

Application of novel complexing agent in sorption
of heavy metal ions from wastewaters on ion exchangers
of various types*

D. Kołodyńska and Z. Hubicki

Department of Inorganic Chemistry, Faculty of Chemistry, Maria Curie-Skłodowska University, pl. Marii Curie-Skłodowskiej 2, 20-031 Lublin, Poland

Ethylenediaminetetraacetic acid (EDTA) and nitrilotriacetic acid (NTA) are very effective chelating agents used in many branches of industry. However, they are characterized by low biodegradability (EDTA) and carcinogenic effect (NTA), additionally they are quite persistent in the environment. The search for a cost effective alternative to these two most frequently used chelating agents has long been an industry target. One of them is N,N-bis(carboxymethyl)-L-glutamic acid whose tetrasodium salt known as Dissolvine GL-38. The aim of our work was to investigate Dissolvine GL-38 as a potential alternative for EDTA or NTA in effective removal of heavy metal ions from waters and wastewaters. In the presented paper there were used for the sorption of heavy metal ions two commercially available ion exchangers: Lewatit MonoPlus MP 64 and PuroLite S-920. A series of experiments was conducted to optimise the method for the Cu(II), Zn(II), Ni(II) and Cd(II) removal from industrial effluents. It was found that the sorption efficiency of the monodisperse polystyrene anion exchanger as well as the chelating ion exchanger varied depending on metal ions concentration, pH, phase contact time, agitation, temperature and properties of ion exchangers.

*This article is dedicated to Professor Roman Leboda on the occasion of his 65th birthday

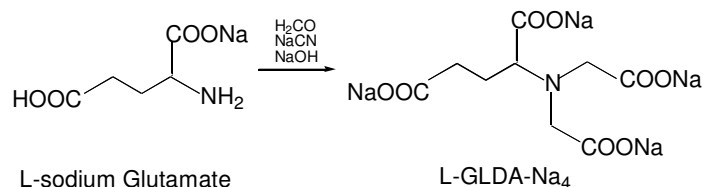
1. INTRODUCTION

Complexing agents are extensively applied in many fields. They are used as components of detergents and cosmetics, in the pulp industry, they are utilized to form stable water soluble chelates with transition metal ions, and to remove these metals before hydrogen peroxide bleaching [1-3]. In addition to assisting the removal of metals, chelating agents may prevent from their contact with hydrogen peroxide and thus to reduce the catalytic decomposition of the bleach [4, 5]. The use of chelators can be expected to increase further if closure of water cycles and TCF bleaching processes will be applied more extensively.

The behaviour of EDTA and NTA and in wastewater effluents as well as in the natural aquatic environment [6-8] has received much attention. It should be stressed that the widespread use and slow transformation of aminopoly-carboxylic acids have led to concerns regarding the possibility of their persistence in the environment and related to their ability to enhance the mobility and transport of radionuclides and heavy metals once released into the environment. Chelates have also been implicated in eutrophication in natural systems.

The search for a cost effective alternative to the two most frequently used chelating agents has long been an industry target. There are a number of alternative products on market, which claim to be as effective as EDTA, and NTA but most also have 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 EDTA or NTA. It has therefore been difficult to find a good solution that matches the performance profile of traditional chelating agents. As follows from the literature data, biodegradable complexing agents of a new generation such as IDS and DS can be applied for this aim [9-14]. Dissolvine GL-38 seem to be also a perfect solution in sorption of heavy metal ions on ion exchangers.

GLDA – N,N-bis(carboxymethyl)-L-glutamic acid (also called glutamic acid) is produced by the firm Akzo-Nobel Functional Chemicals, Amersfoort. Within the research and development program for new products, Dissolvine GL-38 tetrasodium salt of glutamic acid has been introduced according to the following process [15]:



Dissolvine GL-38 is largely made from sustainable raw materials (molasses). According to the Bra Miljöval protocol of the Swedish Society for Nature Conservation, Dissolvine GL-38 is 86% based on natural, replaceable and sustainable raw materials.

Dissolvine GL-38 as a chelating agent possesses complexing properties comparable to EDTA and NTA. Therefore GLDA is a direct alternative to NTA and EDTA in many industrial processes and consumer products such as detergents, pulp and paper industries (to control the chemistry of metal ions), textile and cosmetic industries, wastewater treatment plants as hard water softening agent, photo processing and food preservative (bonding cofactors of undesirable enzymes). It is readily biodegradable (> 60% degraded within 28 days) possessing good solubility at both low and high pH (Figure 1). Dissolvine GL-38 consists only of L-GLDA. This is significant because the D-form is not biodegradable. This exclusive character of the L form is based on the fact that it is made of the naturally occurring amino acid, L-glutamic acid.

