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New approach to Cu(II), Zn(II) and Ni(II) ions removal at high NaCl concentration on the modified chelating resin

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ABSTRACT

In this study the commercially available chelating ion exchanger Lewatit TP 260 modified for the effective sorption was used for removal of Cu(II), Zn(II) and Ni(II) ions from aqueous acidic solutions. During the modification the resin was converted into Na^+ or $2Na^+$ form. It was found that different conditions such as pH, concentration and form of the functional groups affect the sorption efficiency of the aminophosphonate resin towards the above-mentioned heavy metal ions in aqueous solutions at a low pH value. The maximum sorption capacity of Lewatit TP 260 towards Cu(II), Zn(II) and Ni(II) was obtained for the $2Na^+$ form. The sorption kinetic data were found to fit the pseudo-second-order model as compared with the pseudo-first-order model. The intraparticle diffusion model suggested that the sorption process was dominated by the external mass transfer of Cu(II), Zn(II) and Ni(II) ions to the surface of Lewatit TP 260 with the aminophosphonate functional groups in the $2Na^+$ form.

Keywords: Heavy metals; Lewatit TP 260; Waste streams; Ion exchange

1. Introduction

Toxic metals are some of the oldest environmental problems [1,2]. They cause the organ damages and are being classified as human carcinogens and mutagens. Therefore, they should be effectively removed from the environment. A variety of separation processes for heavy metal ions removal have been developed for industrial needs. These are precipitation, evaporation, liquid–liquid extraction, ion exchange, reverse osmosis and electrodialysis [3–5]. Ion exchangers are widely applied in different fields of industries such as industrial and nuclear water treatment, domestic water treatment, catalysts in epoxidation processes, uranium extraction, sugar treatment, pharmaceutical and food processes as well as others [6–9].

The lack of selectivity, sensitivity and capacity of the conventional ion-exchange resins for heavy metal ions led to development of metal ion specific exchange resins known as chelating ion exchangers or chelating ion-exchange resins [10–17]. These exchangers, which are also called complexing or selective resins, combine two analytical processes, i.e., ion exchange and complexing reaction. Therefore, being copolymers of styrene-divinylbenzene, they contain iminodiacetate, amidoxime, aminophosphonate, thiol and other functional groups capable of formation of strong complexes with metal ions. The high selectivity of chelating exchangers is attributed not only to electrostatic forces but also to coordination bonds in the metal-chelating groups [18,19].

In the group of chelating ion exchangers containing phosphorus, the aminophosphonate resins such as Duolite C 467, Duolite ES 469, Lewatit OC 1060, Purolite S 940, Purolite S 950 or Chelite P are of significant importance. The ion exchangers of this type were synthesized by Kennedy and Ficken in 1956 [20] and independently by Manecke and Heller in 1960 [21]. Since that time they have been produced on the commercial scale. Additionally, bifunctional resins, which combine

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chelating and conventional acidic groups, have also been proposed [22]. One of them is Purolite S 957 with the phosphonic and sulphonate functional groups, used for example for the selective removal of Fe(III) from the Cr(III) passivation baths [23]. Similarly, Diphonix with diphosphonic, sulphonate and carboxylic functional groups, prepared by partial sulphonation of the polystyrene-divinylbenzene matrix containing the phosphinic acid ligands, can be used for effective lanthanides and actinides separation. Sulphonic groups enhance the hydrophilicity of the resin resulting in faster ion-exchange kinetics [24,25].

Accordingly, with an increasing interest in developing processes for the recovery of copper, zinc, cobalt and nickel from secondary sources, the application of aminophosphonate resin is of great interest. Heavy metals are usually present in wastewaters in dilute quantities (1–100 mg/L) and at acidic pH values (<7.0). Moreover, large doses of alkaline chemicals are necessary to increase and maintain pH values to >7.0 for optimal metal removal. Furthermore, this produces secondary wastes in the form of metal hydroxide sludge but it should produce a residue that could be recycled for further processing or safe disposal without affecting the environment [22]. Therefore, in the presented paper, possibility of Cu(II), Zn(II) and Ni(II) removal from acidic waste streams at high concentrations of NaCl using the aminophosphonate resin Lewatit TP 260 was presented. This process is very important from the industrial point of view.

2. Experimental setup

2.1. Exchange resin

Lewatit TP 260 is a macroporous weak acid cation-exchange resin with the aminomethylphosphonate functional groups. It is recommended by the manufacturer for the selective removal of alkaline earth metals from the industrial effluents, the total ion-exchange capacity of 2.4 meq/mL, the particle size of >0.63 mm, the thermal stability up to 313 K (Table 1).

2.2. Static (batch) studies

$CuCl_2{\cdot}2H_2O$, $ZnCl_2$ and $NiCl_2{\cdot}6H_2O$ were used as sources of Cu(II), Zn(II) and Ni(II). Proper amounts of salts were dissolved in the distilled water. The initial pHs of the solutions were adjusted using HCl or NaOH. The stock solution was further diluted to the required experimental concentration. The other used chemicals were of analytical grade.

The static tests were carried out to obtain the sorption percentage (%S) of Cu(II), Zn(II) and Ni(II) ions for Lewatit TP 260 depending on the phase contact time, pH, concentration of NaCl and the form of ion exchanger. The studies were carried out in 250 mL shake flasks, placed in a shaker allowing to achieve 250 rpm (ELPHINE type 357, Poland). 2 g of the ion exchanger was weighed into a dry flask and 100 mL of the aqueous phase containing a mixture of metal ions at a concentration of 6.35 mg/L for Cu(II), 5.87 mg/L for Ni(II) and 6.54 mg/L for Zn, and the established concentration of NaCl (ranging from 0.5 to 40 g/L) was added. To obtain the required pH value, e.g., 1, 2, 3, 4 and 7, the solutions were adjusted by 1 M HCl or 1 M NaOH. The samples were shaken at 298 K in the interval of 0–3,600 s at 180 rpm. For the samples at pH 1 and 2, the interval time was 0–1,200 s. Subsequently, an appropriate amount of the aqueous phase was collected, and the contents of metal ions were analyzed using the atomic absorption spectrometry (AAS) technique. The experiment was conducted in the three parallel series and presented as mean values. The reproducibility of the measurements was within 5%. The concentrations of chloride ions were not determined.

The sorption percentage factor was calculated from the following equation:

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

The amounts of metal ions sorbed at time t on Lewatit TP 260 (q_t, mg/g) were calculated from the mass balance equation:

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

The pseudo-first-order model (PFO) was presented by Lagergren and expressed as follows [26]:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1 t}{2.303} \tag{3}$$

The rate constant, k_1, was obtained from the slope of linear plots of $\log(q_e - q_t)$ against t.

The sorption data was also analyzed in terms of the pseudo-second-order (PSO) mechanism [27]:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e} \tag{4}$$

and the initial rate of sorption h is:

$$h = k_2 q_e^2 \tag{5}$$

The constants q_e, h and k_2 can be determined from the plots of t/q_t against t.

