

# ENHANCED REMOVAL OF METAL IONS IN THE PRESENCE OF GLDA ON PUROLITE S 110

Irmina Pańczuk-Figura, Dorota Kołodyńska\*

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

## Abstract

In this paper the ion exchanger Purolite S 110 has been used for removal of Pb(II), Cd(II) and Zn(II) complexes with Dissolvine GL-38 (GLDA) in order to select the most effective conditions for the removal of heavy metal ions from aqueous solutions in the presence of complexing agents.

Different parameters affected the sorption kinetic such as the initial concentration and the phase contact time. To describe the sorption process the pseudo second order equation as well as the Langmuir and Freundlich adsorption equations were applied. The interactions of M(II) ions with selected ion exchanger was confirmed by the ATR FT-IR method before and after the sorption process.

The determined sorption efficiency of the tested resin with respect to the complexes of Zn(II), Pb(II) and Cd(II) with GLDA depends on the contact time and the concentration of the working solution and accompanying Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> ions. Average sorption efficiency (%S) is as follows: 64% for Zn(II), 62% for Cd(II) and 97% for Pb (II) complexes with GLDA. The kinetic data are well described by the pseudo second order rate equation.

Purolite S 110 can be used for both reducing a content of a complexing agent and metal ions from wastewaters as well as to develop ways for mobilization of heavy metal ions from the soil solution. It is very important because GLDA has excellent stability in the whole pH range, which may have the promising applications in the fields of catalysis, biotechnology and detergents production.

**Keywords:** heavy metal ions, GLDA, Purolite S 110, sorption process

\* Corresponding author: Tel.: +48 81 5375770; Fax: +48 81 5333348  
E-mail address: [kolodyn@poczta.onet.pl](mailto:kolodyn@poczta.onet.pl) (D. Kołodyńska)

## 1. Introduction

Among typical methods of heavy metal ions removal from solutions such as precipitation, coagulation and flocculation, electrolytic methods, evaporation and adsorption ion exchange receive considerable interest due to high efficiency and low operational costs. However, purification of waters and wastewaters containing heavy metal complexes always encounters great difficulties. For example, ethylenediaminediacetic acid (EDTA) is slowly degradable and has been found to "pass through" the wastewater treatment plants due to its poor settling properties. EDTA is used in small amounts in many detergents as a stabilizer for perborate. Such type of complexing agents can also be used: (i) for enhancing detergents application which is very important in everyday use (hard water contains large amounts of calcium and magnesium ions therefore the smaller cleaning effect with the same amount of detergents is observed. The complexing agents 'soften' water by binding these ions in a complex form), (ii) stabilizing the bleaching system by preventing the metal ions from acting as catalysts (catalysts can increase the oxidizing effects of the bleaching agents and in a way that damages the textile fibers). In surface waters, complexing agents are regularly determined in concentrations varying between one digit and double digit µg/dm<sup>3</sup>. Between 1991 and 2002 and within the "Declaration on the Reduction of Water Pollution by EDTA" it was possible to achieve an EDTA emission reduction by 44 % for the German Rhine basin [1]. Increasingly EDTA is being substituted by other complexing agents (e.g. DTPA, NTA phosphonates, etc.). Since 2004 it has been possible to reduce the EDTA emissions of a large chemical plant by further 50 % by putting into work a UV oxidation plant [2].

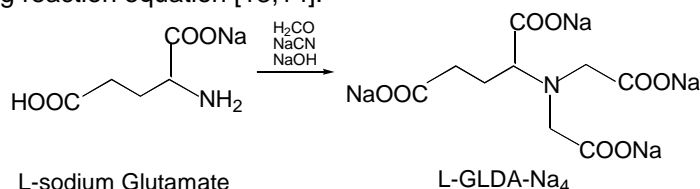
One possible strategy is firstly, precipitation by adding strong acids. Secondly, precipitation of heavy metal ions from such solutions as hydroxides, sulphides or carbonates should be performed. Common coagulants and flocculants are additionally used to increase particle size through aggregation. Another strategy assumes removal of metal ions from solutions by their reduction or electrodeposition (requires separation of heavy metal ions from the complexing agents). These processes are incomplete and additional purification is required after removal of a basic portion. Therefore, more effective solution is application of the ion exchange method.

Although several investigations have been reported on application of ion exchangers for removal of complexes with heavy metals in the presence of a biodegradable complexing agents, more information is still needed for better understanding of the adsorption behaviour of different water soluble and non-biodegradable species of heavy metals, especially Cu(II), Zn(II), Cd(II) and Pb(II).

Our previous papers [3-7] confirmed the usability of well-known strongly and weakly basic anion exchangers for the removal of heavy metal complexes with non-biodegradable and biodegradable

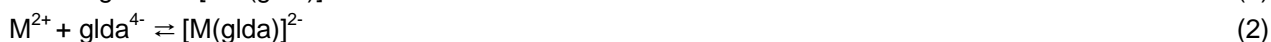
complexing agents from different solutions. In this group the Lewatit MonoPlus ion exchangers (M 500, M 600, MP 500, MP 64, MP 62), Purolite A 520E, Amberjet ion exchangers (4200, 4400, 4600) as well as Amberlite IRA (900, 910, 458, 67 and 958) can be distinguished. From the group of complexing agents the EDTA, NTA and DTPA were studied. For the group of complexing agents that may replace traditional complexones the following can be listed: IDS, also called iminodisuccinic acid; polyaspartic acid (DS), ethylenediaminedisuccinic acid (EDDS), L-glutamic acid N,N-diacetic acid tetrasodium salt (GLDA) as well as methylglycinediacetic acid (MGDA) and N-(2-hydroxyethylene)iminodiacetic acid (HEIDA) [8]. The structure of the typical best known biodegradable complexing agents (IDS, EDDS and GLDA) and their stability constants with metal ions of the M(II)-L=1:1 type are presented in Table 1 [9-12].

GLDA is a new generation of non-toxic biodegradable complexing agent. Synthesis of GLDA is based on the fermentation flavour enhancer - monosodium glutamate, corn molasses. The process takes place in accordance with the following reaction equation [13,14]:



On the commercial scale it is known as Dissolvine GL-38 (AkzoNobel Functional Chemicals, The Netherlands). GLDA is a tetraprotic acid. The acidic dissociation constants determined at an ionic strength 0.1 M and at a temperature 298 K are equal to  $\text{pK}_{\text{a}1}=9.4$ ,  $\text{pK}_{\text{a}2}=5.0$ ,  $\text{pK}_{\text{a}3}=3.5$  and  $\text{pK}_{\text{a}4}=2.6$  [15]. The percentage of individual forms of GLDA depending on the pH value is presented in Fig.1 [6].