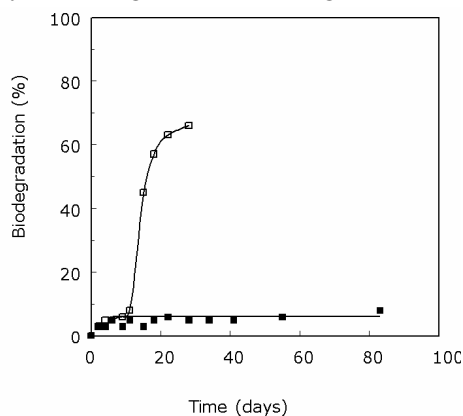


Fig.1. Biodegradation of L-GLDA (open points) and D-GLDA (close points) [16].

The thermal stability of GLDA is high. When tested at temperatures > 300°C, it showed no significant decomposition. This property has been used to develop water treatment systems for operating boilers to reduce the effect of hard water [16]. 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 the hard water ions even at very high pH levels (> pH 11). The tests have shown up to 10 times higher solubility levels in 25% NaOH solution compared to EDTA and NTA.

The aim of this work is to determine the influence of the complexing agent of a new generation Dissolvine GL-38 in the ion exchange removal of heavy metal ions from waters and wastewaters. Its influence on the effectiveness of sorption was tested for the medium basic polystyrene anion exchanger Lewatit MonoPlus MP 64 and the chelating ion exchanger Purolite S-920 with the thiourea functional groups. The evaluation of different chemical conditions on the ion exchange capacity and on the kinetics of copper(II), zinc(II), nickel(II) and cadmium(II) permitted for optimization of heavy metal ions removal.

2. EXPERIMENTAL

2.1. Resins

The medium basic monodisperse polystyrene anion exchanger *Lewatit MonoPlus MP 64* produced by the Lanxess, Germany was used in the investigations. On the contrary, the chelating ion exchanger with the thiourea functional groups *Purolite S-920*, Germany produced by the Purolite was also used. Their brief characteristics are presented in Table 1 [17, 18]. Prior to the use they were washed with 1 M NaOH and 1M HCl to remove organic and inorganic impurities and then washed several times with deionized water.

Tab. 1. Characteristics of the used ion exchangers.

Properties	Lewatit MonoPlus MP 64	Purolite S-920
Matrix	PS-DVB	PS-DVB
Structure	gel	gel
Commercial form	Cl ⁻ /OH ⁻	H ⁺
Functional groups	- ⁺ N(CH ₃) ₃ /-N(CH ₃) ₂	thiourea
Appearance	beige, opaque	cream, opaque
Total capacity (Cl ⁻ form)	1.3 eq/L	200 g Hg(II)/L
Bead size	0.59 mm ± 0.05	0.3–1.2 mm
Max temp. range	40 °C	80 °C
Operating pH range	0–7	1–13

2.2. Chemicals

In order to determine sorption capacity of resins towards copper(II), zinc(II), nickel(II) and cadmium(II) in the presence of Dissolvine GL-38, they were reacted with appropriate solutions of these metals at pH without adjustment. 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 ions, the breakthrough curves were determined using 10 mL of the swollen ion exchanger. The prepared solutions of complexed metal ions were passed continuously downwards through the resin beds keeping the flow rate at $0.8 \text{ mL}\cdot\text{cm}^{-2}\cdot\text{min}^{-1}$. The effluent was collected in fractions in which the metal(II) 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 of M(II) were calculated from the determined breakthrough curves according to equations 1-3 [19]:

$$D_g = \frac{\bar{U} - U_0 - V}{m_j} \quad (1)$$

$$D_v = \frac{\bar{U} - U_0 - V}{V_j} \quad (2)$$

$$C_w = \frac{U \cdot c_0}{V_j} \quad (3)$$

where: \bar{V} is the volume of effluent at $c=c_0/2$ (determined graphically) (mL), V_0 is 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 is the void (interparticle) ion exchanger bed volume which amounts to ca. 0.4 of the bed volume (mL), m_j is the dry ion exchanger mass (g), V_j is the bed volume (mL), V_e is the effluent volume to the break point (L), c_0 is the initial concentration of M(II) solution (mg/L), respectively.

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

2.4. Batch studies

The sorption of divalent metal ions Cu(II), Zn(II), Ni(II) and Cd(II) in the presence of Disslovine GL-38 on the above-mentioned ion exchanger was investigated by batch operation as a function of contact time, different metal-ligand ratios and pH. Batch 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) at the equilibrium, q_e (mg/g) and at the specific time, q_t (mg/g) were obtained according to:

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

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

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

The appropriate amounts of ion exchanger and a solution of known metal ion concentration were shaken in a mechanical shaker (ELPINE type 357) at the constant temperature of 25°C. The experiments were conducted in the two parallel series. The reproducibility of the measurements was within 5%. The concentrations of metals were measured by the AAS method.

2.5. The SEM and FT-IT/PAS studies

The surfaces of the dry samples of the ion exchangers before and after the sorption process were determined by Scanning Electron Microscopy (SEM). The samples were ground into powder and coated with a thin layer of palladium-gold alloy with a sputter coater (Polaron SC 7620). Subsequently, their surfaces were observed and photographed by SEM. The microscope of LEO1430VP trademark and EDX detector of Röntec trademark were used in this study.

