g of resins with 50 mL samples (initial concentration of M(II)–GLDA complexes 1×10^{-3} mol/L) were agitated in a 100-mL conical flasks. The removal rate of complexes was investigated by analysing heavy metal concentrations after 1 min, 3 min, 5 min, 10 min, 20 min, 30 min, 1 h, 2 h and 3 h by the AAS method.

From the group of interfering ions the following were chosen: Ca(II), Mg(II), Cl^-, $SO_4{}^{2-}$, $NO_3{}^-$. The investigations were carried out for the Cu(II)–GLDA complexes on Lewatit MonoPlus MP 500 under the same conditions as previously.

2.3. Column studies

The column sorption experiments were conducted using 10 mL of the swollen ion exchangers Lewatit MonoPlus MP 500 and Amberlite IRA 958 packed in glass columns with glass wool stoppers (the inner diameter 10 mm, the length 25 cm). The feed solutions of Cu(II), Zn(II), Co(II), Ni(II), Pb(II) and Cd(II) complexes with GLDA were passed continuously downwards through the resin beds keeping the flow rate at 0.6 mL/min. The effluents were collected in fractions in which metal contents were determined as previously.

2.4. Regeneration

Regeneration tests were conducted with different regeneration agents (1 mol/L HCl, HNO_3, H_2SO_4 or NaCl solutions). The M(II)–GLDA loaded resins (0.5 g) were put into flasks in contact with 50 mL of different regeneration agents. The flasks were agitated at room temperature. The resins were separated and the solutions were analysed in order to determine the concentrations of metal ions and pHs of the solutions.

2.5. Analytical measurements

The concentrations of heavy metals were measured with the AAS spectrometer ContrAA (Analytic Jena, Jena, Germany) operating with an air–acetylene flame at the wavelengths 324.8 nm for Cu(II), 213.9 nm Zn(II), 240.7 nm Co(II), 232.0 nm Ni(II), 217.0 nm Pb(II) and 228.8 nm Cd(II), respectively. The calibration curves were prepared between 0.01 and 5 mg/L. The precision of the parallel measurements was as ±2%.

3. Results and discussion

3.1. Effects of the stability of the formed complexes and the metal–ligand ratio

Tetrasodium of *N*,*N*-bis(carboxymethyl)glutamic acid is a complexing agent composed of two carboxymethyl groups linked to nitrogen atom of L-glutamate. A major advantage of GLDA relates to its safety profile which is the basis for replacement of phosphates and EDTA by the GLDA in detergents, among others, in the USA. Additionally, it is readily biodegradable (>60% degraded within 28 days) possessing good solubility at both low and high pH. Dissolvine GL-38 consists only of L-GLDA which is very important because the D-form is not biodegradable. Moreover, the thermal stability of GLDA is high [31,32]. This property has been used to develop water treatment systems for operating boilers to reduce the effect of hard water.

In cleaning formulations GLDA behaves similarly to NTA and EDTA making their replacement possible. The benefit of GLDA in such formulations is its broad effective pH range for the chelation of hard water ions, especially at pH >11.

The biodegradability of chelating agents, such as GLDA, appears to depend on the nature of the ligand as well as on the metal ion complexed with it. The metal influence on the biodegradability of chelating agents is partly connected with the thermodynamic stability of the complex. It was proved that complexes with relatively low or moderately high stability constants are readily degradable whereas the chelating agents forming strong complexes are relatively resistant to biodegradation. On the other hand, high resistance of chelating agents to biodegradation is often desired or necessary for the stability of technical processes or products. In the paper by Sýkora et al. [33], it was found that the sequence of the ethylenediamine derivatives possessing methyl ($-CH_3$), ethyl ($-C_2H_5$), hydroxoethyl ($-CH_2CH_2OH$), acetyl ($-COCH_3$) or carboxymethyl ($-CH_2COOH$) groups to biodegradate is the following: $-COCH_3$, $-CH_3$, $-C_2H_5$, $-CH_2CH_2OH$, $-CH_2COOH$ and depends on the character and number of nitrogen atoms in the molecule. On this basis, it was stated that the most stable are complexing agents containing two and more tertiary nitrogen atoms and four or more carboxymethyl groups in the molecule, i.e. EDTA, DTPA, HEDTA, PDTA. However, the N–C bonds are not the cause of biological stability if they can undergo biological hydrolysis.

With regard to GLDA, as mentioned above, it is composed of two carboxymethyl groups linked to nitrogen atom of L-glutamate. On the other hand, the stability constants (log K) for the complexes of $[M(glda)]^{2-}$ in the M(II):GLDA = 1:1 system are low or moderately high and they are equal to: for Ca(II) 5.2, Cd(II) 9.1, Cu(II) 13.1, Co(II) 10.0, Fe(II) 8.7, Fe(III) 11.7, Hg(II) 14.3, Mg(II) 6.1, Mn(II) 7.6, Ni(II) 10.9, Pb(II) 10.5 and Zn(II) 10.0. For Ca(II), Cu(II), Fe(III), Mg(II), Ni(II) and Zn(II) they are close to NTA [19]. In the case of real effluents the stability constants provide only an indication about capability of forming complexes because they are determined under ideal conditions, at room temperature as well as only for free ions. Therefore the impact of other competitive heavy metal ions, different temperatures and pH as well as accompanying complexing ions should be also taken into account. The possibility of not complexing the whole amount of heavy metal ions or formation of different types of complexes besides $[M(glda)]^{2-}$ also exists.

3.2. Ion exchangers characterization by SEM and FT-IR/PAS methods

SEM scans of Lewatit MonoPlus MP 500, Amberlite IRA 958 and Diaion CR-20 are typicaly of macroporous materials (therefore not presented). They indicate the presence of many pores and a rough structure favourable for sorption, especially of large molecules. However, the SEM scans after the sorption of Cu(II)–GLDA complexes on Lewatit MonoPlus MP 500 and Amberlite IRA 958 are presented in Fig. 2. Furthermore, the exemplary FT-IR/PAS spectra of Lewatit MonoPlus MP 500 before and after the sorption of Cu(II)–GLDA complexes are given in Fig. 3. A broad, intensive peak at 3420 cm^{-1} is characteristic of hydroxyl and amine groups. The bands at 3044 cm^{-1} and 2934 cm^{-1} are ascribed to the asymmetric and the corresponding symmetric stretch vibrations of the $-CH_2$ groups (they are not presented). The bond related to the presence of water in the ion exchanger phase was found at 1640 cm^{-1}. The ring carbon–carbon stretching $\nu_{as}(C{=}C)$ and the scissoring vibrations of the methylene groups occur at 1483 cm^{-1}, 1486 cm^{-1} and 1417 cm^{-1} as well as at 1382 cm^{-1}. At 978 cm^{-1} and 890 cm^{-1} the deformation vibrations of 1,4-disubstituted benzene ring (ST-DVB) were also observed. A peak at 1385 cm^{-1} represents the oxygen functional groups connected with stretching vibrations in the carboxylic groups. These functional groups (hydroxyl, amine and carboxyl) are available for the binding of metal ions. Therefore, the bands at 1611 cm^{-1} and 1385 cm^{-1} can be assigned to the asymmetrical and symmetrical stretching of the COO^- group, respectively. These bands are connected to the complexes $[M(glda)]^{2-}$ [34,35].

