Chemical Engineering Journal 159 (2010) 27–36

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Diphonix Resin® in sorption of heavy metal ions in the presence of the biodegradable complexing agents of a new generation

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ARTICLE INFO

Article history:
Received 21 September 2009
Received in revised form 26 January 2010
Accepted 6 February 2010

Keywords:
GLDA
EDDS
Heavy metal ions
Diphonix Resin®

ABSTRACT

This paper presents the equilibrium and kinetic studies of Cu(II), Zn(II), Co(II), Pb(II) and Cd(II) complexes with Dissolvine GL-38 (GLDA) and Enviomet™ C140 (EDDS) from aqueous solution by the chelating ion exchanger Diphonix Resin®. The selected complexing agents Dissolvine GL-38–tetrasodium salt of N,N-bis(carboxylmethyl)-L-glutamic acid and Enviomet™ C140–trisodium salt of ethylenediaminedisuccinic acid belong to the group of a new generation of complexons which easily undergo biodegradation but their complexes are not biodegradable. The effect of pH, phase contact time and concentration has been studied using the batch technique at room temperature. After achieving the best conditions for complexes sorption, isotherms were obtained and fitted to the Langmuir, Freundlich, Temkin and Dubinin–Radushkevich (D–R) models. The kinetic data were fitted using the pseudo-first-order, pseudo-second-order and intraparticle diffusion models. The respective characteristic rate constants were presented. The results showed that the sorption processes of Cu(II), Zn(II), Co(II), Pb(II) and Cd(II) complexes with Dissolvine GL-38 and Enviomet™ C140 on Diphonix Resin® followed well the pseudo-second-order kinetics.

1. Introduction

Ion exchange has been identified as one of the most promising technologies widely applied for heavy metal ions removal. Among advantages of this method the simplicity of equipment, operation and regeneration should be listed. For these reasons and the fact that a large number of new ion exchange resins, e.g. cationic, anionic and chelating resins are produced, the ion exchange chromatography is commonly applied for sorption, separation, recovery and concentration of heavy metal ions.

In general, sorption selectivity of a resin can be affected by both sorbate–sorbent and sorbate–solvent interactions. It has been well recognized that resin matrix and functional groups can strongly affect ion exchange capacity and selectivity. Therefore in the presented paper the chelating ion exchanger Diphonix Resin® containing diphosphonic, sulphonic and carboxylic acid groups bonded to the polymer matrix was used for the sorption of Cu(II), Zn(II), Co(II), Pb(II) complexes with Dissolvine GL-38 (GLDA) and Cu(II), Zn(II), Cd(II), Pb(II) complexes with Enviomet™ C140 (EDDS) [1]. The presence of the sulphonic functional groups determines better hydrophilic properties of Diphonix Resin® compared to the traditional monofunctional ion exchangers.

Diphonix Resin® exhibits high affinity and fast ion exchange kinetics of actinide ions on both +4 and +6 oxidation states (Th(IV), U(VI), Pu(VI)) even from the solutions of very low pH. It was found that for Am K_d is as high as 10^8 from 0.1 M HCl and 10^6 to 10^7 for Pu(IV), Th(IV) and U(VI) in acid up to 1 M HCl. High capacity of the chelating ion exchanger Diphonix Resin® for actinide ions results from large stability of their complexes [2–8].

Owing to its very good separation capability, Diphonix Resin® was also applied for separation and determination of lanthanides and rare elements from their mixtures in various types of wastewaters, soils and biological samples. Of particular importance is its application for separation of the above-mentioned elements from wastewaters originating from nuclear industry, particularly of isotope ^{99}Tc [9].

In the paper by Phillips et al. it was demonstrated that Diphonix Resin® can be successfully used for removal of uranium from the solutions of pH > 5 including high concentration of NO_3^- ions as it is less sensitive to interference by such ions as carbonates, nitrates(V), sulphates(VI), Fe(III), Ca(II) and Na(I) [10].

Smolik et al. [11] investigated separation of zirconium(IV) from hafnium(IV) sulphuric acid solutions on Diphonix Resin®. It was found that the best medium for separation of hafnium(IV) and zirconium(IV) is 0.5 M sulphuric acid. A decrease in temperature lowers the degree of metals separation, while lower flow rates through the column increases zirconium(IV) from hafnium(IV) separation.

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doi:10.1016/j.cej.2010.02.017

Nomenclature

EDDS	Enviomet^{TM} C140
GLDA	Dissolvine GL-38
IDS	iminodisuccinic acid
b_T	the Temkin constant related to the heat of sorption [J/mol]
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_0	the initial concentration of M(II) solution [mg/L]
C	the constant related to the thickness of the boundary layer [mg/g]
k_i	the intraparticle diffusion rate constant [mg/g min$^{1/2}$]
k_1, k_2	the equilibrium rate constant [1/min] and [g/mg min], respectively
K_d	the distribution coefficient [L/g]
K_F	the Freundlich adsorption capacity [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]
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	Hall parameter
S (%)	the sorption percent [%]
T	the temperature [K]
V	the volume of the solution [L]
X_m	the D–R sorption capacity [mg/g]
β	the constant related to the sorption energy [mol^2/kJ^2]
ε	the Polanyi potential

Recent studies have shown that Diphonix Resin® can also be used for removal of Cd(II) and Cr(III) from phosphoric acid solutions through column tests. Kabay et al. [12] found that the acid concentration strongly determines the resin behaviour with respect to the sorption/elution of Cd(II) and Cr(III). In the paper by Cavaco et al. it was pointed that Diphonix Resin® has strong affinity for Cr(III) ions and high selectivity towards Fe(III) and Ni(II) [13]. However, according to literature, Diphonix Resin® has the best selectivity for transition metals such as Fe(III), Cu(II) and Ni(II) over Cr(III) [14,15].

Table 1
Comparison of the relative selectivities of Diphonix Resin® for calcium(II).

Metal ion	Selectivity
Ca(II)	1.0
Cd(II)	1.2×10^3
Co(II)	4.5×10^3
Cu(II)	$>10^3$
Hg(II)	3.5×10^3
Mn(II)	4.1×10^3
Ni(II)	2.7×10^2
Pb(II)	9.9×10^3
Zn(II)	1.4×10^4
U(VI)	1.3×10^4

High affinity of Diphonix Resin® for Fe(III) compared to the mono- and divalent ions, e.g. Ca(II) was reported in several papers [16–21]. Comparing the selectivity relative to Ca(II), it is evident that for Mn(II), Co(II), Ni(II), Zn(II), Cd(II) and U(VI) it is significantly higher (Table 1). The obvious disadvantage of this ion exchanger is the fact that it is difficult to remove iron(III) ions. To this aim 1-hydroxyethane-1,1-diphosphonic acid (HEDP) is used. In the case of Cr(III), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II), Sn(II) and Pb(II) ions 2 M H_2SO_4 can also be applied.