The FT-IR/PAS spectra of the ion exchangers before and after the sorption processes were recorded by means of a Bio-Rad Excalibur 3000MX spectrometer equipped with the photoacoustic detector MTEC 300 (in the helium atmosphere in a detector) over the 4000–400 cm^{-1} range at the resolution of 4 cm^{-1} and the maximum source aperture. The spectra were normalized with reference to the MTEC carbon black standard.

3.1. Complexes with Dissolvine GL-38

In a metal-ligand system, metal-ligand bond formation can be explained by electrostatic interaction and π bond formation between the metal subshell and the vacant ligand orbital. In the case of application of anion exchangers, the removal of metal ions in the presence of organic ligands occurs mainly due to formation of negatively charged complexes between the ligand and the metal ion, which

interact with the ionized functional groups linked with the matrix of anion exchanger. Formation of an insoluble metal-ligand species, especially hydroxocomplexes may also increase the apparent sorption of metal ions, whereas metal uptake may be reduced in the presence of ligands due to competition for functional groups between the ligand and the negative metal complexes. Formation of positively charged metal-ligand complexes, which pass through the anion exchanger bed without any reaction makes this process ineffective. In the case of chelating ion exchangers possible decomposition of studied complexes and sorption of heavy metal ions with forming the coordination bond should also be taken into account.

In the case of Disslovine GL-38 the following reactions are possible [20]:

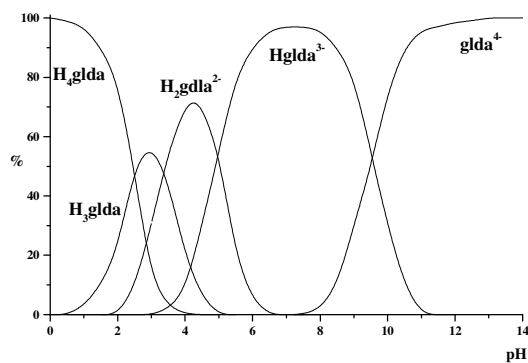
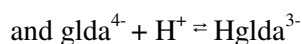
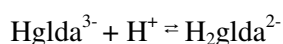
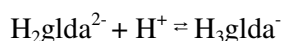


Fig.1. The percentage of individual forms of GLDA depending on the pH value.

Tab. 2. The stability constants of complexes of ML type (log K) for heavy metal ions with GLDA.

M(II)/M(III)	L=gl ⁴⁻
<i>Ca(II)</i>	5.2
<i>Cd(II)</i>	9.1
<i>Cu(II)</i>	13.1
<i>Co(II)</i>	10.0
<i>Cr(III)</i>	—
<i>Fe(II)</i>	8.7
<i>Fe(III)</i>	11.7
<i>Hg(II)</i>	14.3
<i>Mg(II)</i>	6.1
<i>Mn(II)</i>	7.6
<i>Ni(II)</i>	10.9
<i>Pb(II)</i>	10.5
<i>Zn(II)</i>	10.0

The complexation of polydentate Dissolvine GL-38 is characterized by the formation of stable 1:1 metal to ligand complexes as the major species. The comparison of stability constants of heavy metal complexes with Dissolvine GL-38 is presented in Table 2.

The test at pH 10 with a competing complexing agent (hydroxy naphthyl blue) showed that Dissolvine GL-38 possesses quite good chelating power (Figure 2).

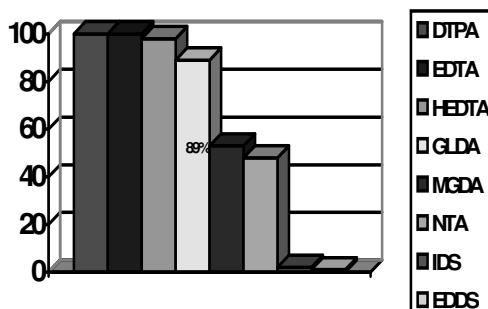
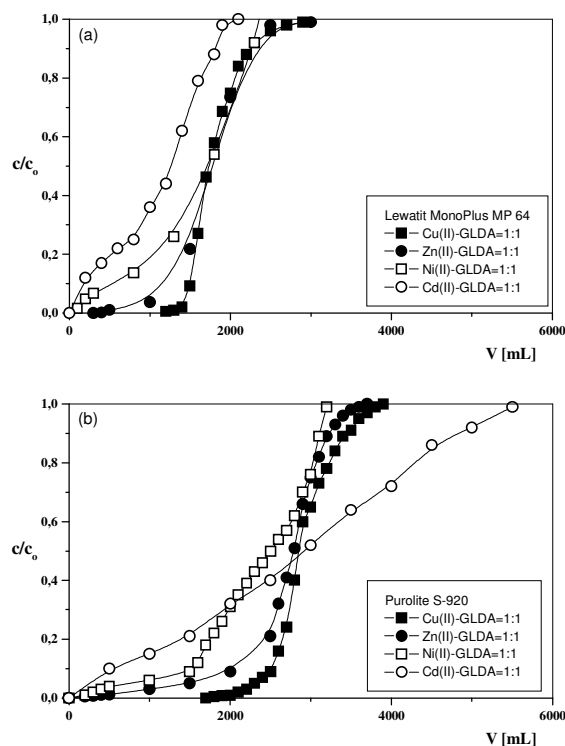


Fig. 2. The chelating power of different complexing agents [21].