Complexation is characterized by the formation of stable 1:1 metal to ligand complexes as the major species. According to the mechanisms of Eqs.1-3, heavy metal complexes with GLDA can be as follows:



or generally:



where  $n=0-3$ .

Based on the stability constants ( $\log K$ ) for the complexes of  $[\text{M}(\text{glDa})]^{2-}$  (Table 1) it was found that over 98 % of metal ions existing in the system is chelated. The residual part due to the decomposition or lower stability constant of M(II)-GLDA chelate as compared to EDTA and DTPA can occur in the form of aqua ions or hydroxides (at higher pH). It should be noticed that in the case of real solutions, the results of speciation calculations should be considered critically taking into account occurrence of other complexing ions. The effective range of complexation of heavy metal ions with GLADA ion is 7-10 for Mg (II), 6-14 for Ca(II), 3-10 for Zn(II), 2-11 for Cu(II), 5-11 for Mn(II) and 2-4 for the Fe(III).

It should be mentioned that low toxicity ( $\text{LD}_{50} > 2000 \text{ mg / kg}$ ) makes that GLDA is safe for humans. In comparison with the phosphate it does not contribute to eutrophication and as a component of various types of detergents it removes stains better.

In the presented paper the kinetic and adsorption studies of heavy metal Pb(II), Cd(II) and Zn(II) complexes with GLDA removal from aqueous solutions using the synthetic macroporous ion exchanger Purolite S 110 were presented. Different parameters affected the sorption kinetics and equilibrium studies such as the effect of the initial concentration and the phase contact time. To describe the sorption process the pseudo first order, the pseudo second order and the intraparticle model equations as well as the Langmuir and Freundlich adsorption equations were applied. The interactions of M(II) ions or its complexes with a selected ion exchanger was confirmed by ATR FT-IR method before and after the sorption process. The results can be used in the future to develop the ways to mobilize the heavy metal ions contained in the soil solution and select the best performance sorption and sorbents for the removal of heavy metal ions from aqueous solutions.

## 2. Experimental

### 2.1. Materials and chemicals

Purolite S110 (Purolite Ltd.) is a macroporous polystyrene based resin, with functional groups specially designed for the selective removal of boron from concentrated aqueous solutions and wastewaters. It is effective for such solutions over a wide range of pH values and over a wide range of boron concentrations. The presence of boron ions in the process streams and in wastewaters can give rise to major problems. Purolite S110 will reduce boron concentrations by an order of magnitude even where concentrations of other ions are reasonably high. It contains the N-methyl-D-glucamine functional group [16, 17]. According to the Zingg classification as can be seen from the measurements using the optical-electronic analyzer almost 98% of the beads are of disc shape. The bead size distribution of Purolite S 110 is presented in Fig.2. The quotient  $c/b$  is a measure of the flatness of the particles. Knowing the three

dimensions of beads correlated with the three main axes, namely the long axis - the length (a) and the medium axis - width (b), the short axis - thickness (c) and based on the b/a and c/b ratio, these shapes are defined as follows: blade ( $b/a < 2/3$  and  $c/b < 2/3$ ), disc ( $b/a > 2/3$  and  $c/b < 2/3$ ), rod ( $b/a < 2/3$  and  $c/b > 2/3$ ), sphere ( $b/a > 2/3$  and  $c/b > 2/3$ ) [18]. The SEM micrographs of the Purolite S 110 are shown in Figs.3.

Stock solutions of  $1 \times 10^{-3}$  mol/L in the M(II)-GLDA=1:1 system (where M(II) is the metal ion) were made from  $Pb(NO_3)_2$ ,  $CdCl_2 \cdot 4H_2O$  and  $ZnCl_2$ , respectively. The metal-chelate solutions were prepared by adding equimolar amounts of respective metal salts to the GLDA solutions. GLDA was obtained from Akzo Nobel Functional Chemicals (Amersfoort, The Netherlands). In the studies the obtained solutions were used without pH adjustment which were as follows: Pb(II) 9.30, Cd(II) 8.74 and Zn(II) 9.17. In order to study the effect of accompanying ions  $Cl^-$ ,  $SO_4^{2-}$ ,  $NO_3^-$  on sorption of heavy metal complexes from aqueous solutions, the initial solutions were enriched by  $200 \text{ mg/dm}^3$  and  $500 \text{ mg/dm}^3$  of their sodium salts. All chemicals were used of analytical grade. They were purchased from POCh Gliwice (Poland).

## 2.2. Kinetic parameters determination

Batch experiments were carried out to measure the adsorption characteristics of anionic complexes onto Purolite S 110. Prior to their use, the ion exchanger was washed by 1 M HCl and 1 M NaOH for 2 h to eliminate traces of impurities. For determination of the effect of the resin dose on the effectiveness of the sorption process, Purolite S 110 samples from 0.05 to 0.5 g were added to the solutions of Pb(II) complexes with GLDA and shaken for 2 h at 298 K. In order to determine the effect of the phase contact time an ion exchanger the dose of 0.5 g was added to the M(II) complexes with GLDA solutions (the initial concentration  $1 \times 10^{-3}$  M -  $7 \times 10^{-3}$  M) and shaken for 2 h at 298 K. At the prescribed time intervals, the solutions were filtered and the M(II) concentration in the filtrate was determined. Equilibrium experiments were performed at the initial concentrations varying from  $1 \times 10^{-3}$  M to  $2 \times 10^{-2}$  M and the solutions were shaken for 2 h at 298 K. The effect of pH on the amount of Pb(II) complexes with GLDA adsorbed onto ion exchanger was investigated over the pH range of 1.0 to 12.0. The pH was adjusted using NaOH and/or HCl solutions. The samples were shaken for 2 h at 298 K, prior to removal, filtration and analysis of Pb(II). After experiments the samples were filtered and the Pb(II), Cd(II) and Zn(II) concentrations in the filtrate were determined. The obtained results were utilized to evaluate the kinetic and adsorption parameters using well known equations.