3.3. Kinetic studies

The effect of time on the sorption of Cu(II), Zn(II), Co(II), Ni(II), Pb(II) and Cd(II) complexes with GLDA was investigated. The obtained results suggest that the process was rather quick.

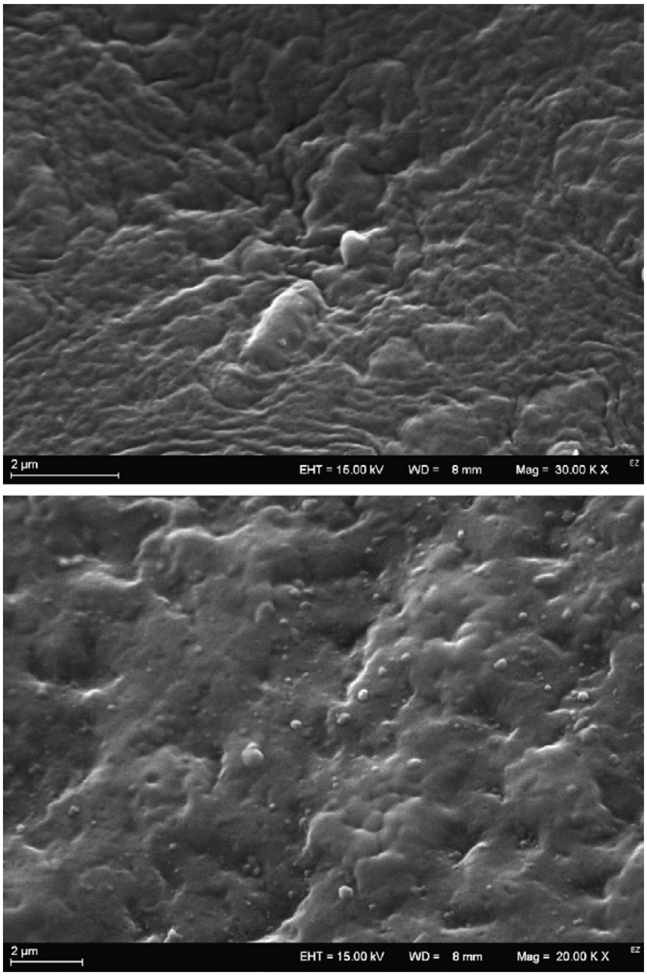


Fig. 2. SEM analysis of the macroporous anion exchangers Lewatit MonoPlus MP 500 and Amberlite IRA 958 after the sorption of Cu(II)–GLDA complexes.

Nearly 100% of the sorption capacity was reached within 10–20 min (Fig. 4a–c). During the sorption process, pH changes were also registered (Fig. 4a–c). It was found that the pH of the solutions gradually decreases which confirms that the sorption process on strongly basic anion exchangers Lewatit MonoPlus MP500 and Amberlite IRA 958 proceeds according to the proposed exchange reactions:

$$R{-}CH_2{-}N^+(CH_3)_3\,Cl^- + [MH(glda)]^- \rightleftarrows [R{-}CH_2{-}N^+(CH_3)_3][MH(glda)]^- + Cl^- \tag{4}$$

$$2R{-}CH_2{-}N^+(CH_3)_3\,Cl^- + [M(glda)]^{2-} \rightleftarrows [R{-}CH_2{-}N^+(CH_3)_3]_2[M(glda)]^{2-} + 2Cl^- \tag{5}$$

where R – the resin matrix (PST-DVB or A-DVB).

The initial rapid removal gives way to a relatively slow rate of approach to the equilibrium. The data for the time interval up to 20 min were fitted to the pseudo first-order and pseudo second-

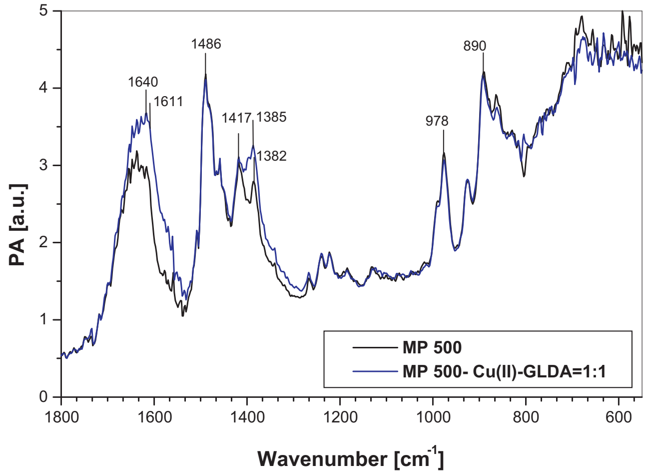


Fig. 3. The FT-IR/PAS spectra of macroporous anion exchanger Lewatit MonoPlus MP 500 after the sorption of Cu(II)–GLDA complexes.