Diphonix Resin® has never been tested previously for sorption of Cu(II), Zn(II), Co(II), Pb(II) and Cd(II) complexes with the biodegradable complexing agents of new generation that is Dissolvine GL-38 (GLDA) and Enviomet^{TM} C140 (EDDS) from aqueous solution. Therefore, the aim of this work is to determine their influence on the sorption of heavy metal ions under such conditions as pH, phase contact time and concentration. The experimental data were correlated to the Langmuir, Freundlich, Temkin and Dubinin–Radushkevich (D–R) models and the kinetic pseudo-first-order and pseudo-second-order models as well as the intraparticle diffusion model.

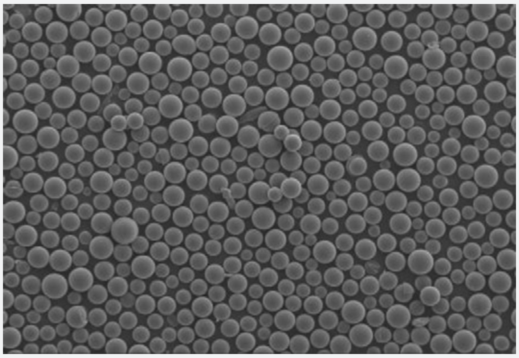
2. Materials and methods

2.1. Chemicals and instruments

Diphonix Resin® is a commercially available chelating ion exchanger manufactured by EiChrom Industries (France). Its short characteristic is presented in Table 2. Before the experiments, the resin was washed with hydrochloric acid (0.1 M) and sodium hydroxide (0.1 M) to remove impurities from its synthesis. After pre-treatment it was washed with deionised water.

The solutions of Cu(II), Zn(II), Co(II), Pb(II) and Cd(II) complexes with Dissolvine GL-38 and Enviomet^{TM} C140 with the desirable concentrations were prepared by mixing of appropriate metal

Table 2
Physicochemical properties of Diphonix Resin®.

Diphonix Resin®		
Matrix	PS-DVB	
Structure	Gel	
Functional groups	Diphosphonic, sulphonic, carboxylic	
Commercial form	H$^+$	
Appearance	Beige, opaque	
Total capacity	5.6 [mmol/g]	
Moisture content	58.3%	
Bead size	0.074–0.150 [mm]	
Density	1.05–1.11 [g/mL]	
Wet particle porosity	0.7	
Max temp.	313 K	
Operating pH range	0–12	
Total costs	3000 \$/ft^3	

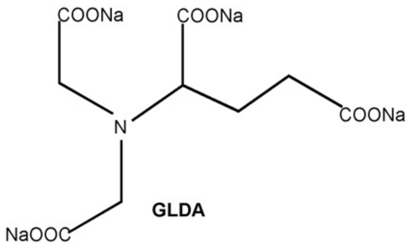


Fig. 1. Chemical structure of GLDA.

chlorides or nitrates with Dissolvine GL-38 and Enviomet^{TM} C140 solutions, respectively. For studies the obtained solutions were used without pH adjustment. The pHs of the solutions of Cu(II), Zn(II), Co(II) and Pb(II) complexes with GLDA were as follows: 7.6, 7.5, 7.7 and 9.3, respectively. For Cu(II), Zn(II), Cd(II) and Pb(II) complexes with EDDS these values were equal to 4.2, 4.5, 5.1 and 4.7. The other chemicals used were of analytical grade.

Dissolvine GL-38–tetrasodium salt of N,N-bis(carboxylmethyl)-L-glutamic acid is produced by the firm Akzo-Nobel (CAS No. 51981-21-6). It is readily biodegradable (>60% degrades within 28 days), possessing good solubility at both low and high pH. Dissolvine GL-38 consists only of the L form of GLDA. According to the Swedish Society for Nature Conservation GLDA is 86% based on natural, raw materials. Fig. 1 shows its chemical structure [22].

Enviomet^{TM} C140–trisodium salt of ethylenediaminedisuccinic acid on a commercial scale is produced by the firm Innospec Inc. (formerly Octel) (CAS No. 144538-83-0). S,S-EDDS is a biodegradable complexing agent that is a structural isomer of EDTA (ethylenediaminetetraaceitic acid). Its chemical structure is presented in Fig. 2 [23].

The pH values were measured with a PHM 84 pH meter (Radiometer, Copenhagen) with the glass REF 451 and calomel pHG 201-8 electrodes.

The concentrations of heavy metals were measured with the AAS spectrometer ContrAA (Analytic Jena, Germany).

Surface morphology of ion exchanger was studied by scanning electron microscope LEO1430VP (Carl Zeiss, Germany) with the EDX detector (Röntec, GmbH).

2.2. Batch experiments

In batch experiments, 50 mL of sample solution and ion exchanger (0.5 g) were put into a conical flask and shaken at different time intervals using the laboratory shaker Elpin type 357 (Elpin-Plus, Poland). After the pH of solutions was stabilized and equilibrated, the ion exchanger was filtered. The experiments were conducted in the two parallel series. The reproducibility of the measurements was within 5%. The sorption percent S (%), the metal complexes concentration at time t (q_t, mg/g) and the distribution coefficient (K_d, L/g) were calculated using the relationships:

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

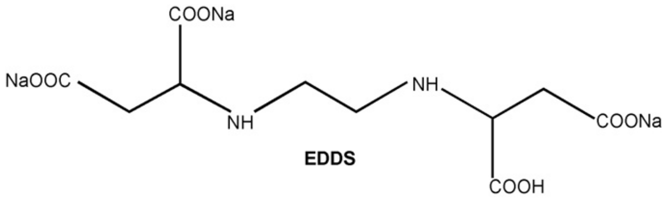


Fig. 2. Chemical structure of EDDS.

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

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

In order to investigate the effect of pH on the sorption of Cu(II), Zn(II), Co(II), Pb(II) and Cd(II) complexes GLDA and EDDS on Diphonix Resin® 50 mL of 1.0×10^{-3} M metal solutions and the constant resin amount (0.5 g) were used. Experiments were performed in the pH range 2–12. The solutions were shaken for 3 h at 180 rpm.

2.2.1. Adsorption studies

Adsorption isotherm studies were carried out using the batch equilibrium technique. The initial concentrations of the studied solutions were prepared in the range 1.0×10^{-3} to 2.5×10^{-2} M. The contents of 0.5 g ion exchanger sample and 50 mL solution of Cu(II), Zn(II), Co(II), Pb(II) and Cd(II) complexes with GLDA and EDDS were mixed in 100 mL flasks for 3 h until equilibrium was reached.