## 2.3. Apparatus

In the studies the shaker Elpin type 357 (Elpin-Plus, Poland) was used. The samples were weighed using the analytical balance weight XA 60/220/X (Radwag, Poland). The solution pH values were measured by means of a pH-meter CPI-505 (Elmetron, Poland). The contents of Pb(II), Cd(II) and Zn(II) complexes with GLDA were determined using the atomic absorption spectrometry method by means of a spectrometer SpectrAA 240 FS (Varian, Australia). The analysis parameters were as in [19]. The experiments were conducted in the three parallel series. The precision of the parallel measurements was  $\pm 5\%$ SD. The specific surface area, total pore volume, average pore diameter as well as pore size distribution were determined by  $N_2$  adsorption/desorption isotherms at 77.5 K using ASAP 2420 Micromeritics, Norcross, USA. Before each measurement, the sample was degassed at  $105^\circ\text{C}$  for at least 2 h. pH of zero charge (pHpzc) of the samples was determined using pH drift method [20]. The surface structure and morphology of Purolite S 110 were characterized using a scanning electron microscope (Tescan Vega, USA) after gold plating by using a sputter coater (K-550X, Emitech). The FT-IR spectra were obtained by the ATR (Attenuated Total Reflection) method using a spectrometer Cary 630 FTIR (Agilent Technology, USA) in the region of  $400\text{-}4000 \text{ cm}^{-1}$ .

## 2.4. Data evaluation

The rate of Pb(II), Cd(II) and Zn(II) complexes with GLDA is expressed as percentage of the amount of metal ions adsorbed after a certain time related to that required for the state of equilibrium. It can be described as follows:

$$S\% = \frac{(c_0 - c_e)}{c_0} \times 100\% \quad (4)$$

The metal complexes with GLDA at equilibrium,  $q_e$  (mg/g) and at time t,  $q_t$  (mg/g) were obtained according to the following equations:

$$q_e = (c_0 - c_e) \times \frac{V}{m} \quad (5)$$

$$q_t = (c_0 - c_t) \times \frac{V}{m} \quad (6)$$

where:  $c_0$  is the initial concentration of metal complexes with GLDA in the aqueous phase ( $\text{mg/dm}^3$ );  $c_t$  is the concentration of metal complexes with GLDA in the aqueous phase at time t ( $\text{mg/dm}^3$ );  $c_e$  is the concentration of metal complexes in the aqueous phase at equilibrium ( $\text{mg/dm}^3$ ); V is the volume of the solution ( $\text{dm}^3$ ); m is the mass of Purolite S 110 (g).

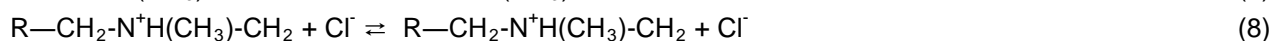
### 3. Results and discussion

In order to effectively remove heavy metals from aqueous solutions by anion exchangers, the formation of stable complexes with these ions should be assumed. For this purpose, various types of aminopolycarboxylic complexing agents as EDTA or DTPA were used. However, EDTA or DTPA were found to be negligibly biodegradable (Table 2). Therefore new biodegradable complexing agents are an important alternative to the poorly biodegradable chelates used so far mainly in such areas as household chemicals, agricultural chemistry and wastewater treatment. The ion exchanger Purolite S 110, similarly to other commercially available ion exchangers of this type, Amberlite IRA 743 or Purolite S-108 possess the N-methyl-D-glucamine functional groups  $-\text{CH}_2-\text{N}(\text{CH}_3)-\text{CH}_2-\text{C}_6\text{H}_8(\text{OH})_5$  which comprises tertiary amine and polyol ends (it consists of five hydroxyl groups) [21]. It exhibit high selectivity to boron in the form of trioxoboric acid [22, 23]. Therefore it should be also characterized for affinity to anionic complexes of Pb(II), Cd(II) and Zn(II) with GLDA.

It was found that the specific surface area ( $S_{\text{BET}}$ ) of Purolite S110 was equal to  $13.34 \text{ m}^2/\text{g}$  and after the sorption process decreased to  $12.89 \text{ m}^2/\text{g}$ . From the SEM analysis (Fig.3) it was shown that Purolite S 110 possesses the spherical beads with the particle size ranging from 0.4 mm to 0.6 mm and showed rough surface with a dense pore structure at higher magnification. The sorption process was confirmed by the ATR-FTIR analysis. The presence of O-H bonds from the N-methyl-D-glucamine group is reflected by the vibration bands at  $3343 \text{ cm}^{-1}$  before and at  $3365 \text{ cm}^{-1}$  after the sorption process. Analogously, the peaks at  $1455 \text{ cm}^{-1}$  and  $1456 \text{ cm}^{-1}$  are ascribed to the C-N stretching vibration of this group. After the sorption process the new band at  $1608 \text{ cm}^{-1}$  appears. It is connected with the presence of the carboxyl groups in the GLDA molecules (Fig.4).

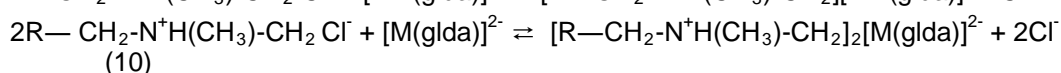
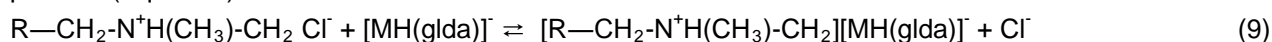
In the preliminary results it was shown that a larger dose of Purolite S 110 can provide more active sites, thus the sorption percentage (S%) was higher until a 0.5 g ion exchanger dose when the sorption efficiency does not increase sufficiently and reaches the value 96 % (data not presented). It can be stated that not all adsorption sites are available for binding or exchanging anionic complexes of metal ions with GLDA because of overlapping, so a portion of the sorption capacity of Purolite S 110 will not be used. In this study, when the dose is more than 0.5 % the theoretical ion exchange capacity it makes the pH solution value higher than 5.5. When the complexing agent GLDA was not present M(II) would start to precipitate e.g. transform into hydroxide of a low solubility.

Besides the physicochemical properties of the used ion exchanger affecting the sorption effectiveness pH is very important. It is well known that pH affects the ion exchanger surface charge and the degree of ionization of the functional groups. Under acidic conditions, Purolite S 110 surface will be covered with  $\text{H}^+$  ions and the M(II) ions in the presence of GLDA can compete for adsorption sites:



where: R- is the resin matrix

Therefore the N-methyl-D-glucamine functional groups should take part in the anion exchange process (Eqs.9-10):



The increase in the complexes removal as the pH increases can be explained on the basis of the increasing competition between different types of complexes for the functional groups (in the case of heavy metal complexes those of higher negative charge are the most preferred by the anion exchanger). Therefore, in the next stages of investigations, the optimal pH value was maintained without any additional adjustment. The obtained solutions of the studied Cd(II), Zn(II) and Pb(II) complexes with GLDA possess the following pH values: 8.74, 9.17 and 9.30, respectively. It should be mentioned that the precipitation of heavy metal ions was not observed.

However, with increasing pH, this competition decreases and the positively charged Pb(II) ions can be adsorbed at the negatively charged sites on the ion exchanger.