There was also applied the Weber–Morris kinetic equation, i.e., the intraparticle diffusion (IPD) model [28]:

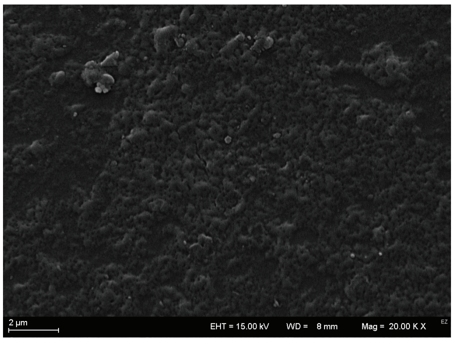
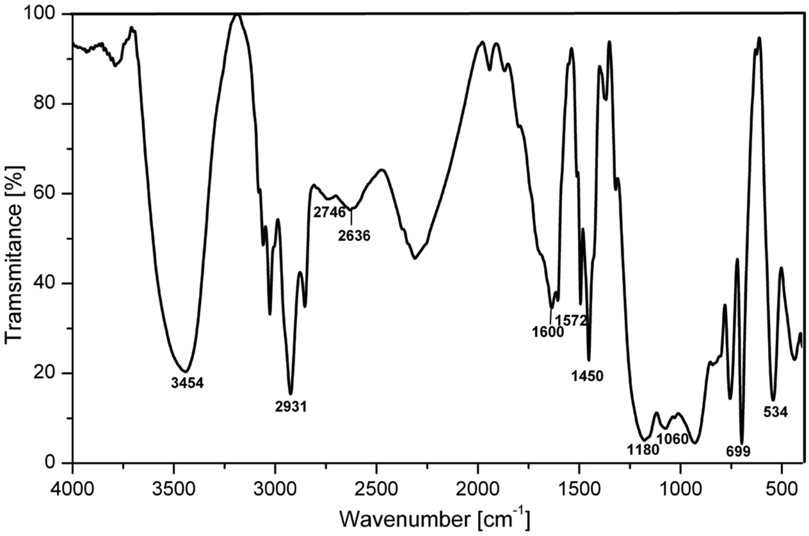
$$q_t = k_i t^{1/2} + C \tag{6}$$

Efficiency of the ion exchanger regeneration was tested using the HCl solution. In this part of study, Lewatit TP 260 was contacted with 1 M HCl. The sorption–desorption experiments were conducted totally for 50 cycles.

2.3. Dynamic (column) studies

In order to measure the affinity of the above-mentioned Cu(II), Zn(II) and Ni(II) ions, the breakthrough curves were determined using 10 mL of the swollen ion exchanger in the Na^+ and $2Na^+$ forms placed in the glass column with a

Table 1
Detail characteristic of the Lewatit TP 260 (Lanxess technical information)

Properties	Lewatit TP 260
Matrix	PS-DVB macroporous
Functional groups	$–CH_2NH–CH_2–PO(OH)_2$
Physical form	Opaque, white-beige
Ionic form as shipped	Na^+
Beads size, mm	>0.65
Total exchange capacity, eq/L	2.4 (H^+)
Moisture holding capacity, %	58–62
Shipping weight (±5%), g/L	720
Uniformity coefficient	1.1
Swelling $Na^+ > H^+$, %	35
pH range	0–14
Maximum temperature, K	313
Physical appearance	SEM image
	
FT-IR scan	
	

Note: SEM – scanning electron microscopy and FT-IR – Fourier transform infrared.

diameter of 1 cm. The Na^+ and $2Na^+$ forms were achieved by passing the appropriate amount of 1 M NaOH by the resin bead. The concentrations of the metal ions were established as 40 mg/L. The water phase flow rate was set at 100 mL/h and controlled by a peristaltic pump coupled to a rotameter. The temperature process was 298 K. In order to reproduce the conditions of industrial process, the ion exchangers were stripped of <0.2 mm grain fractions. The eluate was collected in fractions of 10 mL and analyzed by AAS.

The mass (D_g) and bed (D_v) distribution coefficients as well as the working (C_w) and total ion-exchange capacities (C_t) of M(II) were calculated from the determined breakthrough curves according to the equations presented below (Eqs. (7)–(9)) [29]:

$$D_g = \frac{\overline{V} - (V_0 - V_i)}{m_j} \tag{7}$$

$$D_v = \frac{\overline{V} - (V_0 - V_i)}{V_j} \tag{8}$$

$$C_w = \frac{V_e c_0}{V_j} \tag{9}$$

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

2.4. Apparatus

An AAS SpectrAA-FS 240 (Varian, Australia) was used for quantitative determination of Cu(II), Zn(II) and Ni(II) concentration. The AAS was equipped with a deuterium lamp; background correction; hollow cathode lamps for Cu, Zn and Ni; and an air-acetylene burner. The Fourier transform infrared (FT-IR) spectra of Lewatit TP 260 were recorded using the FT-IR spectrometer of the Cary 630 type (Agilent Technologies, Australia). Surface morphology of the ion exchanger was studied using the scanning electron microscope LEO1430VP (Carl Zeiss, Germany) with the EDX detector (Röntec, GmbH; Table 1).

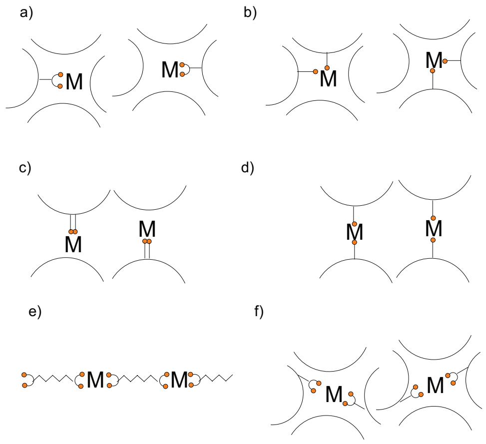
3. Results and discussion

3.1. Aminophosphonate resins behaviour

In the group of the ion exchangers of the phosphorous-containing functional groups, the following can be distinguished: phosphate $–OPO(OH)_2$, phosphonic $–PO(OH)_2$ and phosphinic $–PO(OH)H$ [30]. In the process of synthesis of the aminophosphonate resins such as Lewatit TP 260, Purolite S 940 and Purolite S 950, in the first stage the polystyrene-divinylbenzene matrix is obtained. The next stage is introduction of the primary amines and the methylenephosphone groups into the matrix (Mannich reaction with phosphoric(III) acid and formalin; Eq. (10)):

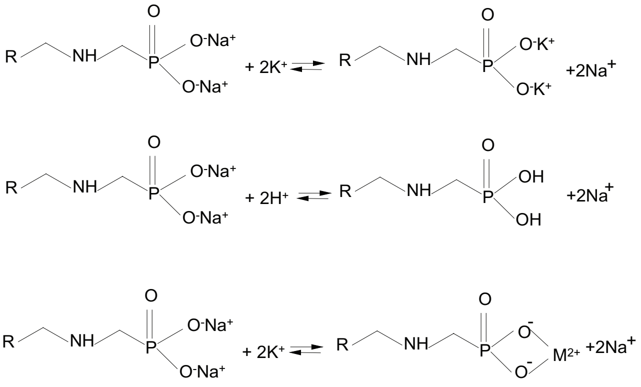
$$\begin{aligned} &R—CH_2—NH_2 + CH_2O + HP(O)(OH)_2 \\ &\rightarrow R—CH_2—NH_2—P(O)(OH)_2 + H_2O \end{aligned} \tag{10}$$

The obtained chelating ion exchanger can contain the functional groups attached to one point (a). The other chelate-containing polymers include cross-linkers and ligands attached to two or more positions in the network (b) and the linear polymers with pendent ligands forming either intramolecular chelating groups (c) or intermolecular chelating groups (d). In the case of metallopolymers (e), the polymeric chelate complex is formed by metal-ion bridging of monomeric or oligomeric ligands, and also chemically inert polymers with the sorbed low molecular-weight ligands (f):



Depending on the chemical system many chelating functional groups can act in the same way as the ion-exchange group without exhibiting any chelating properties.