The equilibrium between the solid and liquid phases was modelled by the Langmuir, Freundlich, Temkin and Dubinin–Radushkevich (D–R) equations. The Langmuir equation may be written as [24]:

$$q_e = \frac{q_0 K_L c_e}{1 + K_L c_e} \qquad (4)$$

The Freundlich model can be as follows [25]:

$$q_e = K_F c_e^{1/n} \qquad (5)$$

The Temkin adsorption isotherm is expressed as [26]:

$$q_e = \left(\frac{RT}{b_T}\right) \ln(K_T c_e) \qquad (6)$$

The D–R isotherm model is based on the Polanyi theory. It relates the fractional coverage to the Polanyi potential as given below [27]:

$$\frac{q_e}{X_m} = e^{-\beta\varepsilon^2} \qquad (7)$$

2.2.2. Kinetic studies

The kinetic studies were conducted using Diphonix Resin® by shaking 0.5 g of resin with 50 mL of sample (initial concentration of M(II) 1×10^{-3} M) in a conical flask (100 mL capacity). In this experiment, the removal rate of heavy metal complexes with biodegradable complexing agents was investigated by extracting and analyzing heavy metal concentration by the AAS method after 1, 3, 5, 10, 20, 30 min, 1, 2 and 3 h. The amount of heavy metal complexes sorbed onto the resin was calculated by the difference between the amounts added and/or already present in the solution and that left in solution after equilibrium. The pseudo-first-order and pseudo-second-order linear equations can be as follows [28,29]:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1 t}{2.303} \qquad (8)$$

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2} \qquad (9)$$

Additionally, the intraparticle diffusion model, which refers to, the theory proposed by Weber and Morris was also tested.

2.3. Regeneration

Regeneration tests of Diphonix Resin® were conducted with different regeneration agents. Several acid solutions (HCl, HNO_3, H_2SO_4) and NaCl were tested at the three concentration levels 0.5, 1 and 2 M. The saturated Diphonix resin with Cu(II) complexes with GLDA or EDDS (0.5 g) was put in flasks in contact with 50 mL of

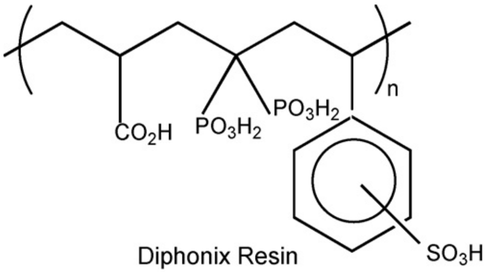


Fig. 3. Chemical structure of Diphonix Resin®.

different regeneration agents. The flasks were shaken at constant temperature (295 K). The resin was separated and the liquid was analysed in order to determine the concentration of metal ion and pH of the solution.

3. Results and discussion

3.1. Complexing agents and ion exchanger characterization

The complexing agents Dissolvine GL-38 (tetrasodium salt of N,N-bis(carboxylmethyl)-L-glutamic acid–GLDA) and Enviomet^{TM} C140 (trisodium salt of ethylenediaminedisuccinic acid–EDDS) selected in this paper are not toxic, biologically neutral, with good solubility compounds. They are characterized by excellent biodegradability. These properties promote their common use as components of detergents including those used in dishwashers, where their concentrations is relatively high. In lower concentrations these compounds are found in many cosmetics and household chemical products. They are also used in the process of heavy metal ions removal by phytoextraction and as effective agents stabilizing hydrogen peroxide in paper industry [30–32]. It should be stressed that despite being safe for the natural environment the above-mentioned agents, reacting with heavy metal ions form non-biodegradable complexes. The stability constants ($\log K$) for the studied Cu(II), Zn(II), Co(II) and Pb(II) complexes with GLDA are as follows: 13.1, 10.0, 10.0, 10.5, respectively, while for the Cu(II), Zn(II), Cd(II) and Pb(II) complexes with EDDS they are equal to: 18.4, 13.4, 16.4, 12.7 [33]. Thus these factors affect heavy metal ions toxicity and solubility. Conventional methods of heavy metal ions removal, e.g. precipitation are of small effectiveness in the case of wastewater originating from paper, galvanic, textile or cosmetic industries containing besides heavy metal ions various types of complexing agents. However, adsorption methods based on novelty sorption materials create many new possibilities.

According to the data presented in Table 2, Diphonix Resin® possesses diphosphonic, sulphonic and carboxylic acid groups bonded to the polymer matrix that was developed by Argonne National Laboratory and the University of Tennessee [11,12]. Its structure is presented in Fig. 3. Diphonix Resin® is synthesized by a patented process involving copolymerization of tetraalkylvinylidene diphosphonate with styrene, divinylbenzene, and acrylonitrile followed by sulphonation with concentrated sulphuric acid. Determining a method for effective copolymerization vinylidene-1,1-diphosphonate (VDPA) ester was a major achievement because of the steric hindrance imposed on the vinylidene group by the diphosphonate group. This difficulty was overcome by using another relatively small monomer, acrylonitrile, as a carrier to induce polymerization of vinylidene-1,1-diphosphonate [1,2]. The protonation constants of Diphonix Resin® which are pK_1 and $pK_2 < 2.5$, $pK_3 = 7.24$ and $pK_4 = 10.46$ appear almost equal to the protonation constants of the starting material VDPA which are $pK_1 = 1.27$, $pK_2 = 2.41$, $pK_3 = 6.67$ and $pK_4 = 10.04$ [34].

3.2. Kinetic studies

In the case of chelating ion exchanger, where the formation of coordination bonds is the basis of the sorption process, besides the parameters related to physicochemical properties of the resin, additionally in the presented paper the effect of the presence of complexing agents is taken into account. The sorption effectiveness will be dependent on the decomposition of neutral or anionic species of $[MH_2L]$, $[MHL]^-$ and $[ML]^{2-}$ type, where $L = \text{gdla}^{4-}$, edds^{4-} as well as the sieve effect (large species will be excluded from the resin phase). The effect of the complexing ligands on the uptake of metal cations should be predicted based on the values of the complex formation constants.

The sorption of Cu(II), Zn(II), Co(II) and Pb(II) complexes with GLDA from their single solutions in the system M(II)–GLDA = 1:1, the pseudo-first-order as well as the pseudo-second-order kinetic plots are presented in Fig. 4a–c. The analogous data for Cu(II), Zn(II), Cd(II) and Pb(II) complexes with EDDS in the M(II)–EDDS = 1:1 system are presented in Fig. 4d–f. The straight lines of t/q_t vs. t suggest the applicability of the pseudo-second kinetic model to determine the q_e, k_2 and h parameters (from intercept and slope of the plots). These kinetic parameters are presented in Table 3. The pseudo-first-order parameters were not shown because the coefficients of determination for this model are low (0.672–0.731 for GLDA complexes and 0.636–0.693 for EDDS complexes).