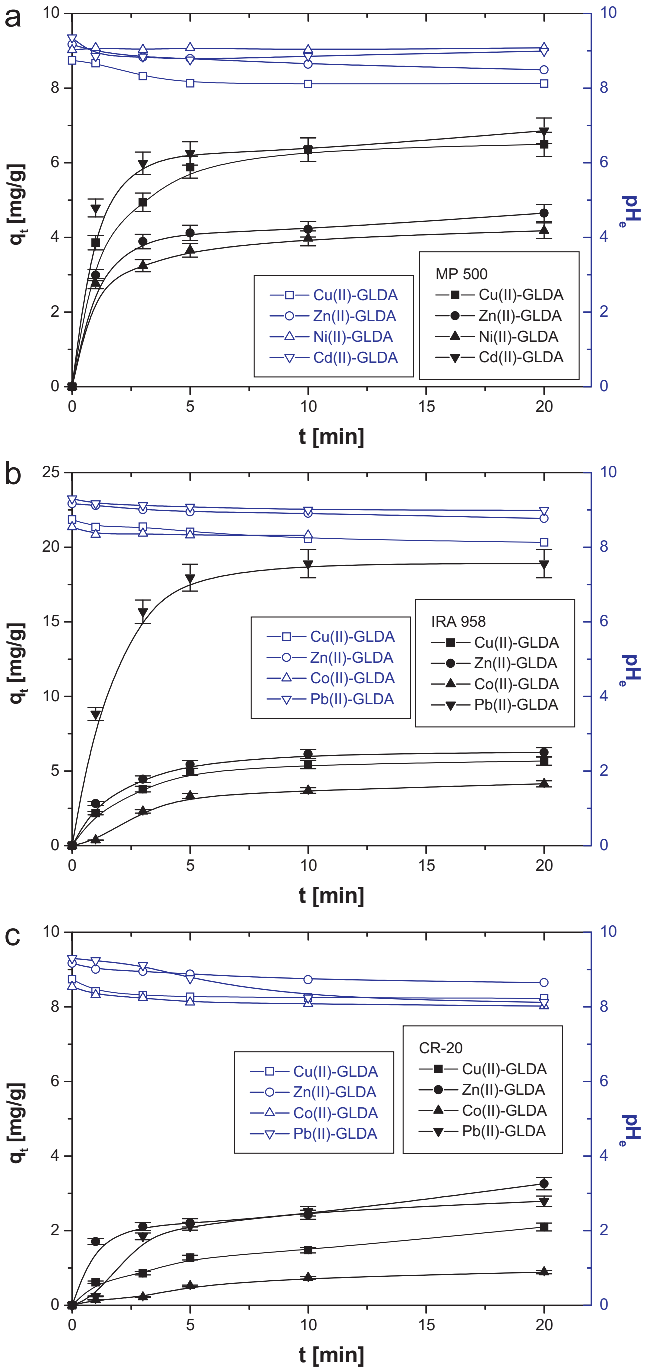


Fig. 4. (a–c) The effect of the phase contact time as well as pH changes on the sorption of Cu(II), Zn(II), Co(II), Ni(II), Cd(II) and Pb(II) complexes with GLDA on Lewatit MonoPlus MP 500 (a), Amberlite IRA 958 (b) and Diaion CR-20 (c) (c_0 1×10^{-3} mol/L, agitation speed 180 rpm, room temperature).

Table 2
The kinetic parameters for Cu(II), Zn(II), Co(II), Ni(II), Cd(II) and Pb(II) complexes with GLDA on Lewatit MonoPlus MP 500, Amberlite IRA 958 and Diaion CR-20.

System M(II)–GLDA		Pseudo first-order model			Pseudo second-order model				Intraparticle model	
M(II)	$q_{e,\mathrm{exp}}$	q_1	k_1	R^2	q_2	k_2	h	R^2	k_i	R^2
Lewatit MonoPlus MP 500										
Cu(II)	7.35	1.74	0.052	0.9024	6.36	0.790	3.54	0.9999	0.573	0.8274
Zn(II)	5.01	1.00	0.036	0.8955	5.04	0.160	4.07	1.0000	0.125	0.6349
Ni(II)	4.52	1.07	0.336	0.7771	4.53	0.141	2.88	0.9998	0.112	0.6658
Cd(II)	7.31	1.26	0.027	0.8901	7.34	0.111	5.97	0.9999	0.150	0.6476
Amberlite IRA 958										
Cu(II)	5.76	3.11	0.193	0.9557	5.75	0.153	5.05	0.9998	0.179	0.6008
Zn(II)	6.35	2.46	0.144	0.9306	6.43	0.189	7.82	0.9999	0.186	0.6273
Co(II)	4.99	2.38	0.032	0.7138	5.02	0.134	2.86	0.9956	0.253	0.5694
Pb(II)	19.32	11.26	0.348	0.9540	19.31	0.069	2.77	0.9999	0.438	0.6114
Diaion CR-20										
Cu(II)	4.36	3.71	0.025	0.9671	4.74	0.014	0.32	0.9994	0.329	0.8554
Zn(II)	4.00	1.96	0.038	0.9614	4.08	0.060	1.00	0.9993	0.186	0.8004
Co(II)	1.49	1.19	0.036	0.9047	1.58	0.051	0.12	0.9971	0.107	0.8093
Pb(II)	3.47	2.01	0.043	0.9614	3.60	0.044	0.56	0.9972	0.188	0.6336

order equations. They can be written as follows [36–39]:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1 t}{2.303} \tag{6}$$

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2} \tag{7}$$

Based on the plots of $\log(q_e - q_t)$ vs. t and t/q_t vs. t the kinetic parameters were calculated and they are summarized in Table 2.

The intraparticle diffusion model is also tested in the studied system. It is well-known that if the plot of q_t versus $t^{1/2}$ gives a straight line, then the sorption process is controlled by intraparticle diffusion only. However, if the data exhibit multi-linear plots, then more steps can influence the sorption process. The slope of these plots is defined as a rate parameter, characteristic of the rate of sorption in the region where intraparticle diffusion is rate controlling (the former represents the macro-pore diffusion and the latter the micro-pore diffusion). The rate constants of intraparticle transport k_i were calculated using the following equation:

$$q_t = k_i t^{1/2} + C \tag{8}$$

The values of rate parameter as well as correlation coefficients (R^2) obtained for sorption of the above-mentioned complexes are also presented in Table 2.

The higher correlation coefficient (R^2) for a pseudo second-order equation implied that the sorption of the above-mentioned complexes on the strongly basic macroporous anion exchangers Lewatit MonoPlus MP 500 and Amberlite IRA 958 proceeds accordingly to the chemisorption mechanism. It is worth mentioning that the sorption capacity ($q_{e,\mathrm{exp}}$) obtained based on the pseudo second-order equation was consistent with the experimental capacities ($q_{2,\mathrm{cal}}$) and the other kinetic data correspond well to this equation. For the studied anion exchangers the sequence of the complexes sorbed can be as follows: Lewatit MonoPlus MP 500: Cd(II) > Cu(II) > Zn(II) > Ni(II) and Amberlite IRA 958: Pb(II) > Zn(II) > Cu(II) > Co(II). In the case of the chelating ion exchanger Diaion CR-20, the obtained sequence of the metal ions sorbed is in agreement with the selectivity order known from the literature data: Hg(II) > Fe(III) > Cu(II) > Zn(II) > Cd(II) > Ni(II) > Co(II) > Ag(I) > Mn(II). Diaion CR-20 with the polyamine functional groups in the pH range from 4 to 10 acts as a chelating ion exchanger therefore decomposition of the $[\mathrm{M(glda)}]^{2-}$ and $[\mathrm{MH(glda)}]^{-}$ complexes in the resin phase is very probable. Another explanation of the sorption of the metal ions by Diaion CR-20 is incomplete complexation of metal ions by GLDA and their sorption. This would also account for not 100% sorption complexes (%S) in the case of Lewatit MonoPlus MP 500 (for Cu(II) 99.9%, Zn(II) 76.6%, Ni(II) 76.9% and Cd(II) 65.8%, respectively) and Amberlite IRA 958 (for Cu(II) 90.66%, Zn(II) 97.6%, Co(II) 84.6% and Pb(II) 93.2%, respectively).