The aminophosphonate chelating resins can also act as conventional non-specific ion exchangers or chelating polymers [31]. Therefore, the following reactions can be proposed for such ion exchangers (Eq. (11)):

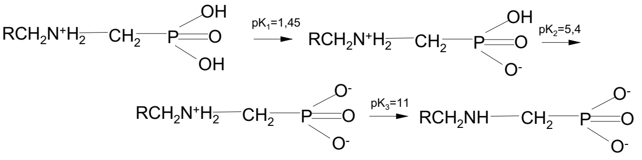


(11)

It should be emphasized that different ion exchangers bearing the same groups can exhibit significantly different properties because the strength of the group depends on the nature of the supporting matrix structure. For the aminophosphonate functional groups, the following pK changes can be obtained for different matrices: from 8.0 for phosphonate acid $–PO_3H_2$ to 7.5 in the case of phosphonate group attached to the benzene ring $Ar–PO_3H_2$ and 7.7 for $p–H_3C–Ar–PO_3H_2$ [32–34].

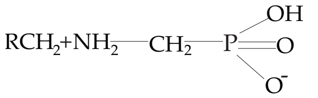
3.2. pH effect

The sorption efficiency for metal ions decreases with the decreasing pH value. Depending on the pH the aminophosphonate group occurs in the following forms [30,35–38]:



(12)

It is interesting that such ion exchanger changes its selectivity with the increasing pH value because of the presence of two ionizable –OH groups [30]. The aminophosphonate ion exchangers are characterized by large selectivity towards heavy metal ions, and their sorptive properties are determined by the extent of phosphonic groups' ionization. This is due to the electron-acceptor effect of the cationic centre ≡N or ≡P= through the alkyl fragment. As follows from the literature, lengthening of the alkyl fragment of the aminoalkylphosphonic group leads to insignificant increase of sorption capacity towards heavy metal ions [33]. The presence of methylene group increases electron density of the nitrogen atom of the amine group, which promotes its protonation:



$$RCH_2{}^+NH_2—CH_2—P(OH)(=O)(O^-)$$

Therefore, the most favourable mode of chelation when the pH value increases in the weak acid range is formation of four-membered rings by the aminophosphonate groups. In this case it acts as the tridentate ligand. Under the acidic conditions because of strong protonation, the amino-nitrogen atom does not participate in the bond formation, and the complexes without amine groups' contribution are formed [38]. The stability constants of copper(II) and zinc(II) complexes with aminomethylphosphonic acid are as follows: log$K$ = 8.12 for Cu(II) and log$K$ = 2.88 for Zn(II) [39].

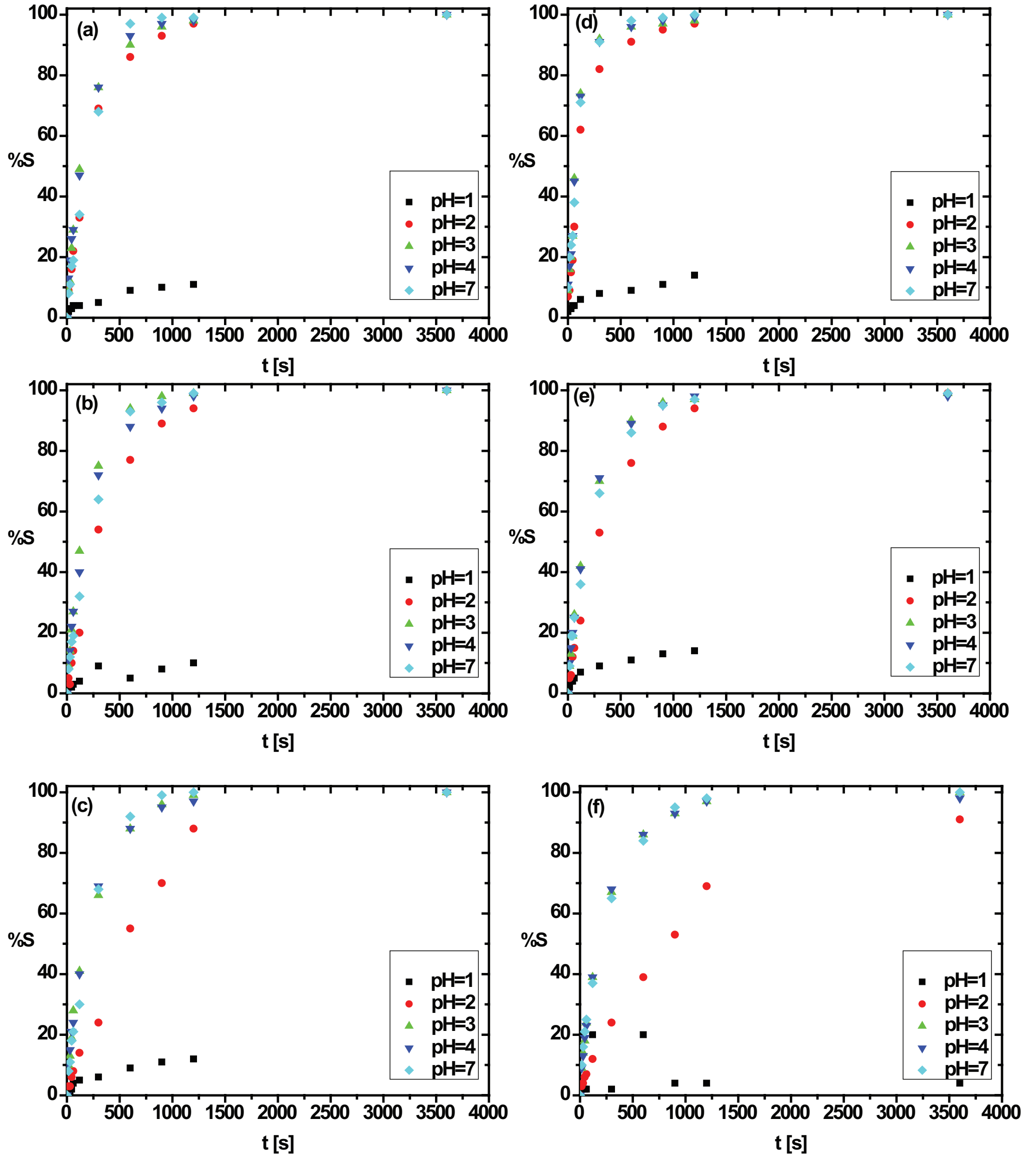


Fig. 1. Comparison of the sorption effectiveness of (a) Cu(II), (b) Zn(II) and (c) Ni(II) in the presence 0.5 g/L (a–c) and 40 g/L (d–f) of NaCl on the Lewatit TP 260 in the Na$^+$ form depending on the pH ($c_{cu(II)}$ = 6.35 mg/L, $c_{Zn(II)}$ = 6.54 mg/L, $c_{Ni(II)}$ = 5.87 mg/L; T = 298 K; m = 2 g; V = 100 mL; A = 7; 180 rpm).