For both systems very rapid initial sorption was observed during the first few minutes. Thereafter negligible amount of metal complexes is sorbed on Diphonix Resin® and the time required for obtaining the plateau for the metal complexes ranges from 10 to 20 min. For the M(II)–L = 1:1 system and the initial concentration 1×10^{-3} M, about 77, 100, 89 and 97.5% of Cu(II), Zn(II), Co(II) and Pb(II) complexes with GLDA are sorbed at this time, respectively. However, with increasing the phase contact time, the K_d values were changed in the range for the complexes: Cu(II) 0.15–0.35 L/g, Zn(II) 5.37–6.55 L/g, Co(II) 0.14–0.79 L/g and Pb(II) 0.13–3.88 L/g. For Cu(II), Zn(II), Cd(II) and Pb(II) complexes with EDDS the adequate values are as follows: 96, 81, 100 and 98% as well as 0.59–2.52 L/g, 0.38–0.46 L/g, 0.13–1.55 L/g and 1.13–4.4 L/g. The correlation coefficients (R^2) obtained for the pseudo-second-order kinetic model are greater than 0.999 for all metal complexes. The theoretical $q_{e,cal}$ values of the pseudo-second-order kinetic model for Diphonix Resin® are also close to the experimental values $q_{e,exp}$.

Table 3
The pseudo-second-order kinetic parameters for the sorption of Cu(II), Zn(II), Co(II), Cd(II) and Pb(II) complexes with GLDA and EDDS on Diphonix Resin®.

System	$q_{e,exp}$ [mg/g]	$q_{e,cal}$ [mg/g]	k_2	h	R^2
Cu(II)–GLDA = 1:1	4.96	4.95	0.41	10.05	1.000
Zn(II)–GLDA = 1:1	6.55	6.55	2.16	92.59	1.000
Co(II)–GLDA = 1:1	5.22	5.25	0.15	4.07	0.999
Pb(II)–GLDA = 1:1	20.21	20.34	0.04	17.06	0.999
Cu(II)–EDDS = 1:1	6.11	6.12	0.50	18.73	1.000
Zn(II)–EDDS = 1:1	5.37	5.38	1.60	46.51	1.000
Cd(II)–EDDS = 1:1	12.25	12.25	4.16	625.00	1.000
Pb(II)–EDDS = 1:1	20.28	20.28	0.97	400.01	1.000

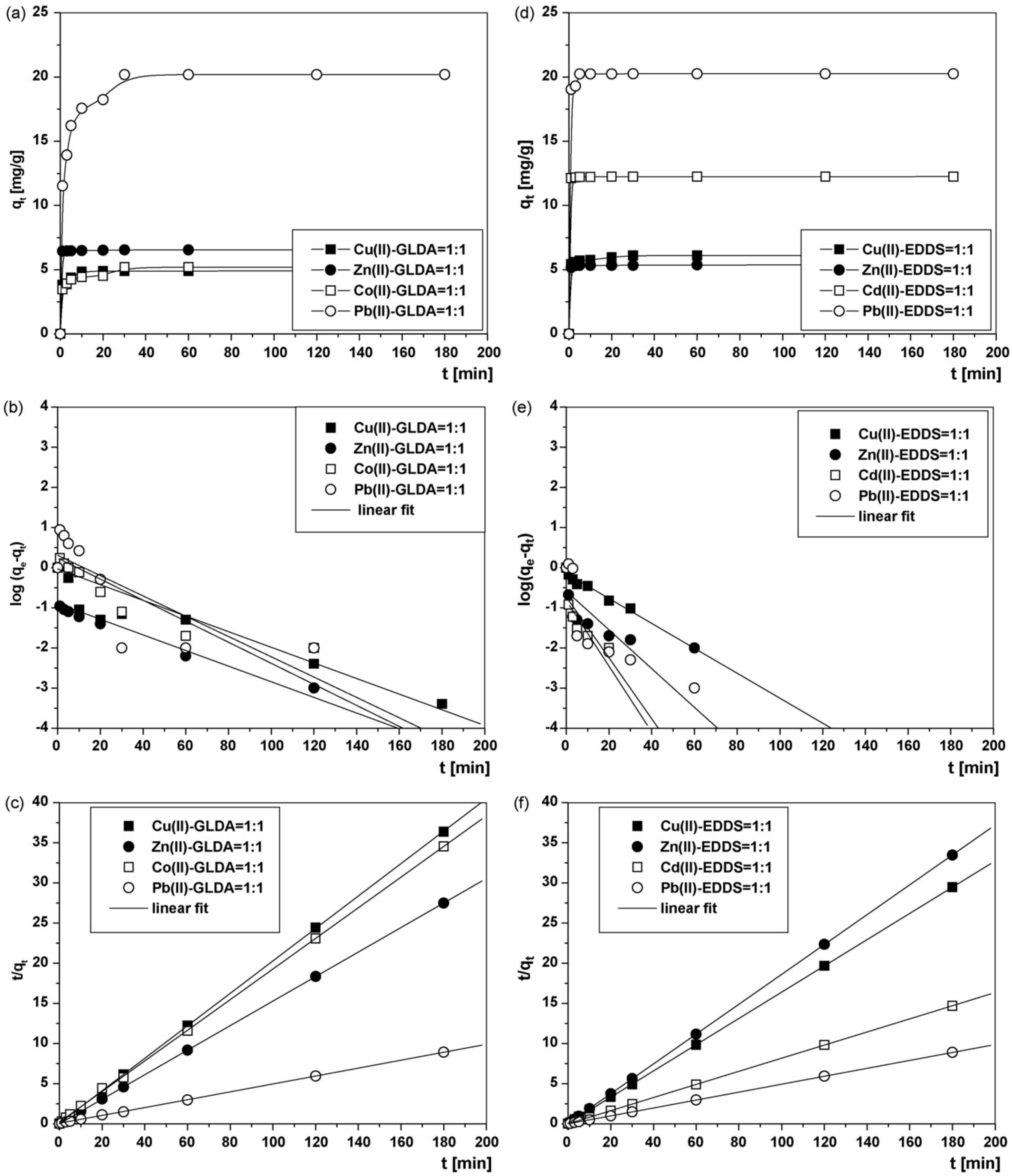


Fig. 4. (a–f) The effect of the phase contact time, the pseudo-first-order and pseudo-second-order kinetic plots for the sorption of Cu(II), Zn(II), Co(II), Cd(II) and Pb(II) complexes with GLDA (a–c) and EDDS (d–f) on Diphonix Resin® (c_0 1×10^{-3} mol/L, ion exchanger dose 10 g/L, shaking speed 180 rpm and temperature 295 K).