3.2. Sorption of M(II) complexes with Dissolvine GL-38 – the dynamic method

The mass (D_g) and volume (D_v) distribution coefficients as well as the working (C_w) ion exchange capacities were calculated from the breakthrough curves. The breakthrough curves of Cu(II), Zn(II), Ni(II) and Cd(II) in the

presence of Dissolvine GL-38 using Lewatit MonoPlus MP 64 and Purolite S-920 are presented in Figures 3a-b.



Figs. 3a-b. Breakthrough curves of Cu(II), Zn(II), Ni(II) and Cd(II) in the presence of Dissolvine GL-38 determined for Lewatit MonoPlus MP 64 and Purolite S-920. ($c_0 = 1\text{mM}$; 10 mL of swollen ion exchanger; flow rate $0.8\text{ mL/cm}^2\text{min}^{-1}$; pH for Cu(II) 8.24, Zn(II) 9.17; Ni(II) 9.02 and Cd(II) 9.35).

For Lewatit MonoPlus MP 64 the calculated D_g and volume D_V are equal to 731 and 170 for Cu(II), 751 and 174 for Zn(II), 721 and 168 for Ni(II) and 533 and 124 for Cd(II), respectively. The values under discussion are higher for the chelating ion exchanger Purolite S-920 with thiourea functional groups. They are as follows: 1079 and 283 for Cu(II), 1062 and 278 for Zn(II), 936 and 246 for Ni(II) and 1243 and 294 for Cd(II), respectively. From the values of C_w in the range from 2 mg/mL to 6 mg/mL and the values of C_t in the range from 1.3 mg/mL to 11.5 mg/mL for Lewatit MonoPlus MP 64 as well as for Purolite S-920 the values of C_w in the range from 3 mg/mL to 10.8 mg/mL and the values of C_t in the range from 3.2 mg/mL to 18.6 mg/mL, the studied ion exchangers can be presented in the following series:

Purolite S-920 > Lewatit MonoPlus MP 64.

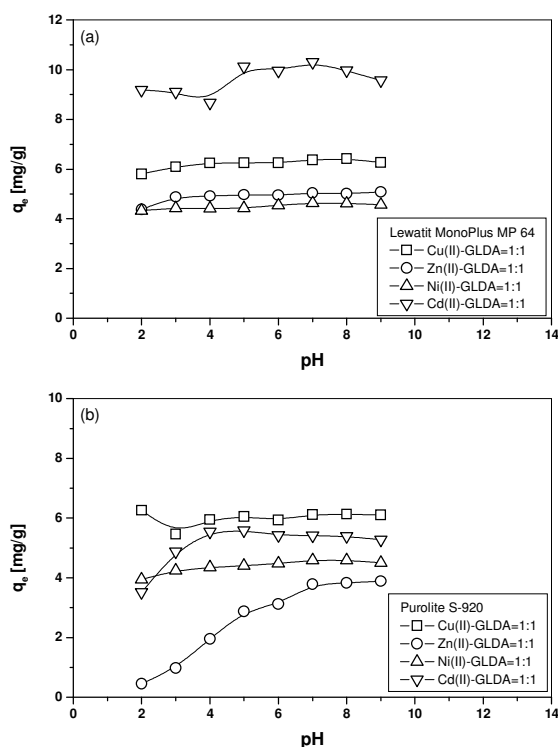
For the individual heavy metal ions the affinity series for the above-mentioned ion exchangers can be as follows:

Lewatit MonoPlus MP 64: $Zn(II) > Cu(II) > Ni(II) > Cd(II)$,

Purolite S-920: $Cd(II) > Cu(II) > Zn(II) > Ni(II)$.

3.3. Sorption of M(II) complexes with Dissolvine GL-38 – the batch method

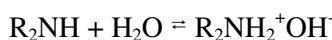
Figures 4a-b show the relationship between the initial pH of heavy metal ion solutions in the presence of Dissolvine GL-38 and the maximum mass of sorbed complexes at the equilibrium (adsorption capacity) using Lewatit MonoPlus MP 64 and Purolite S-920.



Figs. 4a-b. Effect of initial pH on Cu(II), Zn(II), Ni(II) and Cd(II) in the presence of Dissolvine GL-38 determined for Lewatit MonoPlus MP 64 and Purolite S-920 ($c_0 = 1\text{mM}$; $t = 3\text{h}$).

In the range from 2 to 9 for the medium basic anion exchanger Lewatit MonoPlus MP 64 with $\text{—}^+\text{N}(\text{CH}_3)_3/\text{—N}(\text{CH}_3)_2$ functional groups the sorption capacity slightly depends on the initial pH.