The point of zero charge (PZC) describes a condition where the electric charge density on the surface of the test material is equal to zero. PZC is the pH at which the solid material immersed in the electrolyte has a zero electric charge on the surface. When the pH is less than the PZC, the water gives more protons than the hydroxyl groups, and thus the surface of the adsorbent is positively charged and allows to sorb (attract) anions. The situation is reversed when the pH of the solution is higher than the PZC, the surface is negatively charged and the attraction of cations dominates. The pH of the PZC for ion exchanger Purolite S110 determined by the drift method is 7.6. (Fig.5). The obtained results are consistent with the measured value because the pH of the solution at the equilibrium was lower than this one.

Kinetic studies are important for understanding reactions and practical implications to improve many processes. A chemical reaction mechanism consists of a series of elementary processes which explain how the overall reaction proceeds. Important parameters in the chemical reaction kinetics studies include the

chemical reaction rate, thermodynamic effects as well as the effect of various process variables. Kinetic studies are not only important in industry, but they are also used to understand biological processes. They also play a role in the environmental chemistry to understand the fate of impurities in wastewaters as well as their quick removal. In the presented studies the pseudo first order, the pseudo second order and the intraparticle diffusion models were used for determination of the sorption parameters. The pseudo first order equation (PFO) is generally represented as follows [24]:

$$\frac{dq_t}{dt} = k_1(q_{e1} - q_t) \quad (11)$$

where:  $k_1$  is the equilibrium rate constant of the PFO kinetics [1/min].

After integration and applying the conditions,  $q_t=0$  at  $t=0$  and  $q_t=q_t$  at  $t=t$ , Eq.11 becomes:

$$\log(q_{e1} - q_t) = \log q_{e1} - \frac{k_1 t}{2.303} \quad (12)$$

The straight line plots of  $\log(q_{e1}-q_t)$  vs.  $t$  were used for the determination of kinetic parameters for the sorption of Pb(II), Cd(II) and Zn(II) complexes with GLDA.

The pseudo second order kinetic equation (PSO) model was applied for determination of kinetic data. It is expressed as follows [25, 26]:

$$\frac{dq_t}{dt} = k_2(q_{e2} - q_t)^2 \quad (13)$$

where:  $k_2$  is the equilibrium rate constant of the PSO [g/mg min].

The linear form of the above equation:

$$\frac{t}{q_t} = \frac{t}{q_{e2}} + \frac{1}{k_2 q_{e2}^2} \quad (14)$$

The linear plots of  $t/q_t$  vs.  $t$  at different metal ions or complexes concentrations were used to calculate the kinetic parameters.

The intraparticle diffusion model was also used to find the effect of the intraparticle diffusion (IPD) resistance to adsorption [27]:

$$q_t = k_i t^{1/2} + C \quad (15)$$

where:  $k_i$  is the intraparticle diffusion rate constant,  $C$  is the intercept.

Comparison of the sorption of Pb(II), Cd(II) and Zn(II) complexes with GLDA on Purolite S 110 depending on the initial concentration and the phase contact time is shown in Figs.6a-c. They show the effect of the phase contact time on the removal efficiency of M(II) complexes with GLDA on Purolite S 110 using the initial concentration ranging from  $1 \times 10^{-3}$  M to  $7 \times 10^{-3}$  M. In this figure fast initial sorption process during the first 5-10 min can be observed followed by slower uptake. Moreover, the optimal sorption time that shows the maximum sorption efficiency (S%) at 180 min was found to be equal to 97 % (Fig.7).

The kinetic parameters of the sorption process of Pb(II), Cd(II) and Zn(II) complexes with GLDA on Purolite S 110 calculated according to the PFO, PSO and IPD models are summarized in Table 3. The kinetic data are well described by the pseudo second order rate equation with higher determination coefficients suggesting that chemical sorption was the rate-controlling step [28]. The equilibrium adsorption amounts ( $q_{e2}$ ) and the initial adsorption rate constant ( $h$ ) increase following the descending order of Pb(II)>Cd(II)>Zn(II) indicating higher affinity of Purolite S 110 towards Pb(II). It was found that the sorption rate constant ( $k_2$ ) decrease in the increasing of the initial concentration. It is significant that the sorption process is also described by the intraparticle diffusion kinetic model (IPD), however it plays a limiting role.

The experimental adsorption data reported for the adsorption of Pb(II), Cd(II) and Zn(II) complexes with GLDA on Purolite S 110 has been analysed using the two most common adsorption models - the Langmuir and Freundlich adsorption isotherms. The nonlinear Langmuir equation can be expressed as Eq.16 [29]:

$$q_e = \frac{q_0 K_L c_e}{1 + K_L c_e} \quad (16)$$

where  $c_e$  (mg/dm<sup>3</sup>) is the equilibrium concentration of the adsorbate in solution,  $q_e$  (mg/g) is the amount adsorbed per unit mass of adsorbent at equilibrium,  $q_0$  (mg/g) is the Langmuir adsorption constant, representing the maximum adsorption capacity,  $K$  (L/mg) is the Langmuir adsorption constant, which is related to the affinity of binding sites and hence the adsorption bonding energy.

Based on the above mentioned equations the plot of  $c_e/q_e$  vs.  $c_e$  should be a straight line with a slope of  $1/q_0$  and an intercept at  $1/Kq_0$ .

The Freundlich adsorption isotherm can be expressed by Eq.17 [30]:

$$q_e = K_F c_e^{1/n}$$

The Langmuir adsorption constants and their correlation regression coefficients ( $R^2$ ) calculated from the plots of  $c_e/q_e$  vs.  $c_e$  are listed in Table 4. From the obtained data the equilibrium parameter ( $R_L$ ) was also calculated. It indicates favourable adsorption at  $0 < R_L < 1$ , unfavourable adsorption for  $R_L > 1$  and irreversible adsorption for  $R_L = 1$ . As follows from the values of  $R_L$  are between 0 and 1 indicating favourable adsorption [31].

The Freundlich adsorption constants ( $K_F$  and  $n$ ) and their correlation regression coefficients ( $R^2$ ) calculated from the plots of  $\log q_e$  vs.  $\log c_e$  are listed in Table 4.

Solutions of the complexes Cd(II) at the concentrations  $3 \times 10^{-3} \text{ M}$  and  $7 \times 10^{-3} \text{ M}$  showed more than 70% of being adsorbed. For other concentrations efficiency of the sorption process decreases to a value of 20% for the solution of the initial ion concentration  $5 \times 10^{-3} \text{ M}$  and  $10^{-2} \text{ M}$ . The sorption of Zn(II) proceeded with the increasing efficiency (from 40% to 98.66%) for the solutions with the initial concentration  $3\text{-}7 \times 10^{-3} \text{ M}$ .