Therefore the pseudo-second-order kinetic model fits the experimental data better than the other kinetic models in this study [35]. The intraparticle diffusion equation can be written as

$$q_t = k_i t^{1/2} + C \tag{10}$$

According to Eq. (10), a plot of q_t vs. $t^{1/2}$ (not presented) should be a straight line with a slope k_i and intercept C when the sorption mechanism follows the intraparticle diffusion process. In a study, sorption of Cu(II), Zn(II), Co(II) and Pb(II) complexes with GLDA as well as Cu(II), Zn(II), Cd(II) and Pb(II) complexes with EDDS exhibits a two step process with various mechanisms since two linear regions on the above-mentioned plots were observed. The correlation coefficients (R^2) for this model were lower and varied from 0.554 to 0.887. It is known that when the data exhibit multi-linear plots, this is indicative of some degree of boundary layer control and further shows that the intraparticle diffusion is not only rate controlling but also other processes may control the rate of sorption [36]. These results are analogous for that obtained for example in the case of Cu(II) ions sorption on the chitosan, chitosan-cross-linking by glutaraldehyde or alginate salts where the pseudo-second-order best describes the adsorption process, which assumes that chemisorption is the rate controlling mechanism [37]. Also in the case of the Cu(II), Co(II), Ni(II) as well as Fe(III) ions sorption in the presence of iminodisuccinic acid (IDS) on strongly, medium and weakly basic anion exchangers the pseudo-second-order model was favourable [38].

The mechanism of sorption is related to decomposition of sorbed complexes and the formation of the coordination bond between the diphosphonic functional groups of Diphonix Resin® and the metal ions. This can be expressed with the following reactions:

$$[ML]^{(4-m)-} \rightleftarrows M^{m+} + L^{4-} \tag{11}$$

$$\begin{aligned} &R\text{–}(PO_3H_2)_2{}^{2-} + 2H^+ + M^{2+} + L^{4-} \\ &\rightleftarrows R\text{–}(PO_3H_2)^{2-} \rightarrow M^{2+} + 2H^+ + L^{4-} \end{aligned} \tag{12}$$

where R, the Diphonix Resin® skeleton (PS-DVB); L, the glda^{4-} or edds^{4-} ligand.

The most likely structure of the M(II)–diphosphonate complexes is shown in Fig. 5. In the case of metal ions with the additional charge, it can be neutralized by the sulphonate functional groups. The minimum energy conformation analysis of the diphosphonate ligand shows that phosphoryl oxygen and acidic oxygen cannot be simultaneously coordinate to the metal ion. In acidic solutions, for example the neutral metal-nitrate(V) species may be bonded to the phosphoryl groups of diphosphonic acid (Fig. 6).

As mentioned earlier, Diphonix Resin® containing the gem-diphosponic acid groups is also characterised by another limitation of chelating resins: operation in low pH ranges. The diphosphonic acid ligands of Diphonix Resin® tend to sorb metal ions by forming protonated metal complexes. As a result, the resin retains its selectivity and capacity for metal ions under conditions that are typically too acidic for appreciable metal complexation by conventional and chelating ion exchange resins [39]. The effect of pH was studied for Cu(II), Zn(II), Co(II), Cd(II) and Pb(II) in the M(II)–GLDA = 1:1 and M(II)–EDDS = 1:1 systems at the pH varied from 2 to 12. The obtained results are shown in Fig. 7a and b. As can be seen from Fig. 7a the optimal sorption range of Cu(II), Zn(II), Co(II) and Pb(II) complexes with GLDA does not change at pH from 4 to 8 whereas, at high pH values, decrease in removal efficiency of Cu(II) can be described with formation of Cu(OH)$_2$. In the case of the Cu(II), Zn(II), Cd(II) and Pb(II) complexes with EDDS a slight decrease in sorption efficiency with the increasing pH was observed (Fig. 7b).

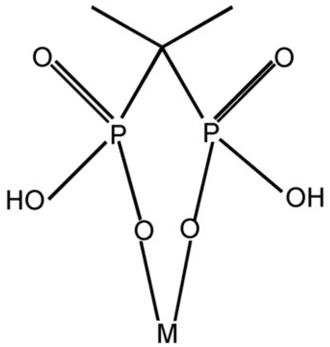


Fig. 5. Chemical structure of the M(II)–diphosphonate complexes.

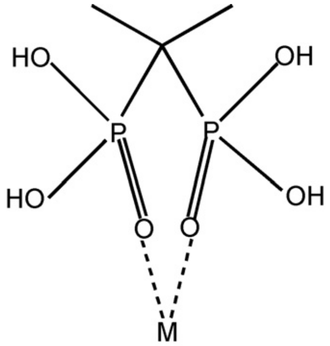


Fig. 6. Chemical structure of the M(II)–diphosphonate complexes in acidic solutions.

3.3. Adsorption studies

Fig. 8a and b illustrates the adsorption isotherms of Cu(II), Zn(II), Co(II), Cd(II) and Pb(II) in M(II)–GLDA = 1:1 and M(II)–EDDS = 1:1 on Diphonix Resin® in the single component system. The equilibrium adsorption q_e increases with increasing the equilibrium concentrations c_e of the Cu(II), Zn(II), Co(II) and Pb(II) complexes with GLDA and the Cu(II), Zn(II), Cd(II) and Pb(II) complexes with EDDS.

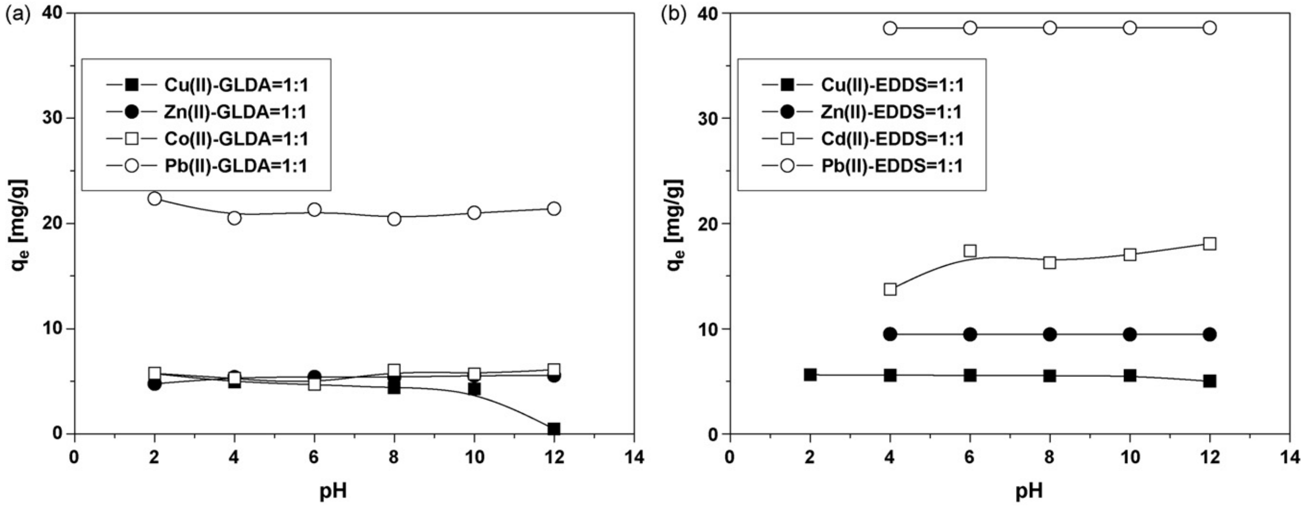


Fig. 7. (a and b) The effect of pH on the sorption of Cu(II), Zn(II), Co(II), Cd(II) and Pb(II) complexes with GLDA and EDDS on Diphonix Resin® (c_0 1 × 10^{-3} mol/L, ion exchanger dose 10 g/L, shaking time 3 h, shaking speed 180 rpm, temperature 295 K).