As follows from the literature data, the mechanism of anion exchange on such a type of anion exchangers involving dissociation reactions was first postulated by Helfferich [22] according to whom the free-base form of e.g. a secondary amino group in neutral and alkaline pH can be characterized by the dissociation equilibrium:

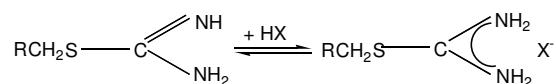


Because of poor dissociation of the free base form in this condition only negligible uptake for example of anions of strong acids is possible, whereas in acidic conditions the amino groups are protonated after reacting with H^+ ions as follows:



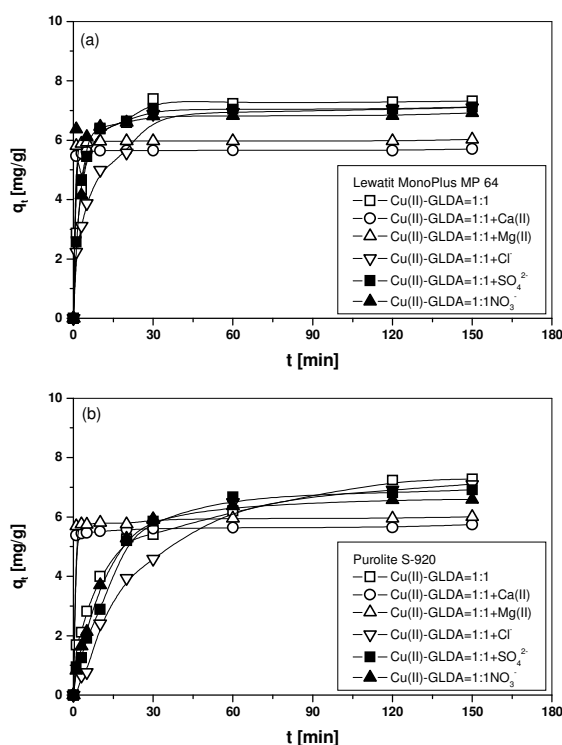
Protonation results into the formation of positively charged surface due to the presence of protonated species on the surface of resin pore walls. The second step, anion association, is a result of electrostatic interactions between the positively charged groups and the negatively charged complexed anions. Specific adsorption of the anions is believed to occur in a region close to the pore walls. Besides the exchange of ions based on the electrostatic interactions with quaternary ammonium groups, medium basic anion exchangers can also bind the transition metal ions through the formation of coordinating bonds (due to the presence of the free pair of electrons). In this case 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 Purolite S-920 containing the thiouronium functional groups, the sorption capacity of Zn(II), Ni(II) and Cd(II) complexes with Dissolvine GL-38 increases with the increasing pH. The maximum sorption was observed for Dissolvine complexes in the pH range 6–9. In the aqueous solution, such selective ion exchangers exhibit high selectivity for metal ions. Depending on the pH, thiouronium functional groups assume the following forms:



They are able to form coordination bonds with metal cations (the first form) but in form 2 the anion complexes are bonded according to the anion exchange mechanism.

A series of contact time experiments for Cu(II) complexes with Dissolvine GL-38 has been carried out in the presence of different interfering cations such as Ca(II), Mg(II) as well as anions Cl^- , SO_4^{2-} and NO_3^- . In Figures 5a-b the contact time curves for sorption of Cu(II) in the presence of Dissolvine GL-38 in the above-mentioned systems using Lewatit MonoPlus MP 64 and Purolite S-920 are presented.



Figs. 5a-b. Effect of phase contact time on Cu(II) in the presence of Dissolvine GL-38 determined for Lewatit MonoPlus MP 64 and Purolite S-920 ($c_0 = 1\text{mM}$; $t = 3\text{h}$; interfering ions Ca(II), Mg(II), Cl^- , SO_4^{2-} and NO_3^-).

Figures 5 a-b show that the amount of Cu(II) complexes sorbed on the medium basic anion exchanger with the $-\text{N}(\text{CH}_3)_3/-\text{N}(\text{CH}_3)_2$ functional groups as well the chelating ion exchanger with the thiourea functional groups increased with contact phase time. The time necessary to reach equilibrium was 30 min for Lewatit MonoPlus MP 64 and 60 min for Purolite S-920. The sorption capacities

q_t are equal to 7.33 mg/g and 6.95 mg/g for Lewatit MonoPlus MP 64 and Purolite S-920, respectively.

For the obtained data, kinetic analysis was also performed. It was shown that the pseudo first order model did not adequately describe the sorption results of studied complexes on Lewatit MonoPlus MP 64 and Purolite S-920 because of low correlation coefficients (R^2) between the predicted and the experimental values (Table 3). Therefore the analysis with the aid of a pseudo second order equation performed. The value of the rate constant k_2 could be calculated using the formula [23, 24]:

$$\frac{dq}{dt} = k_2(q_e - q)^2 \quad (6)$$

where: q_e and q_t are the removal amounts of M(II) ions per unit mass of the ion exchanger at equilibrium and time, respectively. From its linearized form of the pseudo second order model according to the equation:

$$\frac{t}{q} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2} \quad (7)$$

for Cu(II), Zn(II), Ni(II) and Cd(II) ions in the presence of Dissolvine GL-38 on Lewatit MonoPlus MP 64 and Purolite S-920 kinetic parameters were calculated. Additionally, the intraparticle diffusion model was also used. It can be expressed as:

$$q_t = k_i t^{0.5} \quad (8)$$

where: k_i is the diffusion coefficient ($\text{mg/g min}^{0.5}$).

As follows from the data presented in Table 3, the R^2 values for the pseudo second order kinetic model were closer than those for the pseudo first order kinetic model indicating better agreement. The R^2 values for the pseudo second order model of the above-mentioned ion exchangers were 0.9998 and 0.9993 for Cu(II) complexes with Dissolvine GL-38.

The analysis of the isotherm data is important to develop an equation which accurately represents the results and which could be used for design purposes. The most common isotherms applied in the solid/liquid system are the Langmuir and Freundlich models [25, 26]. Using them the equilibrium adsorption of Cu(II), Zn(II), Ni(II) and Cd(II) ions in the presence of Dissolvine GL-38 5 was studied to evaluate sorption capacity of the studied ion exchangers as well as their affinity for the sorbed complexes. The isotherms and their respective linear

forms were shown in Table 4 where the linear form of Langmuir-1 was more common. The analogous data obtained on the basis of the Freundlich model are also presented in this table.

Tab. 3. Kinetic parameters for Cu(II) complexes with Dissolvine GL-38 on Lewatit MonoPlus MP 64 and Purolite S-920.

Cu(II)-GL-38	Lewatit MonoPlus MP 64	Purolite S-920
Pseudo first order		
q_1 (mg/g)	2.218	5.717
k_1 (1/min)	0.038	0.045
R^2	0.8801	0.9633
Pseudo second order		
q_2 (mg/g)	7.374	6.574
k_2 (g/mg min)	0.120	0.012
h (mg/g min)	6.561	0.741
R^2	0.9998	0.9993
Intraparticle diffusion model		
k_i (mg/g min ^{0.5})	0.299	0.498
R^2	0.5827	0.8361

The Langmuir sorption isotherms of Cu(II), Zn(II), Ni(II) and Cd(II) in the presence of Dissolvine GL-38 determined for Lewatit MonoPlus MP 64 and Purolite S-920 are presented in Figures 6a-b. The obtained values of R^2 for the Langmuir-1, Langmuir -2, Langmuir-3 and Langmuir-4 type isotherms suggest that the type 1 isotherm provides a good model of the sorption system. They are in good agreement with the experimental sorption capacities $q_{e,exp}$ for Lewatit MonoPlus MP 64. These values for the complexes with Dissolvine GL-38 are 26.05 mg/g for Cu(II), 14.65 mg/g for Zn(II), 32.89 mg/g for Ni(II) and 15.07 for Cd(II), respectively. In the case of Purolite S-920 these values are as follows: for Cu(II) 31.32 mg/g, for Zn(II) 21.62 mg/g, for Ni(II) 34.58 mg/g and for Cd(II) 36.18 mg/g, respectively. Therefore the sorption capacity order has been found for sorption on Lewatit MonoPlus MP 64 as: Ni(II) > Cu(II) > Cd(II) > Zn(II) whereas for Purolite S-920 as: Cd(II) > Ni(II) > Cu(II) > Zn(II). The obtained results were confirmed by the EDX analysis. The exemplary image for Cu(II) complexes with Dissolvine GL-38 sorbed on Lewatit MonoPlus MP 64 is presented in Figure 7. The registered FT-IR/PAS spectra before and after the sorption of Cu(II) in the presence of Dissolvine GL-38 are presented in Figure 8.

Tab. 4. The linear forms of Langmuir and Freundlich models.

Type	Linear form	Plot
Langmuir-1	$\frac{c_e}{q_e} = \frac{c_e}{q_0} + \frac{1}{bq_0}$	c_e/q_e vs. c_e
Langmuir-2	$\frac{1}{q_e} = \left(\frac{1}{bq_0}\right)\frac{1}{c_e} + \frac{1}{q_0}$	$1/q_e$ vs. $1/c_e$
Langmuir-3	$q_e = q_0 - \left(\frac{1}{b}\right)\frac{q_e}{c_e}$	q_e vs. q_e/c_e
Langmuir-4	$\frac{q_e}{c_e} = bq_0 - bq_e$	q_e/c_e vs. q_e
Freundlich	$\log(q_e) = \log(K_F) + \frac{1}{n}\log(c_e)$	$\log(q_e)$ vs. $\log(c_e)$

where: c_e is the equilibrium M(II) ions concentration in solution (mg/L); q_e is the removal amount of M(II) ions per unit mass of the ion exchanger at equilibrium (mg/g); b is the Langmuir constant related to the energy of adsorption (L/g); K_F is the Freundlich isotherm constant (mg/g)(L/g)ⁿ; n is the Freundlich exponent; q_0 is the maximum sorption capacity (mg/g).

For Purolite S-920 with thiourea functional groups the peaks at 3200–3400 cm⁻¹ are connected with asymmetric and symmetric stretching vibrations of the group–NH₂. The other bands are related to the functional group occurring at 519 cm⁻¹, 1103 cm⁻¹ and 1394 cm⁻¹. The shift of these bands indicates the sorption of Cu(II) complexes with Dissolvine GL-38.

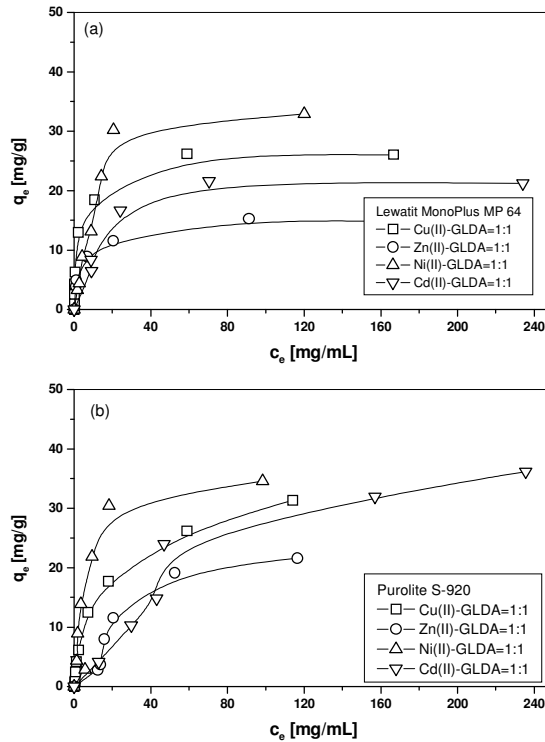


Fig. 6a-b. The Langmuir sorption isotherms of Cu(II), Zn(II), Ni(II) and Cd(II) in the presence of Dissolvine GL-38 determined for Lewatit MonoPlus MP 64 and Purolite S-920 ($t = 3h$).

Summing up, it can be stated that the sodium salt of GLDA (Dissolvine GL-38) can be of great significance in purification of wastewaters from heavy metal ions such as Cu(II), Zn(II), Ni(II) and Cd(II) using the chelating ion exchanger Purolite S-920. It was proved that the initial metal ions concentration, the phase contact time, the appearance of interfering ions influence on the effectiveness of complexes sorption.

Tab. 5. The isotherm parameters obtained by using linear methods.

Type	Parameters	Lewatit MonoPlus MP 64				Purolite S-920			
		M(II)	Cu(II)	Zn(II)	Ni(II)	Cd(II)	Cu(II)	Zn(II)	Ni(II)
Langmuir-1	q_0	26.52	13.83	36.98	21.93	29.52	28.16	39.71	40.16
	b	0.39	1.53	0.02	0.13	0.07	0.03	0.01	0.03
	R^2	0.9998	0.9936	0.9352	0.9988	0.9800	0.9800	0.9976	0.9988
Langmuir-2	q_0	27.26	13.28	33.82	16.17	49.26	34.48	39.76	35.71
	b	2.59	0.47	0.02	0.05	0.04	0.02	0.03	0.01
	R^2	0.8837	0.9788	0.9865	0.9720	0.9306	0.9459	0.9034	0.9667
Langmuir-3	q_0	24.29	15.87	36.25	17.85	34.38	27.39	45.37	39.07
	b	0.71	0.53	0.03	0.66	0.11	0.03	0.15	0.03
	R^2	0.8963	0.8313	0.9292	0.9614	0.9817	0.9370	0.9929	0.977
Langmuir-4	q_0	25.54	16.37	38.73	20.23	34.55	28.02	45.50	28.39
	b	0.64	0.38	0.01	0.18	0.11	0.03	0.15	0.01
	R^2	0.8963	0.8323	0.5292	0.7614	0.9881	0.9381	0.9929	0.8197
Freundlich	K_F	9.40	4.76	2.04	5.90	2.53	1.03	4.79	1.10
	n	2.56	4.02	1.12	3.81	1.07	1.46	1.49	1.51
	R^2	0.9881	0.9345	0.9851	0.7333	0.9497	0.7524	0.9192	0.8494

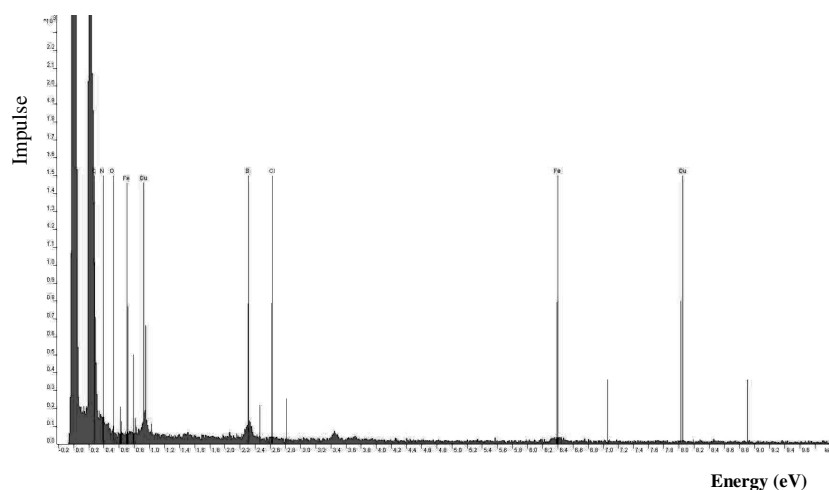


Fig. 7. The EDX analysis for Cu(II) in the presence of Dissolvine GL-38 determined for Lewatit MonoPlus MP 64.

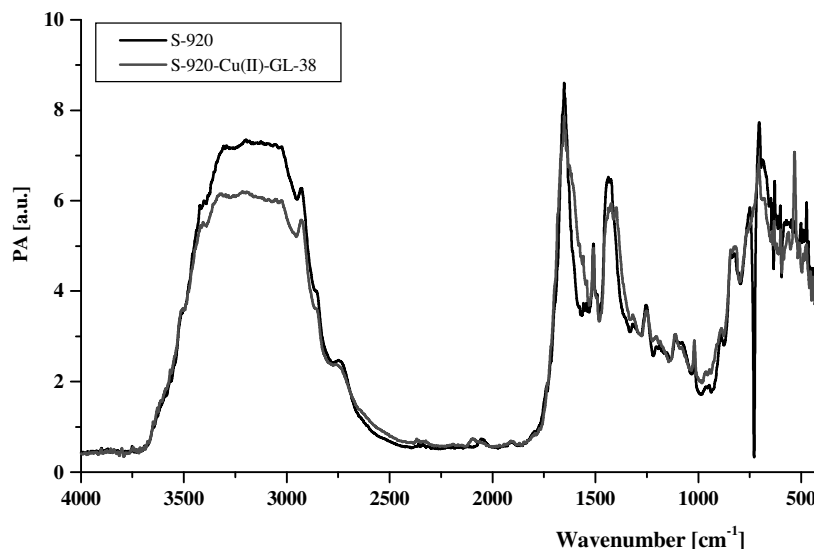


Fig. 8. FT-IR/PA spectra of Purolite S-920 before and after sorption of Cu(II) in the presence of Dissolvine GL-38.

4. REFERENCES

- [1] C. Oviedo, J. Rodríguez, *Quimica Nova*, 26, 901 (2003).
- [2] T. Egli, *J. Biosci. Bioeng.*, 92, 89 (2001).
- [3] T. P. Knepper, *Trends Anal. Chem.*, 22 708 (2003).
- [4] K. Pirkanniemi, S. Metsärinne, M. Sillanpää, *J. Hazard. Mater.*, 147, 556 (2007).
- [5] M. Sillanpää, *Chemosphere*, 33, 293 (1996).
- [6] B. Nörtemann, *Appl. Microbiol. Biotechnol.*, 51 751 (1999).
- [7] B. Nowak, F.G. Kari, H.G. Krüger, *Water, Air Soil Poll.*, 125, 243 (2001).
- [8] H. G. Hauthal, *Tenside Surf. Det.*, 46, 1 (2009).
- [9] D. Kołodyńska, Z. Hubicki, M. Geça, *Ind. Engin. Chem. Res.*, 47, 3192 (2008).
- [10] D. Kołodyńska, Z. Hubicki, M. Geça, *Ind. Engin. Chem. Res.*, 47, 6221 (2008).
- [11] D. Kołodyńska, H. Hubicka, Z. Hubicki, *Desalination*, 239, 216 (2009).
- [12] Dorota Kołodyńska, *Chem. Engin. J.*, 150, 280 (2009).
- [13] D. Kołodyńska, *Przem. Chem.*, 88, 182 (2009).
- [14] D. Kołodyńska, *Chem. Engin. J.*, 2009 doi:10.1016/j.cej.2009.05.002
- [15] J. Seetz, T. Stanitzek, 55th SEPAWA Congress and European Detergents Conference Proceedings, Würzburg, Germany 15-17 October 2008
- [16] J. Seetz, *Soap Perfumery Cosmetics*, 4, 75 (2007).
- [17] Brochure of Lewatite, 2008.
- [18] Brochure of Purolite, 2008.
- [19] D. Kołodyńska, H. Hubicka, Z. Hubicki, *Desalination*, 227, 150 (2008).
- [20] Brochure of Dissolvine GL-38, 2008.
- [21] J. Seetz, Anti-redeposition agents, builders and chelates, BACS Speciality Surfactants Sector Group Meeting, 22 March 2007, Cheshire, Great Britain.
- [22] F.G. Helfferich, *Ion exchange*, Dover Publications Inc., New York 1995.

-
- [23] K.V. Kumar, *J. Hazard. Mater.*, 142, 564 (2007).
[24] Y. S. Ho, G. McKay, *Water Res.*, 34, 735 (2000).
[25] K.V. Kumar, S. Sivanesan, *J. Hazard. Mater.*, 126, 198 (2005).
[26] A. Shafaei, F. Z. Ashtiani, T. Kaghazchi, *Chem. Engin J.*, 133, 311 (2007).