The presence of accompanying ions in the solution such as  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  causes approx. 50% decrease in the sorption efficiency. Sorption of Pb(II), Cd(II), and Zn(II) complexes with GLDA on Purolite S110 was studied for ion solution having a concentration of  $1 \times 10^{-3} \text{ M}$  by adding a  $200 \text{ mg/dm}^3$  or  $500 \text{ mg/dm}^3$  of the above mentioned ions ( $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$ ). The results are summarized in Fig.8a-c. It was found that Pb(II) complexes with GLDA the highest affinity for the resin Purolite S110. The maximum sorption values obtained as a function of the initial concentration of the heavy metal solution is shown in Fig.9.

#### 4. Conclusions

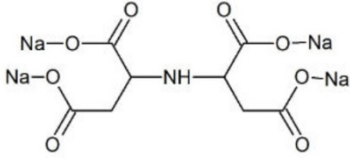
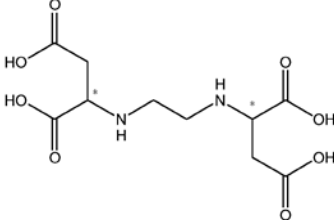
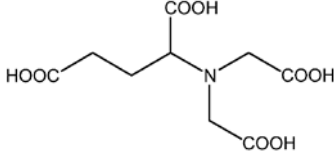
The removal of complexes of  $[\text{M}(\text{glda})]^{2-}$  and  $[\text{M}(\text{glda})]^-$  types from aqueous solutions was investigated using a Purolite S 110. Based on the studies carried out by the static method, the determined sorption efficiency of the tested resin with respect to the complexes of Zn(II), Pb(II) and Cd(II) with GLDA depends on the contact time and the concentration of the working solution and accompanying  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  ions. Average sorption efficiency (S%) is similar and as follows: 64 % for Zn(II), 62 % for Cd(II) and 97 % for Pb(II) complexes with GLDA. In the range of the initial concentration of Pb(II) complexes solution from  $1 \times 10^{-3} \text{ M}$  to  $7 \times 10^{-3} \text{ M}$  these values are not less than 70% and for the concentration of the range from  $1.5 \times 10^{-2}$  to  $2 \times 10^{-2}$  sorption percent decreases rapidly to 3-5%. The kinetic data are well described by the pseudo second order rate equation with higher determination coefficients suggesting that chemical sorption was the rate-controlling step. It has been shown that the ion exchanger Purolite S110 has the high capacity towards the complexes of Pb(II) with GLDA. As an ion exchanger selective for boron it can also find the application in the removal of heavy metal ions in the presence of a biodegradable complexing agent, which is GLDA from different types of water and wastewater. Moreover, from the economical point of view of the purification process of waters containing heavy metal ions, the main advantage is low price of the complexing agent Disolvine GL-38 (38% solution) as well as the possibility of reuse of Purolite S 110. These two aspects cause that the total cost of the purification process is not very high.

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**Table 1.** The names, structures and stability constants (log K) of the complexes of M(II):L=1:1 type for IDS, EDDS and GLDA.

Name	Structure	Stability constant complexes
<p>IDS sodium salt of N- (1,2-dicarboxyethyl)-D,L-aspartic acid</p>		<p>Ba(II) 2.1 Ca(II) 5.2 Cd(II) 8.4 Co(II) 10.5 Cu(II) 13.1 Mg(II) 6.1 Ni(II) 12.1 Pb(II) 11.0 Zn(II) 10.8</p>
<p>EDDS sodium salt of ethylenediamine-N,N'-disuccinic acid</p>		<p>Ba(II) 3.0 Ca(II) 4.6 Cd(II) 16.4 Co(II) 13.6 Cu(II) 18.4 Mg(II) 6.0 Ni(II) 16.7 Pb(II) 12.7 Zn(II) 13.4</p>
<p>GLDA sodium salt of N,N'-bis(carboxymethyl) glutamic acid</p>		<p>Ba(II) 3.5 Ca(II) 5.2 Cd(II) 9.1 Co(II) 10.0 Cu(II) 13.1 Mg(II) 6.1 Ni(II) 10.9 Pb(II) 10.5 Zn(II) 10.0</p>



**Table 2.** Similarities and differences in the physicochemical properties between the GLDA and EDTA.

Properties	GLDA	EDTA
Complexes type	stable complexes of the M(II)-L =1:1 type	
pH	11.0 – 12.0 (1% aq. solution)	8.0 (in 0.5 M aq. solution)
State of matter	liquid	solid
Smell	similar to ammonia	flavorless
Solubility in water at 293 K	miscible in all proportions	100 g/dm <sup>3</sup>
Solubility in 25% NaOH	good	10x słabiej niż GLDA
Origin	natural	synthetic
Boiling point, K	378 – 383	n.a
Crystallization temperature, K	< 285	n.a.
Temperature stability, K	< 573	
Molecular formula	C <sub>9</sub> H <sub>9</sub> NO <sub>8</sub> Na <sub>4</sub>	C <sub>10</sub> H <sub>16</sub> N <sub>2</sub> O <sub>8</sub>
Molar mass, g/mol	351.1	292.24
Density, kg/m <sup>3</sup>	1150-1380	860
Viscosity, mPa·s	41	n.a
Biodegradability	yes	no