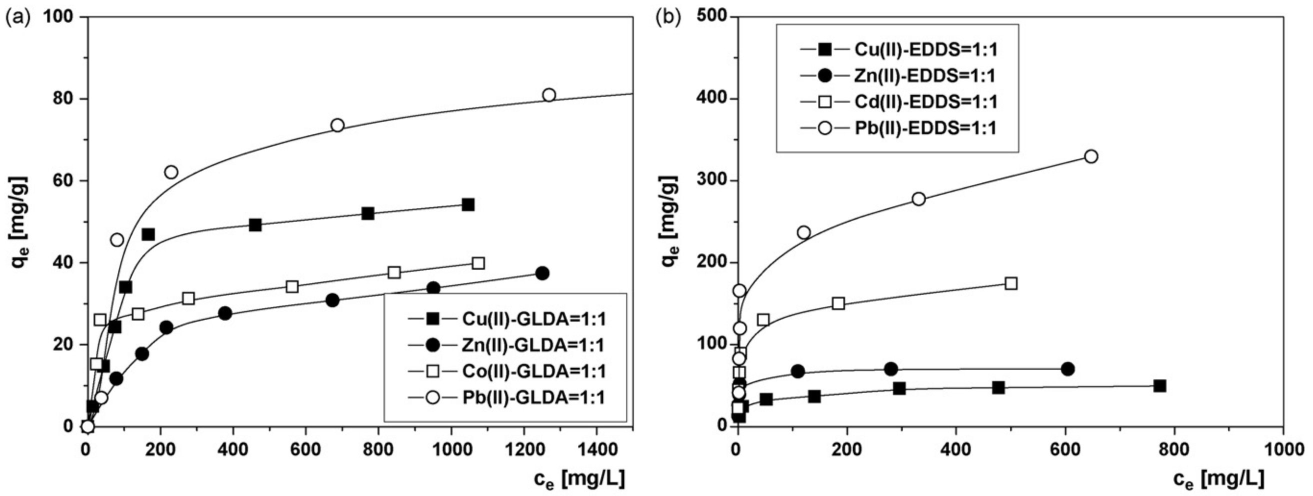


Fig. 8. (a and b) The sorption isotherms of Cu(II), Zn(II), Co(II) and Pb(II) complexes with GLDA (a) and Cu(II), Zn(II), Cd(II) and Pb(II) complexes with EDDS (b) on Diphonix Resin® (1.0×10^{-3} to 2.5×10^{-2} M, ion exchanger dose 10 g/L, shaking time 3 h, shaking speed 180 rpm, temperature 295 K).

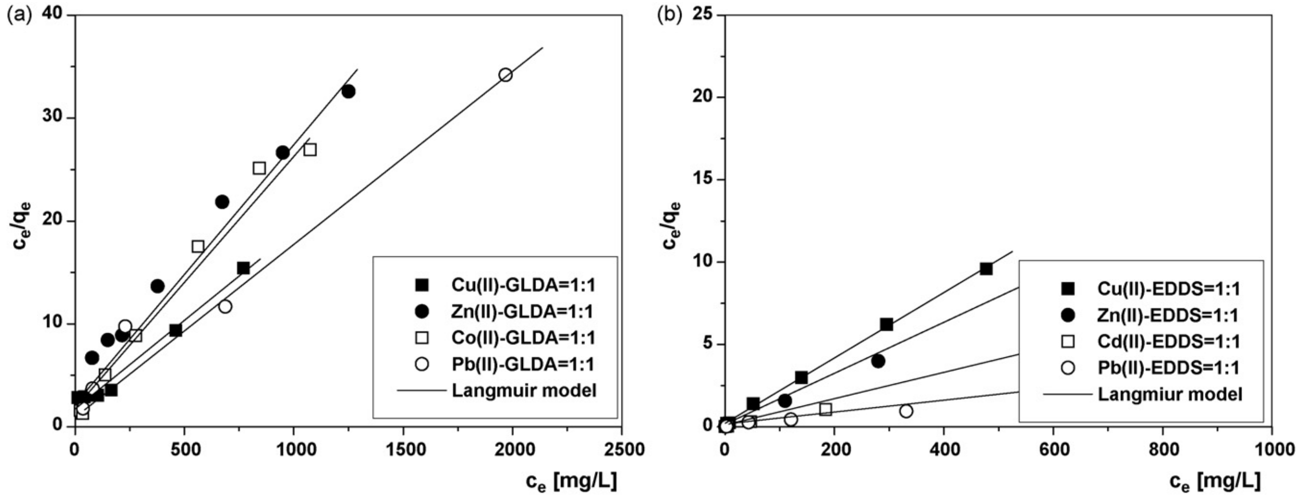


Fig. 9. (a and b) The linearized Langmiur isotherms of Cu(II), Zn(II), Co(II) and Pb(II) complexes with GLDA (a) and Cu(II), Zn(II), Cd(II) and Pb(II) complexes with EDDS (b) on Diphonix Resin® (1.0×10^{-3} to 2.5×10^{-2} M, ion exchanger dose 10 g/L, shaking time 3 h, shaking speed 180 rpm, temperature 295 K).

Comparing the obtained results, Pb(II) adsorption is the highest followed by Cu(II), Co(II) and Zn(II) in the case of the presence of GDLA and Pb(II) followed by Cd(II), Zn(II) and Cu(II) in the case of EDDS.

The adsorption equations, the Langmuir, Freundlich, Temkin and Dubinin–Radushkevich (D–R) were employed to calculate adsorption capacity. The constants q_0 and K_L the characterstics of the Langmuir equation can be determined from the linearized plot of c_e/q_e vs. c_e (from the slope and the intercept) (Fig. 9a and b, Table 4). The highest values of the Langmuir parameter q_0 were obtained in the case of Pb(II) complexes with GLDA and EDDS and they are equal to 114.9 and 357.1 mg/g, respectively. The obtained K_L constants are as follows: 0.003 and 0.056 L/mg, respectively. All values of the experimental sorption capacity ($q_{e,exp}$) for M(II)–GLDA and M(II)–EDDS complexes are in good agreement with the q_0 values obtained based on this model. Comparing the values of K_L parameter for the sorption of Cu(II), Zn(II), Co(II) and Pb(II) complexes with GLDA (0.01, 0.005, 0.02, 0.003, respectively) with those for the Cu(II), Zn(II), Cd(II) and Pb(II) complexes with EDDS (0.09, 0.10, 0.05, 0.06, respectively) it can be implied that the metal ions undergo stronger bonding in the presence of EDDS.