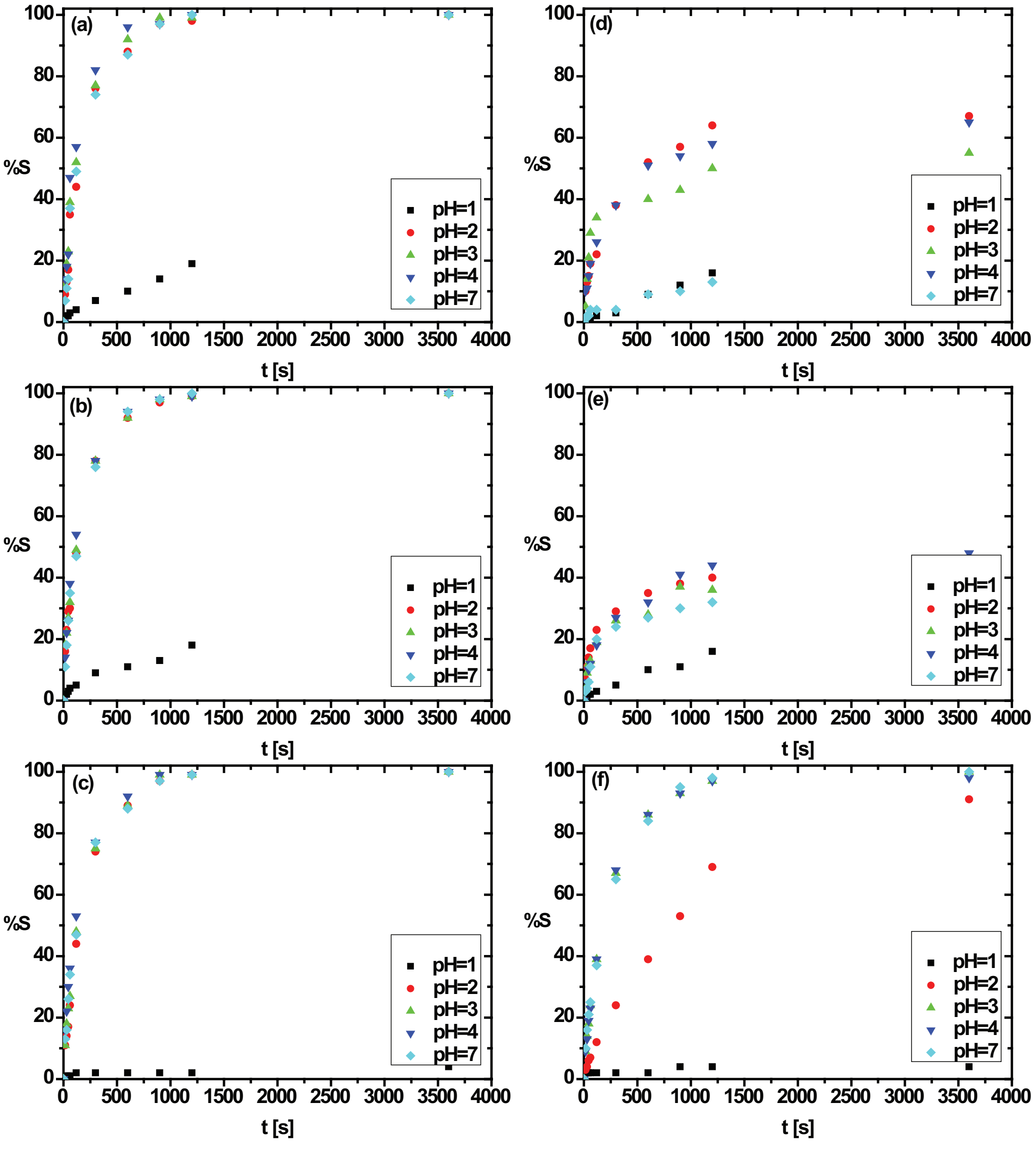


Fig. 2. Comparison of the sorption effectiveness of (a) Cu(II), (b) Zn(II) and (c) Ni(II) in the presence of 0.5 g/L (a–c) and 40 g/L (d–f) of NaCl on the Lewatit TP 260 in the 2Na$^+$ form depending on the pH ($c_{\mathrm{cu(II)}}$ = 6.35 mg/L, $c_{\mathrm{Zn(II)}}$ = 6.54 mg/L, $c_{\mathrm{Ni(II)}}$ = 5.87 mg/L; T = 298 K; m = 2 g; V = 100 mL; A = 7; 180 rpm).

3.3. Kinetic studies

Ion-exchange kinetics involves the diffusion of metal ions through the solution to the surface and particle pores of the ion exchanger followed by the chemical exchange between H$^+$ or Na$^+$ and M(II) in the exchanging sites and the diffusion of the H$^+$ ions displaced from of the interior and surface of the resin to the solution. Both film and particle diffusion mechanisms are prevalent in the ion-exchange process, although normally the slowest step (rate-limiting step) for a given system controls the speed of ion exchange. As it was already mentioned, the chelating process takes place.

Sorption experiments were carried out for Cu(II), Zn(II) and Ni(II) with different initial NaCl concentrations, ranging from 0.5 to 40 g/L. As many plants use saline and hypersaline process water, determining the effect of chloride ions in solution on the resin-metal interaction was deemed important [40]. Figs. 1(a)–(f) show the effect of the NaCl initial concentrations on the sorption kinetics of Cu(II), Zn(II) and Ni(II) at pH 1, 2, 3, 4 and 7 for Lewatit TP 260 in the Na$^+$ form. Figs. 2(a)–(f) show the analogous results obtained for Lewatit TP 260 in the 2Na$^+$ form. It is apparent that the sorption capacity for the studied ion exchanger in these two forms gradually increases with the increase of the phase contact time. It was also found that the higher the NaCl concentration, the longer time is necessary to achieve the sorption equilibrium. Generally, it can be stated that the amount of metal ions sorbed at equilibrium increases from 0.02 to 4.0 mg/g with the increase in the NaCl concentration from 0.5 to 40 g/L. Moreover, the time for the sorption equilibrium is shorter than in the case of Lewatit TP 207 or Lewatit TP 208 [41]. For the Cu(II), Zn(II) and Ni(II) ions sorption, Lewatit TP 208 in the Na^+ form required about 120 min to achieve equilibrium whereas in the present study in the case of Lewatit TP 260 about 25 min is sufficient to obtain the equilibrium. This can be attributed to the macroporous structure of Lewatit TP 260 and the type of functional groups.

Figs. 1(a)–(f) and 2(a)–(f) also show the sorption kinetics of Lewatit TP 260 in the Na^+ and $2Na^+$ forms towards Cu(II), Zn(II) and Ni(II) ions at different pHs. Both in the Na^+ and $2Na^+$ forms, Lewatit TP 260 exhibits capacity for metal ions sorption in the pH range 2–7. It can be seen that the sorption capacity, for example, for Cu(II) increased significantly from 0.04 to 4.0 mg/g when the pH of the solution increased from 2 to 7 (with the NaCl concentration equal to 40 g/L). This increment can be attributed to lower competition between the Cu(II), Zn(II) and Ni(II) as well as H^+ ions. Increasing the solution salinity from 0.5 to 40 g/L, under the above-mentioned pH conditions, did not cause a noticeable change of kinetics. Therefore, it can be stated that in the full range of sodium chloride concentration, good sorption kinetics of the studied metal ions is likely to occur when the process scale is transferred to a half-technological one. For the disodium form a negative effect of NaCl concentration of the sorption of studied metal ions was found. For example, the sorption capacity of Lewatit TP 260 in the $2Na^+$ form decreases with the increasing initial concentration of NaCl. Lewatit TP 260 in the $2Na^+$ form can sorb up to 0.04 mg/g of Cu(II) at pH 7.0, to 4.0 mg/g of Zn(II) and to 0.18 mg/g of Ni(II) in the case of the sorption process carried out at 40 g/L of NaCl. Analogous results were observed for the Na^+ form of Lewatit TP 260 for the multicomponent solutions at pH value 4.0, and therefore, the useful operating range of Lewatit TP 260 in the case of Cu(II), Zn(II) and Ni(II) ions sorption can be as presented in Figs. 3(a)–(c). The obtained results are quite different from those obtained for Lewatit TP 207 and Lewatit TP 208 [41] where the possibility of applying the ion exchangers Lewatit TP 207 and Lewatit TP 208 for removal of Cu(II) ions from the acid brine solutions was only in the pH range 2–4 and low NaCl concentration (up to 10 g/L). Moreover, application of the ion exchanger Lewatit TP 260 in the Na^+ and $2Na^+$ forms enables removal of heavy metal ions from the acid solutions containing sodium chloride of high concentration at pH > 2. Application of the disodium form does not make it possible to separate individual ions.

In order to investigate the sorption rate of Cu(II), Zn(II) and Ni(II) ions, the kinetic data obtained from the static (batch) experiments were analyzed using the PFO, the PSO and the IPD models [42–44]. The PFO model assumes that the sorption rate of sorbate with time is directly proportional to the difference in sorption capacity at equilibrium and the sorbed amount. The PSO model assumes that the rate-limiting step involves chemisorption of sorbate on the sorbent; however, the IPD model shows that the metal ions diffusion process into the interior of the ion exchanger is dependent on $t^{1/2}$ rather than t [45,46].

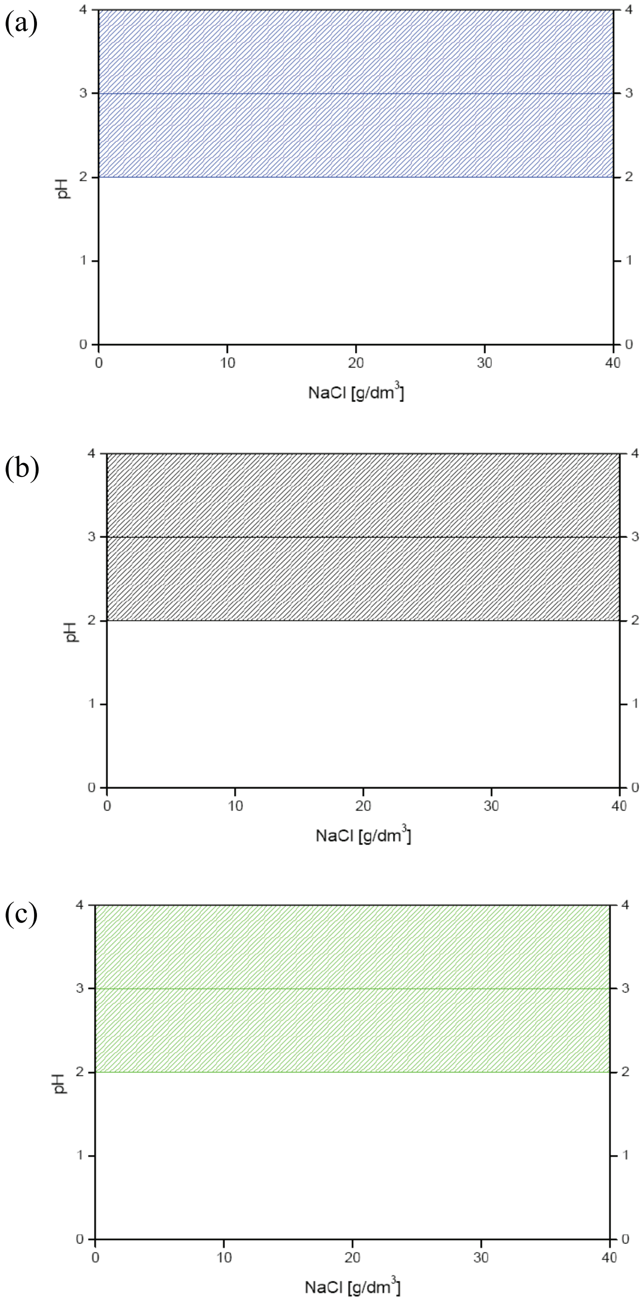


Fig. 3. The useful operating range of Lewatit TP 260 in the case of the Cu(II) ions sorption (blue), Zn(II) (black) and Ni(II) (green) in the Na^+ form ($c_{cu(II)}$ = 6.35 mg/L, $c_{Zn(II)}$ = 6.54 mg/L, $c_{Ni(II)}$ = 5.87 mg/L; pH = 4; T = 298 K; m = 2 g; V = 100 mL; A = 7; 180 rpm).

It was found that the kinetic data were well fitted by the PSO model, as demonstrated by the obtained higher determination coefficients (R^2). In the case of the PFO these values were in the range 0.6551–0.7957. In addition, the calculated $q_{e,\mathrm{cal}}$ values for the PSO model are consistent with the experimental data, $q_{e,\mathrm{exp}}$, compared with those of the PFO model (Table 2). As for the IPD model it was found that there are three linear regions connected with: the bulk diffusion (movement of metal ions from the aqueous phase through the hydrodynamic boundary layer film of the solid, i.e., surface mass transfer (Fig. 4, step 1), IPD or pore diffusion (the metal ions move through the interior solid surface; Fig. 4, step 2) and sorption at the active sites that is chemical interaction between metal ions and active sites (Fig. 4, steps 3 and 4). Due to stirring the first one can be ignored. Moreover, because the plot of q_t vs. $t^{1/2}$ does not give a straight

Table 2
Kinetic parameters for Cu(II), Zn(II) and Ni(II) on Lewatit TP 260 in the Na^+ and $2Na^+$ forms at 0.5 and 40 g/L NaCl ($c_{cu(II)}$ = 6.35 mg/L, $c_{Zn(II)}$ = 6.54 mg/L, $c_{Ni(II)}$ = 5.87 mg/L; T = 298 K; m = 2 g; V = 100 mL; A = 7; 180 rpm)

Cu(II)					Zn(II)				Ni(II)			
pH	q_2	k_2	h	R^2	q_2	k_2	h	R^2	q_2	k_2	h	R^2
TP 260 in the Na^+ form at 0.5 g/L NaCl												
1	0.26	1.48	0.103	0.9804	0.02	12.86	0.008	0.9598	0.04	5.92	0.008	0.9521
2	0.29	1.64	0.069	0.9840	0.43	1.18	0.035	0.9989	0.56	1.17	0.022	0.9923
3	0.27	1.48	0.091	0.9788	0.28	1.17	0.093	0.9859	0.29	1.00	0.082	0.9725
4	4.00	1.25	23.75	0.9804	0.28	1.13	0.098	0.9767	0.28	0.90	0.085	0.9784
7	4.00	0.76	12.238	0.9943	0.31	0.74	0.119	0.9858	0.31	0.72	0.170	0.9827
TP 260 in the $2Na^+$ form at 0.5 g/L NaCl												
1	0.26	0.69	0.116	0.9767	0.05	4.03	0.010	0.9932	0.01	1.87	0.005	0.9997
2	0.27	1.69	0.087	0.9744	0.27	1.56	0.113	0.9794	0.29	1.68	0.084	0.9929
3	0.26	1.56	0.108	0.9747	0.32	1.68	0.113	0.9758	0.28	1.28	0.098	0.9955
4	0.26	1.16	0.116	0.9767	0.27	1.42	0.120	0.9764	0.27	1.39	0.120	0.9927
7	0.31	0.84	0.080	0.9597	0.27	1.23	0.108	0.9766	0.27	1.01	0.103	0.9911
TP 260 in the Na^+ form at 40 g/L NaCl												
1	0.27	1.28	0.092	0.9806	0.04	10.61	0.015	0.9255	0.01	31.74	0.003	0.9577
2	0.29	1.19	0.059	0.9808	0.33	1.45	0.048	0.9756	0.34	16.10	1.910	0.7863
3	0.27	1.16	0.087	0.9848	0.28	1.03	0.083	0.9822	0.29	0.84	0.072	0.9760
4	0.27	1.06	0.086	0.9811	4.00	1.01	16.150	0.9800	0.29	0.83	0.071	0.9784
7	0.28	0.70	0.083	0.9751	4.00	0.90	14.411	0.9739	0.30	0.77	0.069	0.9674
TP 260 in the $2Na^+$ form at 40 g/L NaCl												
1	0.23	0.06	0.003	0.7500	0.06	1.78	0.006	0.7212	0.01	3.38	0.003	0.9950
2	0.18	4.93	0.067	0.9914	0.11	4.04	0.046	0.9510	0.11	3.45	0.021	0.9924
3	0.12	4.72	0.051	0.9962	0.11	3.95	0.028	0.8282	0.12	3.34	0.038	0.9936
4	0.16	2.06	0.046	0.9547	4.00	2.48	32.324	0.9114	0.11	1.42	0.045	0.9403
7	0.04	1.44	0.007	0.9920	4.00	2. 02	63.259	0.9536	0.18	1.99	0.063	0.9784

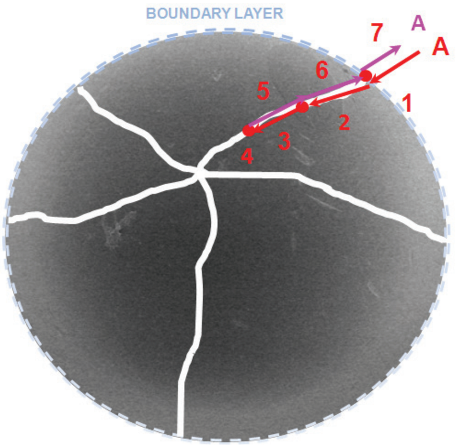


Fig. 4. The scheme of the sorption process: step 1 – diffusion of the adsorbate (A) from the bulk phase through boundary layer to the external surface of the ion exchanger bead (film diffusion or interphase diffusion); step 2 – diffusion of the adsorbent sthrough the pores to the functional groups (pore diffusion or intraparticle diffusion); step 3 – adsorption of adsorbate; step 4 – reaction at specific active sites; step 5 – desorption of adsorbate; step 6 – diffusion from the interior of the ion exchanger bead to the pore at the external surface; and step 7 – diffusion of adsorbate from the external surface to the bulk fluid (interphase diffusion).

line passing through the origin, the IPD is not the only rate-controlling step due to variation of mass transfer in the initial and final stages of sorption. Contribution of the surface sorption in the rate-controlling step is established from the k_i values. Moreover, the plot intercept reflects the boundary layer effect (large values of the intercept indicate greater contribution of the surface sorption in the rate-controlling step). It was found that the IPD coefficients k_i were equal to 0.326, 0.111 and 0.258 mg/g $min^{0.5}$ for Cu(II), Zn(II) and Ni(II) for Lewatit TP 260 in the Na^+ form and 0.283, 0.206 and 0.244 mg/g $min^{0.5}$ for Cu(II), Zn(II) and Ni(II) for Lewatit TP 260 in the $2Na^+$ form, respectively. The values of the intercept were as follows: 22.37, 20.01 and 11.55; and 34.12, 14.95 and 26.08, respectively. It was also found that the values of the IPD rate k_{i2} were smaller than the film diffusion rate k_{i1}. It should be also mentioned that in some cases adsorption kinetics is controlled by film diffusion and IPD simultaneously.

3.4. Sorption selectivity

The chelating resins can be distinguished from the ordinary type of ion exchangers by (i) the dependence of the affinity of a particular metal ion for a functional group on the nature of this group (size of the ion, its charge and physical properties are of secondary importance), (ii) the strength of the binding forces in the chelating resins is much higher than in the ordinary exchangers, (iii) the exchange process in a chelating resin is often slower than in, e.g., strongly acidic or basic resins and is controlled either by a participle diffusion mechanism or a pseudo-second-order chemical reaction as it was mentioned above [47]. In the metal ions separation on the aminophosphonate ion exchangers, the affinity series depends on the pH conditions and is quite different for various pH values. It should be mentioned that this type of ion exchangers similarly to the phosphonate ion exchangers reveals weak affinity for Ca(II) and Mg(II) [48–50]. As follows from the literature data, also in the case of acidic electrolyte solutions (e.g., from copper electrowinning), only the phosphonic resins are suitable for this application [51,52].

3.5. FT-IR analysis

Infrared spectroscopy is a commonly used technique to confirm the presence of various functional groups as well as to correlate some information about the surface activity of ion exchangers with the sorption capacity.

The bands for Lewatit TP 260 related to the amine and hydroxy groups can be assigned to the peak at 3,454 cm^{-1}. As the chelating interactions occurred between the heavy metal ions and –OH groups, there was observed the bands shift from 3,454 cm^{-1} to 3,459, 3,556 and 3,458 cm^{-1} after the Cu(II), Zn(II) and Ni(II) sorption, respectively. This suggests that chelating interactions occur between the –OH and metal ions during sorption. The other characteristic bands are the stretching vibrations at 2,250–2,746 cm^{-1} and the deformation ones in the range 1,572–1,600 cm^{-1}. The C–N absorption is found in the range 1,200–1,350 cm^{-1}. The compounds with the P–OH group have two broad bands of medium intensity at 2,746 and 2,328 cm^{-1}, which are due to the O–H stretching vibrations and a strong band due to the P–O stretching vibration at 1,393 and 1,220 cm^{-1}. Moreover, the presence of absorption bands characteristic of the group $–PO_3H^-$ (asymmetric stretching vibrations for 1,180 cm^{-1} and symmetric stretching vibrations for 1,060 cm^{-1}) was observed [53]. The change of spectra as a function of chloride concentration due to the successive replacement of water with the chloride ligand within octahedral coordination should be also useful for the mechanism of sorption determination [54]. For example, in the case of Ni(II) ions, the three Ni species can be distinguished: Ni^{2+}, $NiCl^+$ and $NiCl_{2(aq)}$.

3.6. Breakthrough curves

As can be seen from Figs. 5(a) and (b) and 6(a) and (b) in the dynamic studies, Lewatit TP 260 demonstrated quite sharp breakdown profiles. The disodium form was characterized by large capacity compared with the monosodium form for individual metal ions (Table 3). The disodium form was characterized by the increased capacity compare with the monosodium form, which was observed only in the case of Cu(II) and Zn(II) ions for the studied values of pH 2.0 and 4.0.

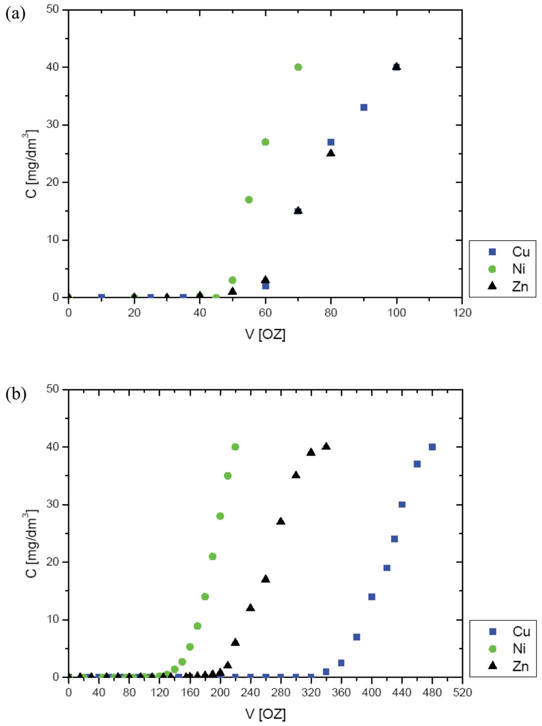


Fig. 5. The breakthrough curves of Cu(II), Zn(II) and Ni(II) ions at (a) pH = 2 and (b) pH = 4 on chelating ion exchanger Lewatit TP 260 in the Na$^+$ form (NaCl concentration 40 g/L) (bed volume = 10 mL; ϕ = 1 cm; flow rate = 100 mL/h; $c_{cu(II)}$ = 40 mg/L, $c_{Zn(II)}$ = 40 mg/L, $c_{Ni(II)}$ = 40 mg/L; pH = 4).

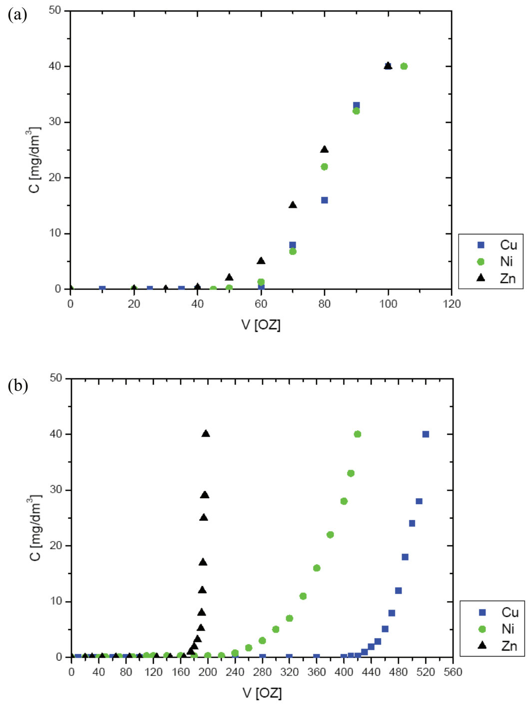


Fig. 6. The breakthrough curves of Cu(II), Zn(II) and Ni(II) ions at (a) pH = 2 and (b) pH=4 on chelating ion exchanger Lewatit TP 260 in the 2Na$^+$ form (NaCl concentration 40 g/L) (bed volume = 10 mL; ϕ = 1 cm; flow rate = 100 mL/h; $c_{cu(II)}$ = 40 mg/L, $c_{Zn(II)}$ = 40 mg/L, $c_{Ni(II)}$ = 40 mg/L; pH = 4).

It was proved that though both operational forms of the ion exchanger can be used for removal of the studied metal ions, they can also be successfully applied for collective separation of the above-mentioned ions from the chloride streams. However, as for the multicomponent solution of Cu(II), Zn(II) and Ni(II), the disodium form was characterized by large capacity (Table 4).

3.7. Desorption studies

The recovery and reusability of the ion exchangers are also an important parameters related to the application of sorption processes potential. In the operation practice the ion-exchange cycle proceeds until the effluent metal ion concentration is greater than the acceptable level [55]. Then the backwash, regeneration and rinse cycles are carried out to restore the ion exchanger capacity for the next ion-exchange cycle. In the case of heavy metal removal only this approach was widely used in water and wastewater treatment practice. In this study, Ni(II)-loaded Lewatit TP 260 was contacted with 1 M HCl solution in order to determine its properties in 50 cycles of sorption–desorption in the plant producing the elements with nickel coating in the system of water recovery from the sewages stream of the yield 10 m^3/h (Fig. 7(a)). The installation includes three main elementary processes: the system of membrane protection against nickel(II) ions (ion-exchange columns), nanofiltration removing the excess of anions and high-pressure reverse osmosis producing demineralized water to satisfy industrial installation requirements. After 50 cycles of sorption–desorption no damages caused by the osmotic shock were found (Fig. 7(b); similarly to Lewatit TP 207 or Lewatit TP 208) [41].

Table 4
The total ion-exchange capacities (meq/mL) for Lewatit TP 260 in the Na^+ and $2Na^+$ forms at the NaCl concentration 40 g/L (Σ denotes the sum of the capacities towards Cu(II), Ni(II) and Zn(II)) (bed volume = 10 mL; Φ = 1 cm; flow rate = 100 mL/h; $c_{cu(II)}$ = 40 mg/L, $c_{Zn(II)}$ = 40 mg/L, $c_{Ni(II)}$ = 40 mg/L; pH = 4)

Ion-exchange capacities (meq/L)				
pH	Cu(II)	Zn(II)	Ni(II)	Σ(Cu, Zn, Ni)
TP 260 in the Na^+ form				
2	0.10	0.09	0.08	0.27
4	0.52	0.37	0.19	1.08
TP 260 in the $2Na^+$ form				
2	0.10	0.09	0.10	0.29
4	0.62	0.49	0.49	1.34

Table 3
The mass (D_g) and volume (D_v) distribution coefficients as well as the working (C_w) (mg/mL) and total ion-exchange capacities (C_t) for Cu(II). Zn(II) and Ni(II) on Lewatit TP 260 in the Na^+ and $2Na^+$ forms (bed volume = 10 mL; Φ = 1 cm; flow rate = 100 mL/h; $c_{cu(II)}$ = 40 mg/L, $c_{Zn(II)}$ = 40 mg/L, $c_{Ni(II)}$ = 40 mg/L; pH = 4)

Cu(II)					Zn(II)				Ni(II)			
pH	D_g	D_v	C_w	C_t	D_g	D_v	C_w	C_t	D_g	D_v	C_w	C_t
TP 260 in the Na^+ form												
2	219.9	84.4	0.003	0.0002	206.9	79.4	0.003	0.0003	154.8	59.4	0.002	0.0003
4	1,118.9	429.4	0.022	0.0014	709.8	272.4	0.008	0.0006	493.5	189.4	0.012	0.0008
TP 260 in the $2Na^+$ form												
2	204.2	78.3	0.003	0.0032	205.4	79.2	0.002	0.0003	203.9	77.64	0.003	0.0002
4	1,301.3	499.4	0.027	0.0013	493.5	189.2	0.011	0.0006	1,027.7	394.2	0.014	0.0011