It was also found that in the presence of the Cl^-, SO_4^{2-} and NO_3^- ions the sorption of Cu(II)–GLDA on Lewatit MonoPlus MP 500 decreased by about 14.3%, 6.6% and 13.5%, respectively (Fig. 5). However, the presence of Ca(II) and Mg(II) ions decreased more significantly the sorption capacity of this anion exchanger towards Cu(II) complexes with GLDA. For the concentrations 20 mg/L Ca(II) and 40 mg/L Mg(II), the sorption capacity decrease was 23% and 18.4%, respectively. It can be explained by the fact that the amount of Ca(II) ions bound to GLDA in the presence of the equivalent amount of hydroxonapthol blue disodium salt is comparable to the standard complexing agents like DTPA, EDTA and HEDTA [19] and therefore these complexes compete with Cu(II) complexes for ion exchange sites.

3.4. Sorption studies

The sorption of the Cu(II), Zn(II), Co(II), Ni(II), Pb(II) and Cd(II) complexes with GLDA was investigated at the pH range from 2 to 12 and presented in Fig. 6a–c. The sorption increases in the pH range 2–6 for strongly basic anion exchangers, then remains almost constant. The maximum sorption percentage in the region of pH > 6 was equal to nearly 100% for Cu(II), 76% for Zn(II), 77% for Ni(II) and 65% for Cd(II) on Lewatit MonoPlus MP 500 and 94% for Cu(II), 63% for Zn(II), 76% for Co(II) and 90% for Pb(II) on Amberlite IRA 958. For Diaion CR-20 the sorption reaction is also pH dependent but

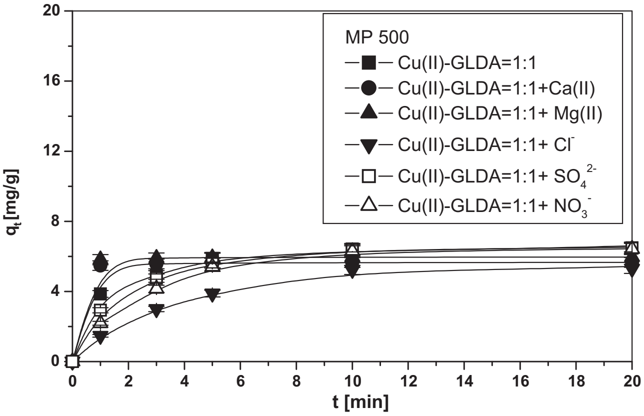


Fig. 5. The effect of the phase contact time on the sorption of Cu(II) complexes with GLDA in the presence of Ca(II), Mg(II), Cl^-, SO_4^{2-}, NO_3^- ions on Lewatit MonoPlus MP 500 (c_0 1×10^{-3} mol/L, agitation speed 180 rpm, room temperature).

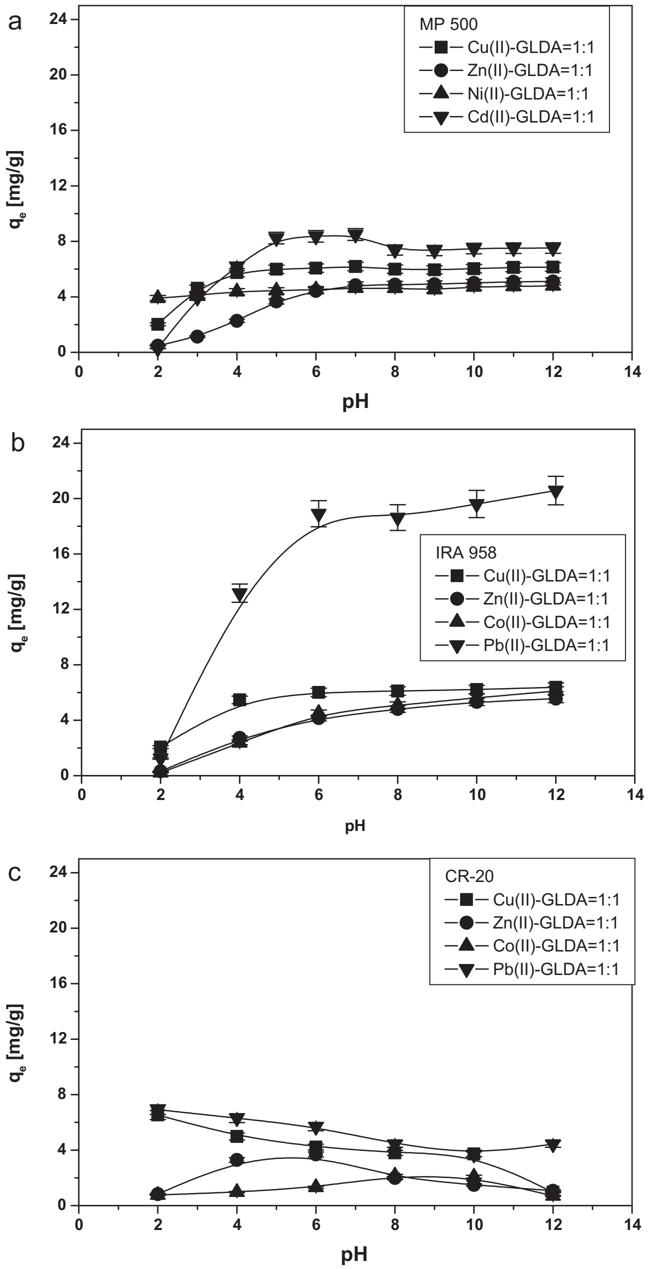


Fig. 6. (a–c) The effect of the pH on the sorption of Cu(II), Zn(II), Co(II), Ni(II), Cd(II) and Pb(II) complexes with GLDA on Lewatit MonoPlus MP 500 (a), Amberlite IRA 958 (b) and Diaion CR-20 (c) (c_0 1×10^{-3} mol/L, agitation time 3 h, agitation speed 180 rpm, room temperature).

the sorption capacity decreases with the increasing pH. The region for maximum sorption capacity was found for pH 2–4.