In order to predict the adsorption efficiency of the adsorption process, the dimensionless equilibrium Hall parameter was also

Table 4
The Langmuir isotherm constants for the sorption of Cu(II), Zn(II), Co(II), Cd(II) and Pb(II) complexes with GLDA and EDDS on Diphonix Resin®.

System	$q_{e,exp}$ [mg/g]	q_o [mg/g]	K_L [L/mg]	R_L	R^2
Cu(II)–GLDA = 1:1	54.19	59.17	0.010	0.06	0.915
Zn(II)–GLDA = 1:1	38.39	44.05	0.005	0.12	0.933
Co(II)–GLDA = 1:1	39.38	38.61	0.018	0.04	0.982
Pb(II)–GLDA = 1:1	112.78	114.94	0.003	0.06	0.979
Cu(II)–EDDS = 1:1	49.78	50.51	0.093	0.01	0.999
Zn(II)–EDDS = 1:1	70.30	70.65	0.098	0.003	1.000
Cd(II)–EDDS = 1:1	174.74	175.55	0.046	0.001	0.998
Pb(II)–EDDS = 1:1	349.67	357.14	0.056	0.004	0.977

Table 5
The Freundlich isotherm constants for the sorption of Cu(II), Zn(II), Co(II), Cd(II) and Pb(II) complexes with GLDA and EDDS on Diphonix Resin®.

System	$q_{e,exp}$ [mg/g]	K_F [mg/g (L/mg)$^{1/n}$]	n	R^2
Cu(II)–GLDA = 1:1	54.19	10.55	4.11	0.752
Zn(II)–GLDA = 1:1	38.39	18.24	2.51	0.699
Co(II)–GLDA = 1:1	39.38	19.16	12.17	0.932
Pb(II)–GLDA = 1:1	112.78	20.40	5.14	0.959
Cu(II)–EDDS = 1:1	49.78	12.67	4.55	0.927
Zn(II)–EDDS = 1:1	70.30	28.87	5.92	0.784
Cd(II)–EDDS = 1:1	174.74	48.55	4.31	0.931
Pb(II)–EDDS = 1:1	349.67	66.87	4.06	0.735

Table 6
The Temkin isotherm constants for the sorption of Cu(II), Zn(II), Co(II), Cd(II) and Pb(II) complexes with GLDA and EDDS on Diphonix Resin®.

System	$q_{e,exp}$ [mg/g]	K_T [L/g]	b_T [J/mol]	R^2
Cu(II)–GLDA = 1:1	54.19	0.32	263.8	0.908
Zn(II)–GLDA = 1:1	38.39	0.05	267.47	0.982
Co(II)–GLDA = 1:1	39.38	0.17	239.48	0.983
Pb(II)–GLDA = 1:1	112.78	0.22	161.75	0.941
Cu(II)–EDDS = 1:1	49.78	4.01	395.38	0.977
Zn(II)–EDDS = 1:1	70.30	5.94	372.85	0.919
Cd(II)–EDDS = 1:1	174.74	22.19	133.87	0.995
Pb(II)–EDDS = 1:1	349.67	7.27	65.12	0.902

determined by using the following equation [40–42]:

$$R_L = \frac{1}{1 + K_L c_0} \tag{13}$$

The value of the R_L indicates the type of the 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 Cu(II), Zn(II), Co(II) and Pb(II) complexes with GLDA and Cu(II), Zn(II), Cd(II) and Pb(II) complexes with EDDS were found to be 0.06, 0.12, 0.04, 0.06 and 0.01, 0.003, 0.001, 0.004, respectively. These values indicate favourable sorption in the case of GLDA presence. For EDDS the sorption is less favourable (the R_L values approach zero).

In the case of Freundlich isotherm, from its linearized form (not presented) the K_F and n parameters were calculated. These constants are related to the sorption capacity of the resin (K_F) and the surface heterogeneity ($1/n$). The higher values of K_F indicate the higher affinity of the ion exchanger for the metal ion. The values of n between 1 and 10 indicate favourable sorption [36]. In the presented paper the obtained Freundlich parameters are listed in Table 5. Taking the correlation coefficients (R^2) into account, it is evident that this model does not fit the experimental data adequately.

The parameters obtained when the Temkin model is applied show that the K_T parameters are higher for the Cu(II), Zn(II), Cd(II) and Pb(II) complexes with EDDS sorption than for the Cu(II), Zn(II), Co(II) and Pb(II) complexes with GLDA. The Temkin constant, b_T, related to heat of sorption decreased successively from Cu(II) to Co(II) and Cd(II), and reached the lowest value for the Pb(II) complexes with GLDA and EDDS (Table 6). For this model the correlation coefficients (R^2) are high.

It is known that the Langmuir and Freundlich adsorption isotherm constants do not give any idea about the adsorption mechanism. Therefore, the equilibrium data were tested with the Dubinin–Radushkevich isotherm (D–R). This model is related to the porous structure of ion exchanger and its linear form can be as follows:

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

In Fig. 10a and b the plots of $\ln q_e$ against ε^2 were shown. They are almost linear with correlation coefficients R^2 in the range 0.831–0.976 (Table 7). The D–R isotherm constants β and X_m were calculated from the negative slope and intercept of these plots, respectively. The values of β were found to be from 2×10^{-9} to 9×10^{-9} mol^2/J^2 in the presence of GLDA and from 2.0×10^{-9} to 2.1×10^{-9} mol^2/J^2 in the presence of EDDS. The maximum X_m values were for Pb(II) in the presence of GLDA and EDDS and they are equal to 131.3 and 481.9 mg/g, respectively.

The mean free energy of adsorption (E) was calculated using the relation:

$$E = \frac{1}{(2\beta)^{-1/2}} \tag{15}$$

It is defined as the free energy change when 1 mol of ion is transferred to the surface of the solid from infinity in solution. The value of E is very useful in predicting the type of adsorption and if the value is less than 8 kJ/mol, then the adsorption is physical in nature and if it is in between 8 and 16 kJ/mol, then the adsorption is due to exchange of ions. The E values in the present study for sorption of the Cu(II), Zn(II), Co(II) and Pb(II) complexes with GLDA were found to be 2.3–15.4 kJ/mol, whereas for Cu(II), Zn(II), Cd(II) and Pb(II) complexes with EDDS they were 15.4–15.8 kJ/mol due to the decomposition of complexes in the resin phase which accompanied by the formation of the coordination bond between the functional groups of Diphonix Resin® and the metal ions.