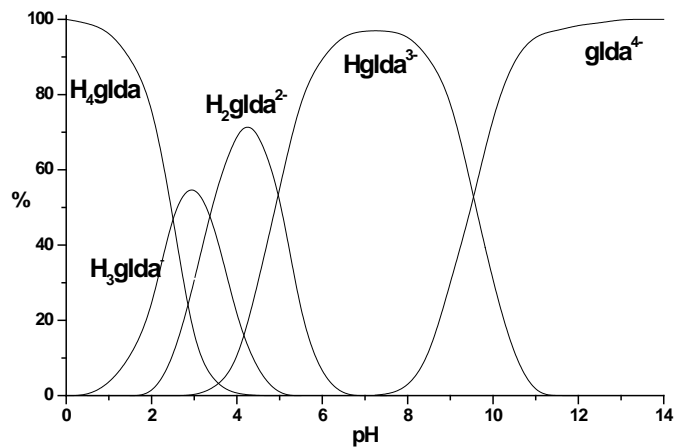
n.a - not available

**Table 3.** The kinetic parameters of the Pb(II), Cd(II) and Zn(II) complexes with GLDA on Purolite S 110.

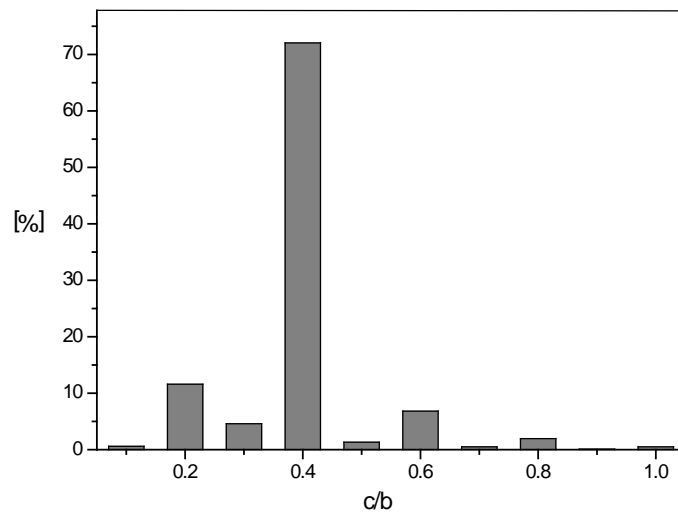
Parameters	$1 \times 10^{-3}$ M	$3 \times 10^{-3}$ M	$5 \times 10^{-3}$ M	$7 \times 10^{-3}$ M
<b>PFO Pb(II)-GLDA=1:1</b>				
$q_{e1}$ , mg/g	1.02	1.31	2.33	2.38
$k_1$ , 1/min	0.103	0.075	0.050	0.035
$R^2$	0.9607	0.6266	0.8444	0.7892
<b>PSO Pb(II)-GLDA=1:1</b>				
$q_{e2}$ , mg/g	17.36	68.94	89.94	117.19
$k_2$ , g/mg min	0.377	0.371	0.363	0.351
$h$ , mg/g min	1.636	1.756	1.892	1.935
$R^2$	1.0000	0.9857	0.9999	0.9956
<b>IPD Pb(II)-GLDA=1:1</b>				
$k_i$ mg/g min	0.136	0.125	0.127	0.169
$R^2$	0.7711	0.7869	0.7562	0.7681
<b>PFO Cd(II)-GLDA=1:1</b>				
$q_{e1}$ , mg/g	3.72	4.30	5.37	6.02
$k_1$ , 1/min	0.051	0.046	0.029	0.010
$R^2$	0.8481	0.6226	0.9724	0.9296
<b>PSO Cd(II)-GLDA=1:1</b>				
$q_{e2}$ , mg/g	13.79	19.45	44.64	70.24
$k_2$ , g/mg min	0.678	0.502	0.444	0.368
$h$ , mg/g min	2.387	2.456	2.650	2.768
$R^2$	0.9182	1.0000	0.9999	1.0000
<b>IPD Pb(II)-GLDA=1:1</b>				
$k_i$ , mg/g min	0.9346	0.7869	0.7228	0.9545
$R^2$	0.8544	0.8125	0.9868	0.7073
<b>PFO Zn(II)-GLDA=1:1</b>				
$q_{e1}$ , mg/g	3.72	3.92	1.36	1.19
$k_1$ , 1/min	0.029	0.021	0.019	0.004
$R^2$	0.8499	0.9871	0.7683	0.8888
<b>PSO Zn(II)-GLDA=1:1</b>				
$q_{e2}$ , mg/g	6.21	26.81	67.56	86.95
$k_2$ , g/mg min	0.059	0.008	0.243	1.323
$h$ , mg/g min	2.266	2.838	3.379	5.379
$R^2$	0.9963	0.9944	1.0000	1.0000
<b>IPD Zn(II)-GLDA=1:1</b>				
$k_i$ , mg/g min	0.9032	0.9619	0.5358	0.6403
$R^2$	0.6740	0.7001	0.8919	0.6102

**Table 4.** The adsorption parameters of the Pb(II), Cd(II) and Zn(II) complexes with GLDA on Purolite S 110.

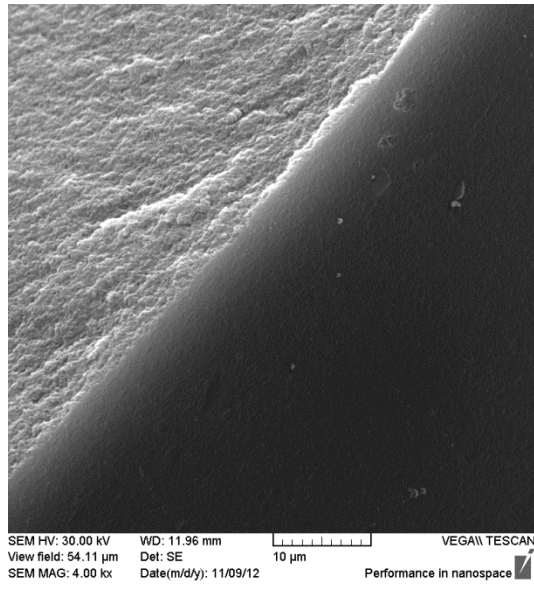
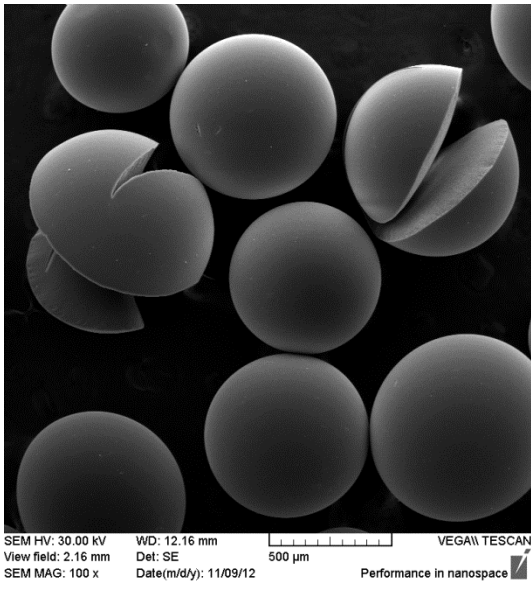
Parameter	Pb(II)-GLDA=1:1	Cd(II)-GLDA=1:1	Zn(II)-GLDA=1:1
<b>Langmuir parameters</b>			
$q_0$	72.45	68.98	56.23
$K_L$	0.043	0.027	0.033
$R_L$	0.56	0.89	0.23
$R^2$	0.9999	0.9893	0.9959
<b>Freundlich parameters</b>			
$K_F$	1.456	2.568	0.998
$n$	1.75	2.85	1.85
$R^2$	0.9156	0.8827	0.8562