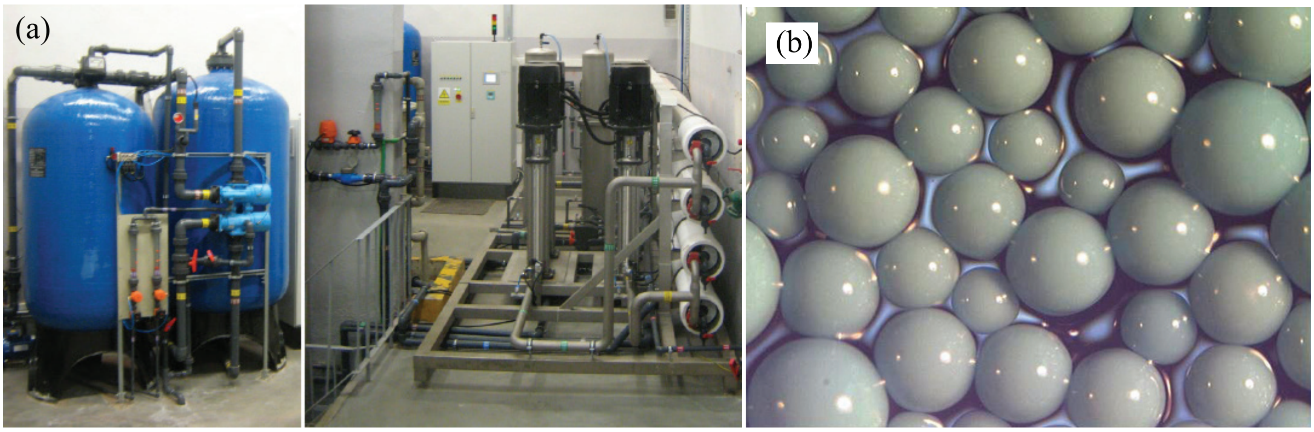


Fig. 7. Installation for water recovery with the ion exchanger protection of membranes (a), Lewatit TP 260 after 50 cycles of Cu(II) ions sorption–desorption process (ion exchanger magnification 40×) (b).

Table 5
Comparison of the heavy metal removal using sorbents with the aminophosphonate groups

Solution components	Sorbent/ion exchanger	Conditions	Sorption capacity	References
Cu(II), Zn(II) and Ni(II)	Lewatit TP 260, Na^+ form	Initial metal concentration for Cu(II), Zn(II) and Ni(II) 40 mg/L; 10 mL bed volume; Φ = 1 cm; flow rate pH = 4	34.3 mg/g	This work
	Lewatit TP 260 $2Na^+$ form		42.5 mg/g	
Ni(II)	Purolite S 950	0.01 M citric acid	18.42 mg/g	[31]
		0.1 M citric acid	14.51 mg/g	
		0.01 M malic acid	14.45 mg/g	
		0.1 M malic acid	11.83 mg/g	
		0.01 M lactic acid	19.42 mg/g	
		0.1 M lactic acid	14.82 mg/g	
Co(II)		0.01 M citric acid	5.39 mg/g	
		0.1 M citric acid	7.31 mg/g	
		0.01 M malic acid	7.54 mg/g	
		0.1 M malic acid	7.38 mg/g	
		0.01 M lactic acid	10.48 mg/g	
		0.1 M lactic acid	7.43 mg/g	
Cu(II), Ni(II), Cd(II), Zn(II), Ca(II), Na(I), NH_4^+	Purolite S 940		47.6 mg/g	[16]
	Purolite S 950		63.2 mg/g	
	Purolite D 3342		65.1 mg/g	
	Purolite D 3343		79.43 mg/g	
Pb(II)	Hydroxyapatite (HAp) Aminophosphonate modified HAP, 2.5N-HAp Aminophosphonate modified HAp, 5N-Hsp	Initial metal concentration 10–2,000 mg/L, 100 mL of solution; 200 mg of sorbent	240 440 450	[59]
Cu(II)	Cross-linked polymer CAPE 5 (cross-linked anionic polyelectrolyte)	Initial metal concentration 3.76–18.8 g/L, 20 mL of solution; 50 mg of sorbent	1,080 mg/g	[60]
Pb(II)		Initial metal concentration 6.6–33.1 g/L, 20 mL of solution; 50 mg of sorbent	1,490 mg/g	
Cu(II), Co(II) or Sr(II)	Zr(IV) phosphate-phosphonate sorbent	Initial metal concentration Cu(II) Co(II) or Sr(II) 63–381 mg/L	26 mg/g	[61]

3.8. Comparison of sorbents with the aminophosphonate groups

The aminophosphonate chelating resins are used, among others, in the process of Th^{4+}, Fe^{3+} and UO_2^{2+} ions separation from alkali and alkali earth elements as well as lanthanides. In reference [56], removal of uranium(VI) ions from the acetate medium in the aqueous solution was investigated using Lewatit TP 260. Moreover, in reference [57], the aminophosphonate ion exchanger Duolite ES 467 was used to investigate the effectiveness of cadmium ions removal from aqueous solutions. In a study by Virolainen et al. [58] it was found that the controlled neutralization to replace H^+ in the acidic phosphonium groups with Na^+ ions enhanced metal ions sorption and helped avoid the undesired pH changes during the metal separation process. Additionally, the comparison of the obtained results with those, reported in the literature, is presented in Table 5. However, the sorption effectiveness is difficult to compare not only due to the lack of the data (pH, sorption concentration range, etc.) but also due to different sorption mechanism.

4. Conclusions

Based on the high sorption rate and capacity, Lewatit TP 260 was found to be a suitable alternative sorbent for the other commercial ion-exchange resins for the removal of metal ions from acidic wastewater effluents. Batch sorption experiments showed that the sorption of Cu(II), Zn(II) and Ni(II) ions onto the aminophosphonate resin was dependent on the ion-exchange form, phase contact time and pH. The sorption data was found to follow the PSO kinetic model suggesting the chemisorption behaviour of metal ions on Lewatit TP 260. The IPD model suggested that the sorption process was dominated by the external mass transfer of Cu(II), Zn(II) and Ni(II) ions to the surface of the selected ion exchanger. Ion-exchange process using Lewatit TP 260 due to its effectiveness, availability, low operating cost, flexibility and simplicity in design and operation can be proposed as an alternative method for heavy metal ions removal at low pH values.

Symbols

c_0 — Initial concentration of metal ion, mg/L
c_t — Concentration of metal ion at time t, mg/L
C — The intercept which reflects the boundary layer effect
h — Initial rate of sorption, mg/g min
k_1 — Rate constant of PFO sorption, min^{-1}
k_2 — Rate constant of PSO sorption, g/mg min
k_i — Intraparticle diffusion rate constant, mg/g $\text{min}^{0.5}$
m — Mass of ion exchanger, g
m_j — Dry ion exchanger mass, g
q_t — Amount of metal ion sorbed at time t on ion exchanger, mg/g
q_e — Amount of metal ion sorbed at the equilibrium on ion exchanger, mg/g
V — Volume of the solution, L
$\overline{V}$ — Volume of effluent at c=c0/2 (determined graphically), mL
V_0 — Dead volume in the column (liquid volume in the column between the bottom edge of ion exchanger bed and the outlet), L
V_i — Void (interparticle) ion exchanger bed volume which amounts to ca. 0.4 of the bed volume, mL
V_e — Effluent volume to the break point, L
V_j — Bed volume, mL

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