The effect of temperature on the sorption of Cu(II) complexes with GLDA on Lewatit MonoPlus MP 500, Amberlite IRA 958 and Diaion CR-20 was investigated and the results are shown in Fig. 7a and b. Slight increase in the sorption of Cu(II)–GLDA complexes with the increasing reaction temperature was observed. Based on the obtained results the thermodynamic parameters for the sorption of Cu(II)–GLDA complexes such as Gibbs free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were determined using the following equations [40]:

$$\log \frac{q_e}{c_e} = -\frac{\Delta H^\circ}{2.303RT} + \frac{\Delta S^\circ}{2.303R} \quad (9)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (10)$$

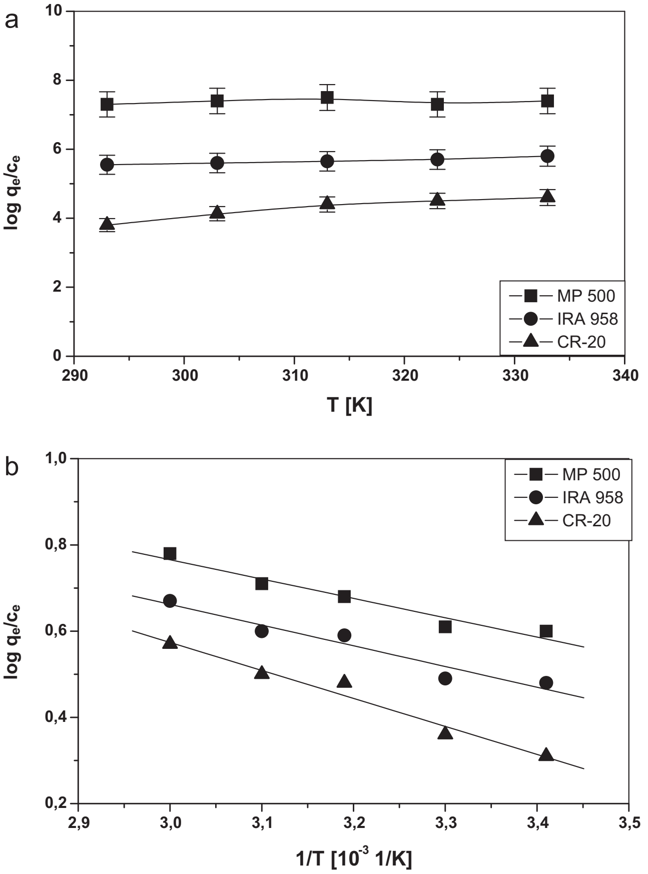


Fig. 7. (a and b) The effect of the temperature on the sorption of Cu(II) complexes with GLDA on Lewatit MonoPlus MP 500, Amberlite IRA 958 and Diaion CR-20 (a) and the plots of log q_e/c_e vs. $1/T$ (b) (c_0 1×10^{-3} mol/L, agitation time 3 h, agitation speed 180 rpm).

The values of ΔH° and ΔS° were obtained from the slope and intercept of the plots of log q_e/c_e vs. $1/T$. In Table 3 the calculated values were collected. The values of ΔG° were more negative with the increasing temperature, which indicates that the sorption process is more favourable at high temperature whereas the positive values of ΔS° indicate that there is an increase in the degree of the randomness during the sorption process. The ΔH° values were found to be 8.43 kJ/mol for Lewatit MonoPlus MP 500, 9.17 kJ/mol for Amberlite IRA 958 and 12.15 kJ/mol for Diaion CR-20, which reveals the endothermic character of the sorption process. In the case of decrease of the sorption of studied complexes with the increasing

Table 3
Thermodynamic parameters for the sorption of Cu(II)–GLDA complexes on Lewatit MonoPlus MP 500, Amberlite IRA 958 and Diaion CR-20.

Ion exchanger	T	ΔG°	ΔH°	ΔS°
Lewatit MonoPlus MP 500	293	−3.30	8.43	40.07
	303	−3.71		
	313	−4.11		
	323	−4.51		
	333	−4.91		
Amberlite IRA 958	293	−2.61	9.17	40.21
	303	−3.01		
	313	−3.42		
	323	−3.82		
	333	−4.22		
Diaion CR-20	293	−1.75	12.15	47.43
	303	−2.22		
	313	−2.69		
	323	−3.17		
	333	−3.64		

temperature these values would indicate the exothermic nature of the process. Additionally, the highest value of change of sorption enthalpy for Diaion CR-20 may indicate formation of coordinate bonds between Cu(II) and the polyamine functional groups.

The sorption studies were also analysed using the Langmuir, Freundlich, Temkin and Dubinin–Radushkevich (D–R) models [41,42]. The appropriate equations can be written as follows:

$$q_e = \frac{q_0 K_L c_e}{1 + K_L c_e} \tag{11}$$

$$q_e = K_F c_e^{1/n} \tag{12}$$

$$q_e = \left(\frac{RT}{b_T}\right) \ln(K_T c_e) \tag{13}$$

$$\frac{q_e}{X_m} = e^{-\beta\varepsilon^2} \tag{14}$$

Based on the Langmuir isotherm model the maximum sorption capacity of Lewatit MonoPlus MP 500, Amberlite IRA 958 and Diaion CR-20 were 89.74 mg/g for Cu(II), 104.17 mg/g Pb(II) and 17.25 mg/g for Cu(II) complexes with GLDA, respectively (Table 4, Fig. 8a–c). The high correlation coefficients ($R^2 > 0.99$) suggest that they can be applicable to describe the sorption process. The adsorption coefficients, that are related to the free energy of sorption (K_L), and Diaion CR-20 for the studied metal ions are presented in Table 4. They were greater for Ni(II) than for Cu(II), Cd(II) and Zn(II) for Lewatit MonoPlus MP 500, greater for Pb(II) than Co(II), Zn(II) and Cu(II) for Amberlite IRA 958 and Pb(II) than Co(II), Zn(II) and Cu(II) for Diaion CR 20. This observation showed that the energy of adsorption is not very favourable for the Ni(II) and Pb(II) complexes with GLDA, probably due to their large size or different structure (hence not all binding sites may be available to them). Additionally, two important factors may govern selectivity in the M(II)–GLDA = 1:1 system, i.e. the spacing of the binging (active) sites and the hydrophobic and hydrophilic nature of the resin matrix (polystyrene–divinylbenzene or acrylic-divinylbenzine).

From the Langmuir parameters at different temperatures (K_L) based on the van't Hoff equation, for Cu(II) complexes with GLDA the enthalpy was also estimated. It was found that for Lewatit MonoPlus MP 500 it was equal to 8.48 kJ/mol, for Amberlite IRA 958 11.04 kJ/mol and for Diaion CR-20 15.02 kJ/mol. These values are very close to those presented in Table 3.

The essential characteristics of the Langmuir isotherm can be also expressed in terms of a dimensionless constant separation factor (Hall parameter) R_L:

$$R_L = \frac{1}{(1 + K_L c_0)} \tag{15}$$

The value of R_L indicates the type of isotherm. It can be either unfavourable $R_L > 1$, linear $R_L = 1$, favourable ($0 < R_L < 1$) or irreversible $R_L = 0$. The R_L values for the studied Cu(II), Zn(II), Ni(II) and Cd(II) complexes with GLDA on Lewatit MonoPlus MP 500 were found to be 0.07, 0.56, 0.46, 0.11, respectively. For the Cu(II), Zn(II), Co(II) and Pb(II) complexes with GLDA on Amberlite IRA 958 they were equal to 0.24, 0.21, 0.04 and 0.01 and for Diaion CR-20 0.33, 0.66, 0.32 and 0.24, respectively. These values indicate favourable sorption in the case of Diaion CR-20 whereas for Lewatit MonoPlus MP 500 and Amberlite IRA 985 it is less favourable.

The parameter K_F related to the sorption density is higher in the case of sorption on Lewatit MonoPlus MP 500 for the Cu(II), Zn(II), Ni(II) and Cd(II) complexes. As for the parameters obtained from the Temkin equation, it can be seen that the values of K_T are larger for Amberlite IRA 958 than for Lewatit MonoPlus MP 500 (Table 4).

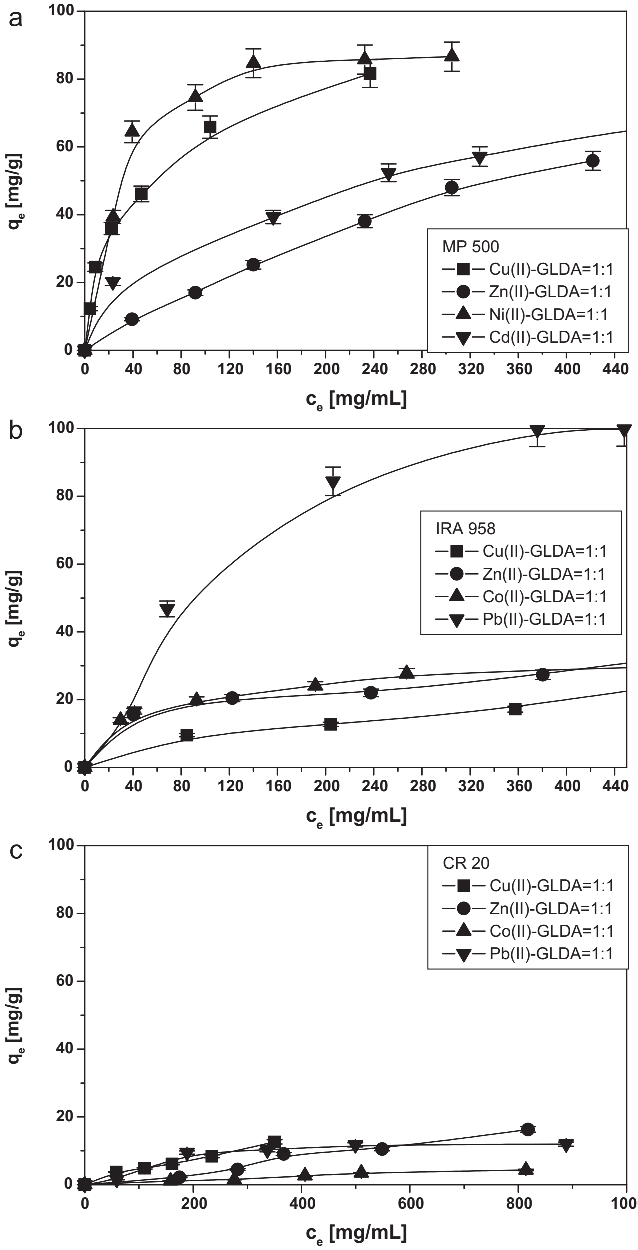


Fig. 8. (a–c) The sorption isotherms of Cu(II), Zn(II), Co(II), Ni(II), Cd(II) and Pb(II) complexes with GLDA on Lewatit MonoPlus MP 500 (a), Amberlite IRA 958 (b) and Diaion CR-20 (c) (1.0×10^{-3}–2.5×10^{-2} mol/L, agitation time 3 h, agitation speed 180 rpm, room temperature).

In order to understand the adsorption type, equilibrium data should be tested with the Dubinin–Radushkevich isotherm (D–R). Radushkevich and Dubinin have reported that the characteristic sorption curve is related to the porous structure of the sorbent and the calculated sorption parameters can be used to distinguish between physical and chemical adsorption [41]. Based on the D–R equation not only the maximum adsorption capacity, but also an average free energy value unique to the adsorbate–adsorbent system can be estimated.

The obtained results indicate that the sorption data are the best fitted by the Langmuir sorption isotherm. However, under industrial conditions the homogeneity requirement of the ion exchanger surface and the assumptions required by the Langmuir isotherm would not be correct. Therefore better fit of the Dubinin–Radushkevich (D–R) isotherm suggests that it could be more appropriate under industrial conditions. The corresponding values of the sorption capacities in the D–R isotherm (X_m)

Table 4
The isotherm parameters for Cu(II), Zn(II), Co(II), Ni(II), Cd(II) and Pb(II) complexes with GLDA on Lewatit MonoPlus MP 500, Amberlite IRA 958 and Diaion CR-20.

System M(II)–GLDA		Langmuir model				Freundlich model			Temkin model			Dubinin–Radushkevich model			
M(II)	$q_{e,\mathrm{exp}}$	q_0	K_L	R_L	R^2	K_F	n	R^2	K_T	b_T	R^2	X_m	β	E	R^2
Lewatit MonoPlus MP 500															
Cu(II)	81.62	89.74	0.03	0.07	0.9917	28.99	2.49	0.9561	2.27	147.56	0.9855	196.41	5.0×10^{-9}	10.11	0.9762
Zn(II)	55.89	55.14	0.002	0.56	0.9986	22.50	1.27	0.9963	2.02	94.96	0.9917	282.86	1.0×10^{-8}	7.07	0.9964
Ni(II)	30.29	26.15	0.05	0.46	0.9974	24.69	1.59	0.8109	2.33	239.14	0.8756	115.70	2.0×10^{-9}	15.58	0.9937
Cd(II)	44.22	44.50	0.01	0.11	0.9932	25.94	2.59	0.9906	8.33	156.67	0.9544	149.35	5.0×10^{-9}	10.02	0.9987
Amberlite IRA 958															
Cu(II)	39.27	37.14	0.002	0.24	0.9985	21.24	1.77	0.9835	17.95	198.53	0.9447	98.03	9.0×10^{-9}	7.45	0.9861
Zn(II)	37.96	41.02	0.004	0.21	0.9965	24.82	3.31	0.9069	20.18	126.23	0.8317	88.78	5.0×10^{-9}	11.08	0.9514
Co(II)	30.38	35.09	0.022	0.04	0.9986	25.61	3.63	0.9818	20.80	425.49	0.9862	72.30	3.0×10^{-9}	12.91	0.9678
Pb(II)	99.80	104.17	0.078	0.01	0.9994	21.87	1.47	0.8968	20.93	172.06	0.9729	102.78	8.0×10^{-9}	7.91	0.9908
Diaion CR-20															
Cu(II)	12.63	17.25	0.002	0.33	0.9967	14.60	1.48	0.9616	34.21	521.03	0.8691	48.86	9.0×10^{-9}	7.45	0.9942
Zn(II)	16.29	14.95	0.001	0.66	0.9955	19.77	1.15	0.9970	21.45	317.66	0.9911	72.47	1.0×10^{-8}	7.04	0.9961
Co(II)	4.34	3.59	0.002	0.32	0.9928	15.85	1.43	0.9985	34.17	535.70	0.9597	25.72	9.0×10^{-9}	7.43	0.9984
Pb(II)	11.97	13.05	0.013	0.24	0.9972	14.03	1.12	0.9018	32.45	633.39	0.9802	94.84	9.0×10^{-9}	7.39	0.9997

compared to the Langmuir isotherm were 196.41 mg/g for Cu(II), 282.86 mg/g for Zn(II), 115.70 mg/g for Ni(II) and 149.35 mg/g Cd(II) on Lewatit MonoPlus MP 500; 98.03 mg/g for Cu(II), 88.78 m/g for Zn(II), 72.30 mg/g for Co(II) and 102.78 mg/g Pb(II) on Amberlite IRA 958, respectively. For Diaion CR-20 the obtained values were lower. The comparison of the obtained values of sorption capacities from the Langmuir and D–R equations suggest that the ion exchangers used possess quite a uniform grain size (D–R equation can not be applied for the adsorbents having a single pore size. A distribution of pore sizes is a prerequisite for the D–R equation).

Based on the D–R equation not only the maximum adsorption capacity, but also an average free energy value unique to the adsorbate–adsorbent system can be estimated. As for the mean sorption energy (E), which gives the information about chemical or physical sorption, it was found to be in the range from 10.02 kJ/mol to 15.58 kJ/mol on Lewatit MonoPlus MP 500, which is typical of the sorption reaction (8–16 kJ/mol). On Amberlite IRA 958 it was found to be from 7.45 kJ/mol to 12.91 kJ/mol.

3.5. Column studies

The sorption process of Cu(II), Zn(II), Co(II), Ni(II), Cd(II) and Pb(II) complexes with GLDA was also investigated by the dynamic method. In Fig. 9a and b the breakthrough curves of the above-mentioned complexes are presented for Lewatit MonoPlus MP 500 and Amberlite IRA 958. The mass (D_g) and bed (D_v) distribution coefficients were calculated from the determined breakthrough curves according to the following equations [40]:

$$D_g = \frac{\overline{V} - (V_0 + V_i)}{m} \tag{16}$$

$$D_v = \frac{\overline{V} - (V_0 + V_i)}{V_j} \tag{17}$$

The comparison of the mass (D_g) and bed (D_v) distribution coefficients as well as the working (C_w) and total (C_r) ion exchange capacities is presented in Table 5. The typical 'S' shaped breakthrough curves were obtained only in the case of the polystyrene anion exchanger Lewatit MonoPlus MP 500. For the polyacrylate anion exchanger Amberlite IRA 958 sorption of different types of complexes is evident. On Lewatit MonoPlus MP 500 larger metal complexes sorption was observed for Cu(II) and Zn(II) compared to Ni(II) and Cd(II) whereas for Amberlite IRA 958 there was found larger sorption of Cu(II) complexes. Therefore the affinity series for these complexes on the macroporous anion exchangers can be as follows:

Lewatit MonoPlus MP 500: Cu(II) > Zn(II) > Ni(II) > Cd(II)
Amberlite IRA 958: Cu(II) > Co(II) > Pb(II) > Zn(II)

It is also worth mentioning, that in the case of the anion exchange process, the affinity of the studied anion exchangers, e.g. Lewatit MonoPlus MP 500 and Amberlite IRA 958 for heavy metal complexes with GLDA (as in the case of anionic complexes of rare earth elements with aminopolycarboxylic acids) is probably independent of the stability constants. For example, in the case of rare earth element complexes with EDTA, HEDTA or IMDA, the unusual

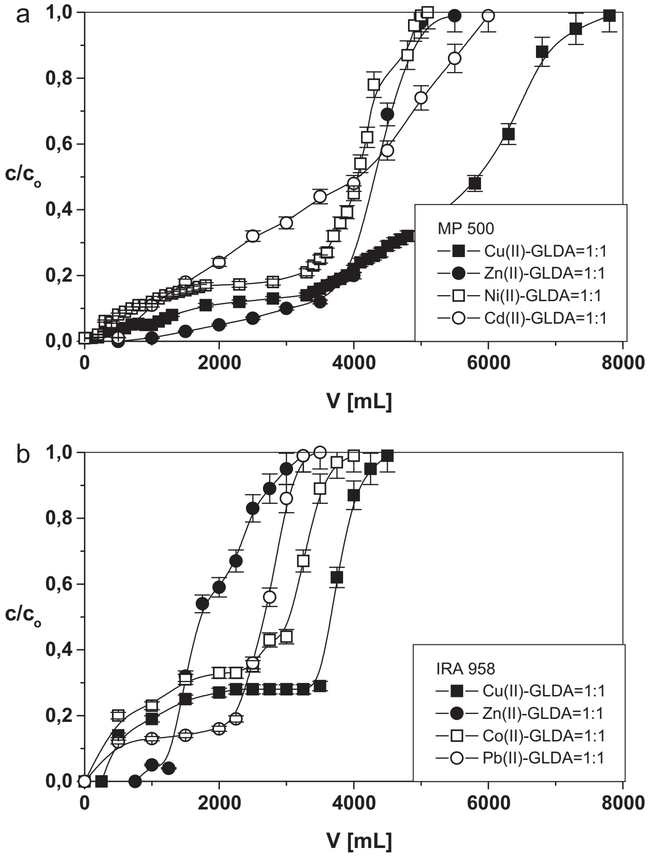


Fig. 9. (a and b) The breakthrough curves of Cu(II), Zn(II), Co(II), Ni(II), Cd(II) and Pb(II) complexes with GLDA on Lewatit MonoPlus MP 500 (a) and Amberlite IRA 958 (b) (c_0 1×10^{-3} mol/L, bed volume 10 mL, flow rate at 0.6 mL/min).

Table 5
The mass (D_g) and volume (D_v) distribution coefficients as well as the working (C_w) and total (C_r) ion exchange capacities for Cu(II), Zn(II), Co(II), Ni(II), Pb(II) and Cd(II) complexes with GLDA on Lewatit MonoPlus MP 500 and Amberlite IRA 958.

System	D_g	D_v	C_w	C_r
Lewatit MonoPlus MP 500				
Cu(II)–GLDA = 1:1	2329.33	582.45	0.0006	0.0329
Zn(II)–GLDA = 1:1	1715.68	429.01	0.0033	0.0270
Ni(II)–GLDA = 1:1	1632.79	408.28	0.0012	0.0208
Cd(II)–GLDA = 1:1	1605.60	401.48	0.0005	0.0040
Amberlite IRA 958				
Cu(II)–GLDA = 1:1	1132.74	367.12	0.0016	0.0194
Zn(II)–GLDA = 1:1	533.03	172.75	0.0016	0.0204
Co(II)–GLDA = 1:1	930.31	301.51	0.0029	0.0152
Pb(II)–GLDA = 1:1	829.50	268.84	0.0010	0.0050

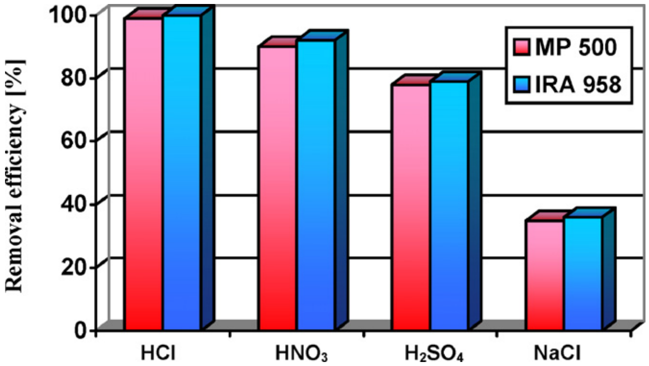


Fig. 10. The regeneration test of the loaded Lewatit MonoPlus MP 500 and Amberlite IRA 958 by Cu(II)–GLDA complexes using 1 mol/L HCl, HNO_3, H_2SO_4 and NaCl solutions (Cu(II)–GLDA = 1:1, c_0 1×10^{-3} mol/L, agitation time 3 h, agitation speed 180 rpm, room temperature).

affinity series was applied to separate some pairs of these elements in the macro–micro system by Dybczyński [43], Kołodyńska and Hubicka [44–46]. The non-typical and non-monotonic character of sorption can be interpreted by differences in the complex structure and anion exchanger matrices. As was mentioned earlier, the flexibility and mobility of functional groups as well as the presence of hydrophilic groups, especially in the case of the polyacrylic anion exchanger, should also be taken into account.

3.6. Regeneration tests

The regeneration tests for Lewatit MonoPlus MP 500 and Amberlite IRA 958 were studied. The investigation was carried out using the anion exchangers loaded by Cu(II)–GLDA complexes. The exemplary results for the desorption of the studied complexes from Lewatit MonoPlus MP 500 and Amberlite IRA 958 obtained using 1 mol/L HCl, HNO_3, H_2SO_4 and NaCl solutions are presented in Fig. 10. It was found that 1 mol/L HCl could be apparently effective for the desorption process and can be used as a regeneration agent. For Lewatit MonoPlus MP 500 and Amberlite IRA 958 more than 99% and 98% of Cu(II)–GLDA complexes were desorbed, respectively.

4. Conclusions

From the environmental standpoint GLDA is a readily biodegradable complexing agent made from renewable raw material—monosodium glutamate. GLDA has low toxicity and aquatic characteristics. The studies show that heavy metal–GLDA complexes, especially with Cu(II), Zn(II), Cd(II) and Pb(II) can be effectively sorbed on the strongly basic, macroporous anion exchangers Lewatit MonoPlus MP 500 and Amberlite IRA 958 from aqueous solutions. These results were confirmed by the FT-IR/PAS studies and SEM analysis. In the case of chelating Diaion CR-20, decomposition of the sorbed complexes in the resin phase should be assumed. Based on the batch studies, sorption was dependent on the initial M(II) and GLDA concentrations and the phase contact time. The sorption process failed to obey the pseudo first-order kinetics whereas followed the pseudo second-order kinetics. pH > 6 was favourable for the sorption process. The sorption was temperature dependent as well as dependent on the presence of Ca(II), Mg(II), Cl^-, SO_4^{2-}, NO_3^- ions. Of the sorption models used, the Dubinin–Radushkevich (D–R) model was found to be appropriate under industrial conditions. The maximum sorption capacity ($q_{e,\mathrm{exp}}$) for the Pb(II) complexes with GLDA on the polyacrylate anion exchanger Amberlite IRA 958 was found to be 99.80 mg/g. For the polystyrene anion exchanger Lewatit MonoPlus MP 500, the maximum value was 81.62 mg/g for Cu(II)–GLDA complexes. Compared the obtained results to the column studies, it was found that the sorption was slightly larger in the column mode. Almost 99% of Cu(II)–GLDA complexes desorption from the spent anion exchangers was possible using 1 mol/L HCl as a desorbing agent. Thus, Lewatit MonoPlus MP 500 and Amberlite IRA 958 could be used as efficient anion exchangers for removal of heavy metal–GLDA complexes from aqueous solutions.

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