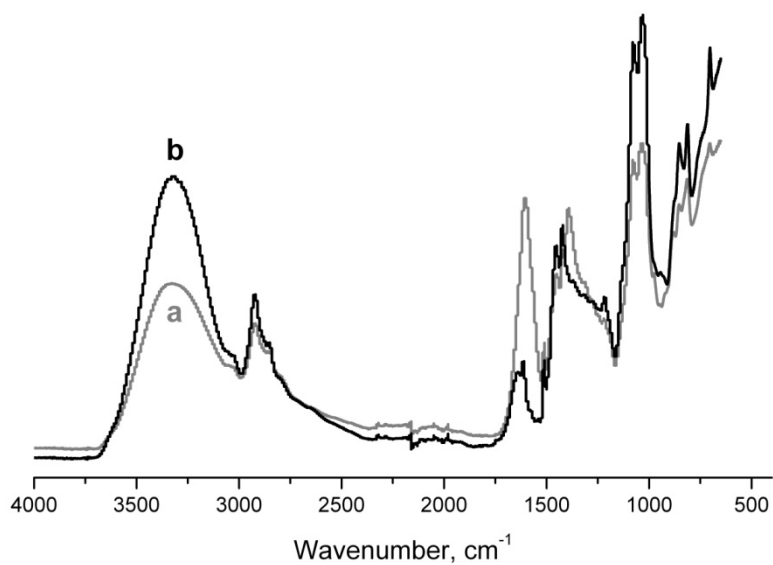
**Fig.1.** The percentage of individual forms of GLDA depending on the pH values [10].



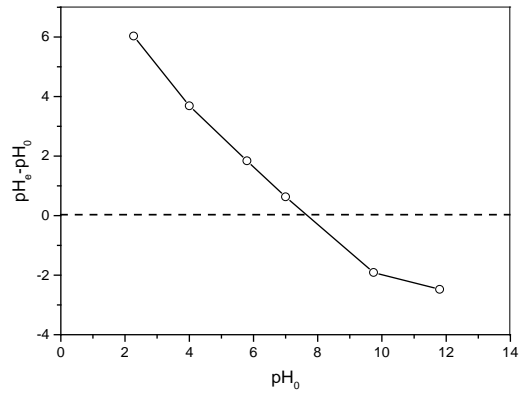
**Fig.2.** Bead size distribution of Purolite S 110 according to the Zingg classification.



**Fig.3.** SEM images of Purolite S 110.

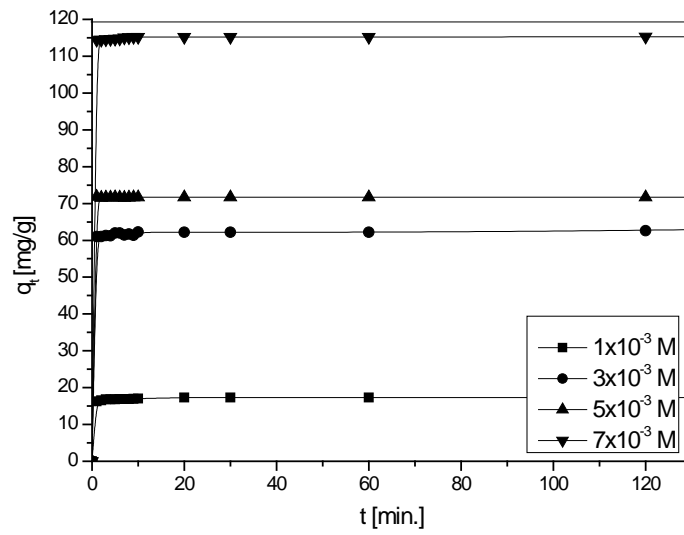


**Fig.4.** The ATR-FT-IR spectra of Purolite S110 a) before and b) after the sorption of Pb(II).



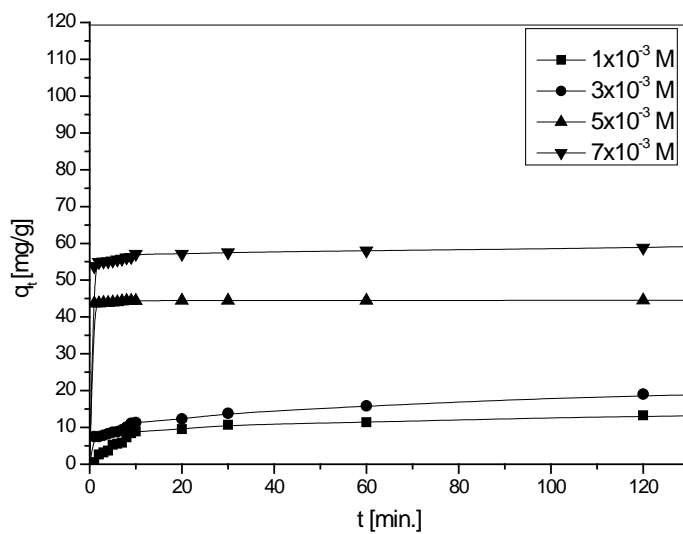
**Fig.5.** Point of zero charge of Purolite S110.

a)