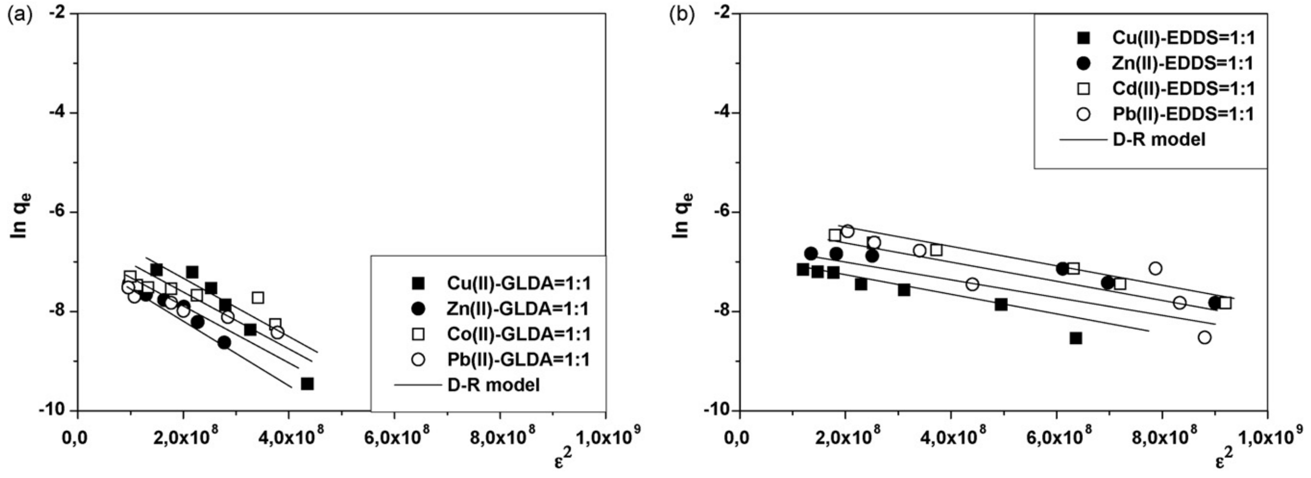


Fig. 10. (a and b) The Dubinin–Radushkevich isotherms of Cu(II), Zn(II), Co(II) and Pb(II) complexes with GLDA (a) and Cu(II), Zn(II), Cd(II) and Pb(II) complexes with EDDS (b) on Diphonix Resin® (1.0×10^{-3} to 2.5×10^{-2} M, ion exchanger dose 10 g/L, shaking time 3 h, shaking speed 180 rpm, temperature 295 K).

Table 7
The Dubinin–Radushkevich isotherm constants for the sorption of Cu(II), Zn(II), Co(II), Cd(II) and Pb(II) complexes with GLDA and EDDS on Diphonix Resin®.

System	$q_{e,exp}$ [mg/g]	X_m [mg/g]	β [mol²/J²]	E [kJ/mol]	R^2
Cu(II)–GLDA = 1:1	54.19	49.22	9.0×10^{-9}	2.26	0.944
Zn(II)–GLDA = 1:1	38.39	42.47	6.0×10^{-9}	9.13	0.963
Co(II)–GLDA = 1:1	39.38	47.34	2.08×10^{-9}	15.47	0.890
Pb(II)–GLDA = 1:1	112.78	131.26	6.0×10^{-9}	9.13	0.969
Cu(II)–EDDS = 1:1	49.78	69.69	2.0×10^{-9}	15.81	0.957
Zn(II)–EDDS = 1:1	70.30	102.42	2.1×10^{-9}	15.43	0.955
Cd(II)–EDDS = 1:1	174.74	272.33	2.08×10^{-9}	15.50	0.976
Pb(II)–EDDS = 1:1	349.67	481.90	2.06×10^{-9}	15.58	0.831

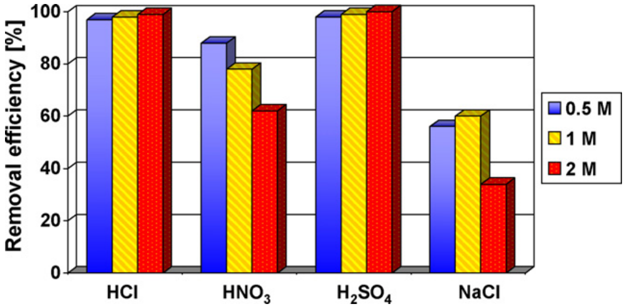


Fig. 11. Regeneration efficiency of Diphonix Resin® using HCl, HNO_3, H_2SO_4 and NaCl solutions at different concentrations (Cu(II)–GLDA = 1:1, c_0 1×10^{-3} mol/L, ion exchanger dose 10 g/L, shaking time 3 h, shaking speed 180 rpm, temperature 295 K).

3.4. Regeneration

Regeneration tests of Diphonix Resin® were conducted for the following regeneration agents, e.g. HCl, HNO_3, H_2SO_4 and NaCl with the three concentrations 0.5, 1 and 2 M. Based on the series of five experiments using known amounts of Cu(II) complexes with GLDA or EDDS sorbed, it was established that the overall recoveries of Cu(II) eluted from Diphonix by 2 M HCl and H_2SO_4 were 99.2 and 96.7%, suggesting that the recovery is quantitative. The exemplary data for the Cu(II)–GLDA complexes are presented in Fig. 11. Additionally, the efficiency is significantly affected by the increasing acid concentration from 1 to 2 M.

4. Conclusions

In the presented paper the studies on the sorption of Cu(II), Zn(II), Co(II) and Pb(II) complexes with GLDA and Cu(II), Zn(II), Cd(II) and Pb(II) complexes with EDDS on the chelating ion exchanger Diphonix Resin® were carried out. Optimal sorption conditions were determined by batch experiments. The obtained results can be summarized as follows:

(1) The presence of biodegradable complexing agent of a new generation GLDA or EDDS affects the sorption process of M(II) ion on Diphonix Resin®.
(2) The effectiveness of sorption depends on the type of complexes and their stability that facilitates their decomposition in the resin phase.
(3) Diphonix Resin® has excellent sorption properties, short contact time, easy regeneration and high sorption capacity toward heavy metal ions in the presence of GLDA and EDDS.
(4) The phase contact time and the concentration affect the sorption process. Sorption efficiency slightly increases with the increasing pH or remains unchanged.
(5) The kinetic results indicate that the values of rate constant of sorption in the case of EDDS complexes are higher than those for GLDA complexes.
(6) Sorption equilibrium data were correlated with the Langmuir, Freundlich, Temkin and Dubinin–Radushkevich (D–R) isotherms. The Langmuir model was found to provide the best fit to the data. In this case the sorption capacities found for Cu(II), Zn(II), Co(II) and Pb(II) complexes with GLDA were as follows: 59.2, 44.1, 38.6 and 114.9 mg/g. For Cu(II), Zn(II), Cd(II) and Pb(II) complexes with EDDS they were: 50.5, 70.6, 175.5 and 357.1 mg/g, respectively.
(7) GLDA and EDDS can be proposed as alternative chelating agents to EDTA. They can be applied for the removal of heavy metal ions from waters and wastewaters on ion exchangers.

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