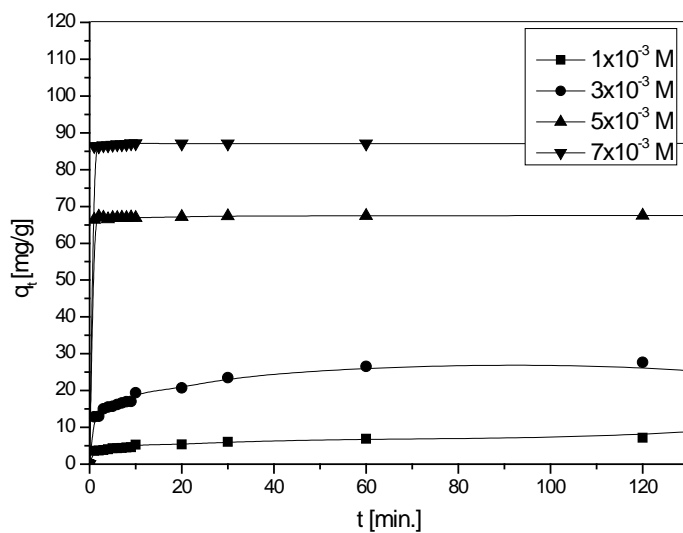




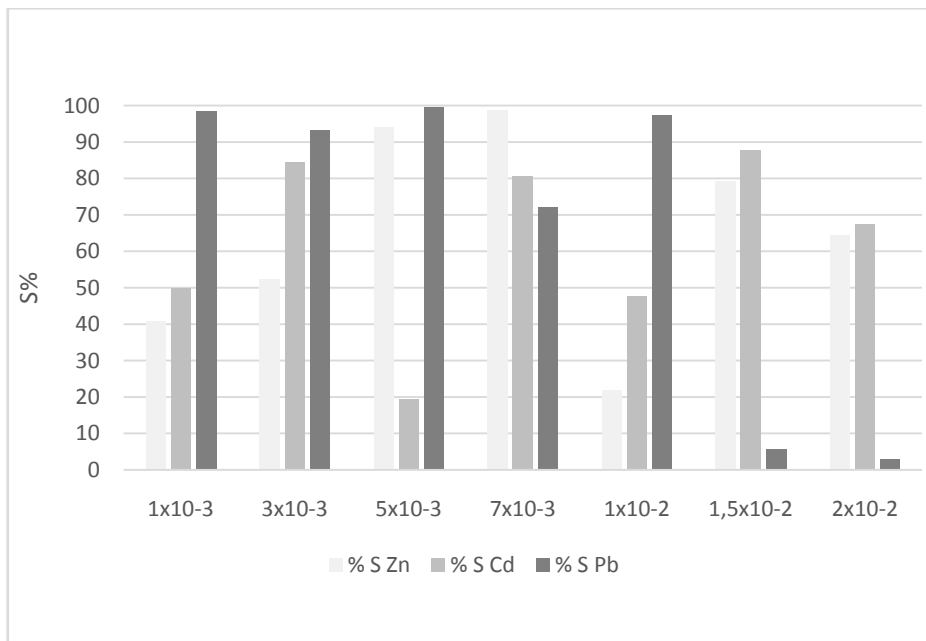
b)



c)

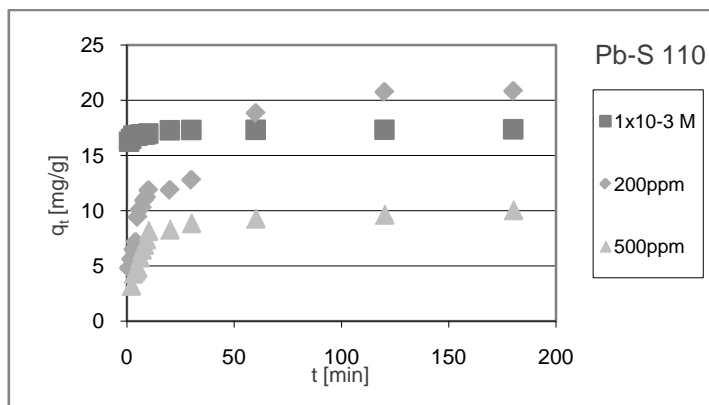


**ys.6a-c.** Comparison of the sorption capacities ( $q_t$ ) of Pb(II), Cd(II) and Zn(II) complexes with GLDA on Purolite S 110 depending on the phase contact time and the initial concentration.

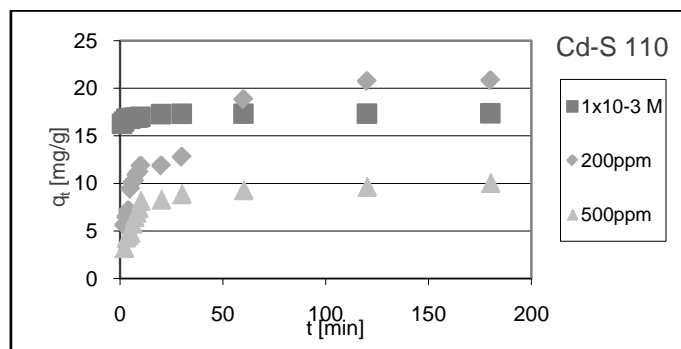


**Rys.7.** Comparison of the sorption percentage (S%) of Pb(II), Cd(II) and Zn(II) complexes with GLDA on Purolite S 110 depending on the initial concentration.

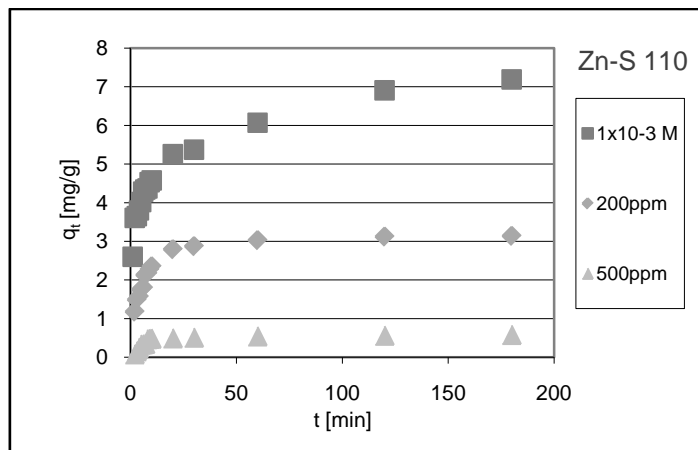
a)



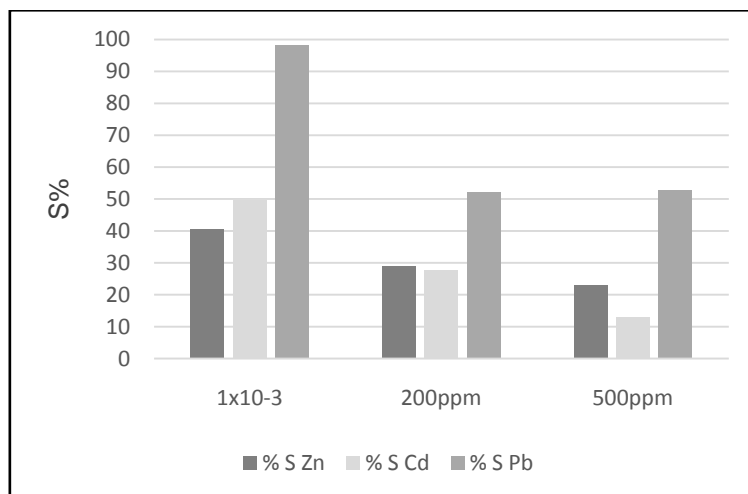
b)



c)



**Rys.8a-c.** Comparison of the sorption capacities of Pb(II), Cd(II) and Zn(II) complexes with GLDA on PuroLite S 110 depending on the presence of accompanying ions  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$  and the phase contact time.



**Rys.9.** Comparison of the sorption percentage (S%) of Pb(II), Cd(II) and Zn(II) complexes with GLDA on Purolite S 110 depending on the presence of accompanying ions  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ .