



# Evaluation of heavy metal ions removal from acidic waste water streams

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## HIGHLIGHTS

- Iminodiacetate resins were used for heavy metals (HM) ions removal from solutions.
- The sorption was favoured at pH range of 4.0–7.0 and high concentrations of NaCl.
- Recommendation to use Lewatit TP 207 and Lewatit TP 208 as effective ion exchangers was made.

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## ABSTRACT

This study presents some purification processes of acidic waste streams including such heavy metals as Cu(II), Zn(II) and Ni(II) in the low and adjusted pH range as well as high NaCl concentrations, which are typical industrial conditions. A novel approach to the assembly of previously used processes skips the step of pH adjustment of the treated waste streams, which further reduces maintenance costs of waste streams.

The study was conducted using macroporous ion exchange resins based on the polystyrene–divinylbenzene matrix: Lewatit TP 207 and Lewatit TP 208 – the chelating ion exchangers with the iminodiacetate functional groups and the medium base anion exchange resin Lewatit MonoPlus MP 64 with the quaternary ammonium and tertiary amine functional groups. Ion exchangers are characterized by high resistance to osmotic shock. The macroporous structure provides an ideal diffusion of Cu(II), Zn(II) and Ni(II), allowing the efficient exhaustion and regeneration. Beside the commercial form, Lewatit TP 207 and Lewatit TP 208 were used in the mono- and disodium forms.

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## 1. Introduction

Due to the increasing deterioration of the environment, European industry is forced to run its business in a manner least disruptive to the surroundings [1]. A major threat to the environment constitute such contaminants as heavy metal ions. Their sources include metal finishing industry, where electrochemical methods are used. In recent years, there has appeared a trend towards elimination of certain heavy metal ions in these processes [2], but this is not always possible due to the lack of alternative technologies. In this case one can only do the activities eliminating hazardous chemicals from waste streams and recycle them [3,4]. In purification of waste waters from metal surface treatment by electrochemical methods the ion exchange method one is of significant importance.

Natural inorganic exchangers such as zeolites, oxides and clay minerals have wide applications especially in treatment of nuclear wastes due to their resistance to decomposition in the presence of ionizing radiation or at high temperatures. They are also characterized by high selectivity towards certain ions therefore they may be suitable for certain hydrometallurgic applications [5–7]. However, waste water treatment technologies generally apply macroporous ion exchangers [8] with the functional groups characterized by chelating properties. The use of chelating resins allows for selective removal of metal ions from waste streams [9]. Selective ion exchange considerably increases the ion exchange capacity due to the fact that the active sites are filled only by specific (not selected) metal ions without unnecessary ballast. The additional advantages of ion exchange include the possibility of recovering valuable metal ions, low amounts of sludge formation and the ability to reach the limit for discharge, small footprint and low installation costs or the concentration factor larger than 200 [10]. For example by using sulfuric acid as regenerating solution copper

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can be directly recovered by electrowinning (at the same time the regenerant acid is recovered). In default of electrowinning the spent regenerant has to be treated by precipitation, but to a much smaller extent than when precipitation is a stand-alone treatment.

The ion exchange method using ion exchange resins is usually used for low and medium levels of metal ions, while extraction is used for medium and high concentrations of metal ions. The combination of both techniques allows for the recovery of metal ions over a range of concentrations. Extraction processes are high-speed ones not requiring a large area for apparatus, but ion exchange techniques require much larger equipment (due to much lower reaction kinetics) [11]. An attempt to avoid these disadvantages is the use of impregnated resins (SIRs) with suitable extractants [12]. In some applications it is possible to use ion exchange resins in the form of fibers, which are characterized by very high ion exchange kinetics due to a large surface area of contact interface [13,14]. Therefore a potential area of fibrous ion exchangers are wastewater treatment processes. So far this method has been in the initial stage of investigations. Numerous studies have been carried out on the removal of metal ions from solutions using strongly acidic cation exchangers (SAC) and chelating ion exchangers [15–17].

This paper presents the possibility of removal from acidic waste streams (such as spent bathing, washing effluents or spent hydrochloric acid from metal etching) of heavy metal ions in the low, deliberately not corrected pH and often high concentrations of NaCl. These conditions are found in industry. To this end the weakly acidic ion exchangers (WAC) were used. There is a clear change in the approach compared to the previous assumptions, since the currently accepted procedures usually require the preliminary, more expensive stage of adjusting the acidity of solutions to the pH range from 1 to 5 or from 9 to 10, causing precipitation of metals [18]. Additionally, the neutralization equipment and supplies must be available. Moreover, it should be also mentioned that some waste waters for example containing cyanides cannot be neutralized because of the possibility of generation of toxic fumes, for example hydrogen cyanide. On the other hand, using NaOH the equilibrium pH control is difficult and over neutralization to pH 13 is possible or using HCl the acid forms a very corrosive mist [19,20].

Preventing from such a phenomenon as well as eliminating one of the stages in the existing technologies, selection of appropriate and stable ion exchangers, checking their resistance to osmotic shock and examination of their selectivity in the process of Cu(II), Zn(II) and Ni(II) separation was proposed. It should be emphasized that in view of the applicable character of the obtained results, the commercially available ion exchange resins were selected to this end. They are characterized by high affinity for divalent metal ions and a much higher capacity than SAC.

## 2. Experimental

### 2.1. Materials and solutions

The following polystyrene–divinylbenzene (PS–DVB) ion exchangers, produced by Lanxess, Germany, were used in the investigations: Lewatit TP 207, Lewatit TP 208 and Lewatit MonoPlus MP 64. Brief characteristics of these chelating resins is presented below and their detailed properties are given in Table 1.

*Lewatit TP 207* is a weakly acidic, macroporous cation exchange resin with the iminodiacetate functional groups used for the selective sorption of heavy metal cations from aqueous solutions, the total ion exchange capacity of 2.2 meq/cm<sup>3</sup>, the particle size of 0.4–1.25 mm and the thermal stability of up to 313 K.

*Lewatit TP 208* is a weakly acidic, macroporous cation exchange resin with the iminodiacetate functional groups used for the selective extraction of heavy metal cations from aqueous solutions, the total ion exchange capacity of 2.9 meq/cm<sup>3</sup>, the particle size of 0.4–1.25 mm and the thermal stability of up to 313 K.

*Lewatit MonoPlus MP 64* is a medium base anion exchange resin with the quaternary ammonium and tertiary amine functional groups. It is recommended by the manufacturer for the selective removal of alkaline earth metals from industrial effluents, the total ion exchange capacity of 1.3 meq/cm<sup>3</sup>, the particle size of 0.59 ± 0.05 mm and the thermal stability of up to 313 K.

Prior to their use they were washed with NaOH and HCl (7.5% in an amount of 140 g per 1000 cm<sup>3</sup>) to remove organic and inorganic impurities and then washed several times with deionized water. The resins were finally converted to the appropriate form. In order to obtain the monosodium and disodium forms, 100 cm<sup>3</sup> of the ion exchanger samples were shaken for 2 h with 160 cm<sup>3</sup> or 320 cm<sup>3</sup> of 4% sodium hydroxide solution, respectively. The amount of NaOH solution was selected based on the manufacturer's data. After that the resins were washed with deionised water.

Copper(II), zinc(II) and nickel(II) salts (POCH, Poland) of analytical grade were used. The stock solutions (1 × 10<sup>−2</sup> M) of the above-mentioned ions were prepared by dissolving the exact quantity of respective salts in distilled water. The stock solutions were further diluted to the required experimental concentration. The other chemicals used were of analytical grade.

### 2.2. Static (batch) studies

The static tests were carried out to obtain the sorption percentage (%S) of Cu(II), Ni(II) and Zn(II) ions for Lewatit TP 207, Lewatit TP 208 and Lewatit MonoPlus MP 64, depending on the phase contact time, pH, concentration of NaCl and the operational form of ion exchanger. The studies were carried out in 250 cm<sup>3</sup> shake flasks, placed in an orbital thermostatted shaker allowing to achieve 250 rpm (ELPHINE type 357, Poland). To a dry flask 2 g of the ion

**Table 1**

Detail characteristic of the Lewatit TP 207, Lewatit TP 208 and Lewatit MonoPlus MP 64.

Properties	Lewatit TP 207	Lewatit TP 208	Lewatit MonoPlus MP 64
Matrix	PS–DVB macroporous	PS–DVB macroporous	PS–DVB macroporous
Functional groups	–CH <sub>2</sub> N(CH <sub>2</sub> COOH) <sub>2</sub>	–CH <sub>2</sub> N(CH <sub>2</sub> COOH) <sub>2</sub>	–N <sup>+</sup> R <sub>3</sub> /–NR <sub>2</sub>
Physical form	Opaque, white	Opaque, white	Opaque, white
Ionic form as shipped	Na <sup>+</sup>	Na <sup>+</sup>	Free base
Beads size mm	0.4–1.25	0.4–1.25	0.59 ± 0.05
Total exchange capacity	2.2	2.9	1.3
Moisture holding capacity (%)	53–58	55–60	61–66
Shipping weight (±5%) (g/dm <sup>3</sup> )	720	790	660
Uniformity coefficient	1.7	1.8	1.04
Swelling Na <sup>+</sup> > H <sup>+</sup> (%)	30	40	n.a.
pH range	0–14	0–14	0–14
Maximum temperature (K)	313	313	313

n.a. – not available

exchanger was weighed and 100 cm<sup>3</sup> of the aqueous phase containing a mixture of metal ions at a concentration of  $1 \times 10^{-4}$  M was added and the concentration of sodium chloride in the range 0.5–40 g/cm<sup>3</sup>. The pH value was adjusted by 1 M HCl or 1 M NaOH. The samples were shaken at 298 K in the interval of 0–3600 s in a temperature controlled shaker. Preliminary tests showed that the adsorption was complete before 1 h. Therefore, in the next step an appropriate amount of the aqueous phase was collected and the contents of metal ions were analysed using the atomic absorption spectrometry technique (AAS). 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.

### 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 cm<sup>3</sup> of the swollen ion exchanger in the appropriate form placed in the glass column with a diameter of 1 cm. The concentrations of the above-mentioned ions were established as 40 mg/dm<sup>3</sup>. The liquid phase flow rate was set at 100 cm<sup>3</sup>/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 used ion exchangers were devoid of grain fractions <0.2 mm. The eluate was collected in fractions of 10 cm<sup>3</sup> and analysed by AAS.

### 2.4. Analytical procedure

An atomic absorption spectrometer SpectraAA-FS 240 (Varian, Australia) was used for quantitative determination of the concentration of Cu(II) and Zn(II). The AAS was equipped with a deuterium lamp, background correction, hollow cathode lamps for Cu, Ni and Zn and an air-acetylene burner.

### 2.5. Calculations

#### 2.5.1. Sorption percentage

The sorption percentage factor was calculated from the equation:

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

The resin phase concentrations of metal ions at equilibrium,  $q_e$  (mg/g) and at time  $t$ ,  $q_t$  (mg/g) were obtained according to:

$$q_e = (c_0 - c_e) \times \frac{V}{m} \quad (2)$$

$$q_t = (c_0 - c_t) \times \frac{V}{m} \quad (3)$$

where  $c_0$  – the initial concentration of M(II) in the aqueous phase (mg/dm<sup>3</sup>);  $c_t$  – the concentration of M(II) in the aqueous phase at time  $t$  (mg/dm<sup>3</sup>);  $c_e$  – the concentration of M(II) in the aqueous phase at equilibrium (mg/dm<sup>3</sup>);  $V$  – the volume of the solution (dm<sup>3</sup>);  $m$  – the mass of the ion exchanger (g).

#### 2.5.2. Kinetic parameters

The sorption kinetic parameters for the studied systems were determined by using:

- (a) the Lagergen kinetic equation, i.e. the pseudo first order (PFO) [21,22]:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1 t}{2.303} \quad (4)$$

where  $k_1$  – the rate constant of PFO sorption (1/min);

- (b) the Ho and McKay kinetic equation, i.e. the pseudo second order (PSO) [23,24]:

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2} \quad (5)$$

where  $k_2$  – the rate constant of PSO sorption (g/mg min).

- (c) the Weber–Moriss kinetic equation, i.e. the intraparticle diffusion model (IPD) [25,26]:

$$q_t = k_i t^{1/2} + C \quad (6)$$

where  $k_i$  – the intraparticle diffusion rate constant (mg/g min<sup>0.5</sup>),  $C$  – the intercept which reflects the boundary layer effect.

#### 2.5.3. Distribution coefficients

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 procedure presented below [27,28]:

$$D_g = \frac{\bar{V} - (V_0 - V_i)}{m_j} \quad (7)$$

$$D_v = \frac{\bar{V} - (V_0 - V_i)}{V_j} \quad (8)$$

$$C_w = \frac{V_e c_0}{V_j} \quad (9)$$

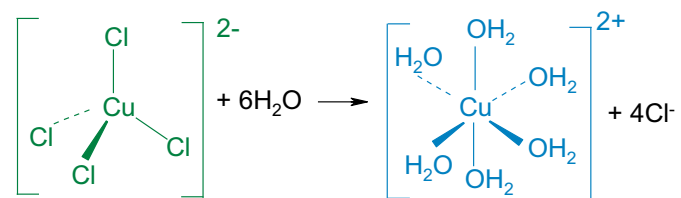
where  $\bar{V}$  – the volume of effluent at  $c = c_0/2$  (determined graphically) (cm<sup>3</sup>);  $V_0$  – the dead volume in the column (liquid volume in the column between the bottom edge of the ion exchanger bed and the outlet) (cm<sup>3</sup>);  $V_i$  – the void (interparticle) ion exchanger bed volume which amounts to ca. 0.4 of the bed volume (cm<sup>3</sup>);  $m_j$  – the dry ion exchanger mass (g),  $V_e$  – the effluent volume to the break point (dm<sup>3</sup>);  $c_0$  – the initial concentration of M(II) solution (g/dm<sup>3</sup>) and  $V_j$  – the bed volume (cm<sup>3</sup>).

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

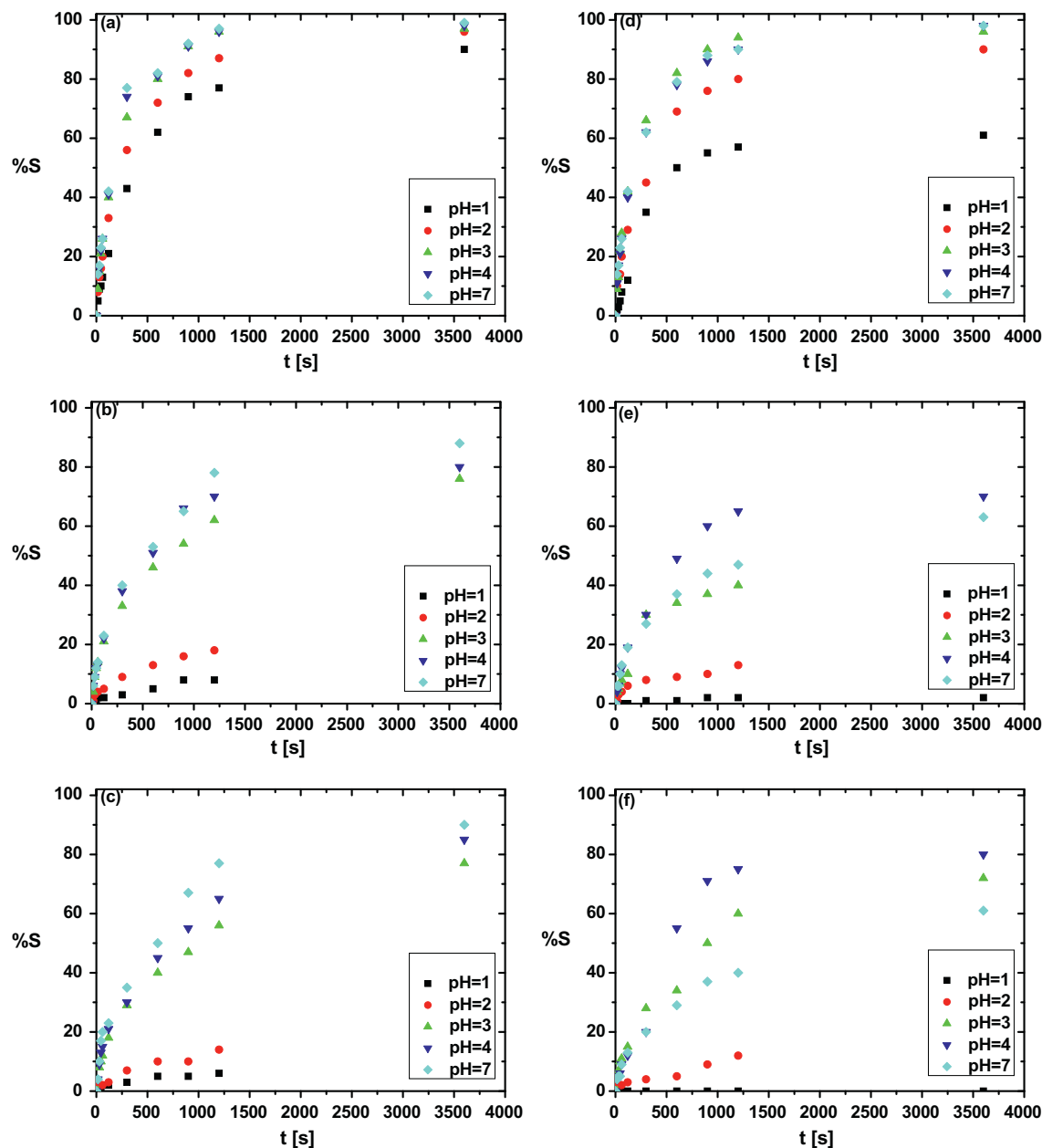
## 3. Results and discussion

### 3.1. Types of chlorine complexes

Similar to platinum metal ions, copper(I) ions form strong complexes with chloride ions while with copper(II) forms rather weak chloride complexes in solution. In the aqueous system from  $10^{-4}$  to  $10^{-6}$  M concentration of copper(II) and 0.2 and 1.5 M for chlorides they can be as follows [29–31]:  $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2(\text{s})$ ,  $\text{CuCl}_{(\text{aq})}$ ,  $[\text{CuCl}_2]^-$ ,  $[\text{CuCl}_3]^{2-}$ ,  $[\text{CuCl}]^+$ ,  $\text{CuCl}_{2(\text{aq})}$ ,  $[\text{CuCl}_3]^-$  and  $[\text{CuCl}_4]^{2-}$ . There is a significant geometrical difference between the hexaaquacopper(II) and tetrachlorocopper(II) complexes:



These two complexes also differ in complex sphere charges: the aquacomplex is doubly positively charged, while the chlorocomplex is doubly negative (consequently, the solutions of these two complexes differ in colour). However, the structure of the chloride complexes of copper(II) is still an open question due to the fact that



**Fig. 1.** Comparison of the sorption effectiveness of Cu(II) (a), Zn(II) (b) and Ni(II) (c) in the presence 0.5 g/dm<sup>3</sup> (a–c) and 20 g/dm<sup>3</sup> (d–f) of NaCl on Lewatit TP 207 in the H<sup>+</sup> form depending on pH.

the structural data were obtained for crystalline chlorocomplexes, for example for  $[\text{CuCl}_4]^{2-}$  with the coordination number 4, and rarely for  $[\text{CuCl}_5]^{3-}$  or as a dimer or polymers. It was found that the stability constants for the  $[\text{CuCl}_i]^{(2-i)+}$  complexes are equal to  $\beta_1 = 9.6 \pm 0.5$ ,  $\beta_2 = 4.92 \pm 0.5$ ,  $\beta_3 = 3.52 \pm 0.3$  and  $\beta_4 = 1.0 \pm 0.5$ , where  $\beta = \frac{[\text{CuCl}_i^{(2-i)+}]}{[\text{Cu}^{2+}][\text{Cl}^-]^i}$ ,  $i = 1, 2, 3, 4$  [32,33]. Compared to the chlorocomplexes of Co(II), Ni(II) and Zn(II) the stability constants decrease in the order: Cu(II) > Co(II) > Ni(II) > Zn(II) (for the  $\text{MCl}^+$  species) [34,35].

As follows from the literature data in the case of application of the ion exchanger resins such as Wofatit L-150, a small sorption of copper chloride complexes in the presence of sodium(I) or calcium(II) chlorides was observed. In this case the mechanism is not clearly described (it can be exchange of the chloride ions for preformed chlorocomplexes). The sorption from the mixture of hydrochloric acid-lithium(I) chlorate solutions has

been interpreted in terms of the formation of undissociated  $\text{HClCl}_4$  ions in the aqueous phase. The ratio of  $\text{CuCl}_4^{2-}$  to total Cu(II) ions concentration in 6 M LiCl is equal to 13%. The sorption of Cu(II) from HCl solutions indicates that there are formed the following species:  $[\text{CuCl}]^+$ ,  $[\text{CuCl}_3]^-$  and  $[\text{CuCl}_4]^{2-}$ . Copper(II) chlorides can be sorbed on a weak basic anion exchanger from acetone or dimethylformamide solutions due to complex formation with the resin functional groups [36]. The sorption from organic aqueous hydrochloric acid solutions (especially from acetone, then ethanol and isopropanol) was found to be much larger than from pure aqueous hydrochloric acid.

Zinc(II) also forms rather weak complexes with chloride ions, although somewhat stronger than those of e.g. Co(II) and Cu(II). They can be as follows:  $[\text{ZnCl}]^+$ ,  $\text{ZnCl}_2$ ,  $[\text{ZnCl}_3]^-$  and  $[\text{ZnCl}_4]^{2-}$ . Contrary to copper(II), nickel(II) forms chloride complexes in concentrated solutions more readily [37–40]. It was found that in 1 M nickel(II)–calcium(II) chloride–nitrate(V) solution the  $[\text{NiCl}]^+$

species are formed ( $\log \beta = -0.66$ ) [37], whereas in the 0.69 M perchloric–hydrochloric acid media the  $[\text{NiCl}]^+$  ( $\log \beta = 0.23$ ) and  $\text{NiCl}_2$  are formed ( $\log \beta = -0.04$ ) [38]. It was also found that tetrahedral complexes, e.g.  $[\text{NiCl}_3(\text{H}_2\text{O})]^-$  and/or  $[\text{NiCl}_4]^{2-}$ , are formed at high temperature and high salinity [41]. Moreover, Liu et al. [42] stated that  $[\text{NiCl}]^+$  and  $\text{NiCl}_2$  are the dominant species up to 523 K, with a small amount of  $[\text{NiCl}_3]^-$  present above 423 K at high salt concentrations. Therefore, nickel is not sorbed on anion exchangers from hydrochloric and lithium solutions even in the case of the resins with high cross linkage (16% or 24% DVB). This suggests that anionic complexes are not formed in aqueous hydrochloric acid or lithium chloride solutions. Similarly, the addition of ethanol to the system does not improve the sorption efficiency. However, in 95% isopropanol–2 M HCl and in 96% acetone–0.05–0.1 M HCl systems the distribution coefficients equal to 100 and 1000 are obtained.

### 3.2. Effect of the phase contact time, pH and NaCl concentration

Application of the batch or static equilibrium technique at different phase contact times is one of the most important controlling factors commonly used in order to evaluate the kinetics of adsorption processes and to determine metal sorption capacity values. In this section, several phase contact times (0, 15, 30, 60, 120, 300, 600, 900, 1200 and 3600 s) were used to evaluate the sorption efficiency of Lewatit TP 207, Lewatit TP 208 and Lewatit MonoPlus MP 64 for Cu(II), Zn(II) and Ni(II) ions in the chloride ion media. The effects of pH (1, 2, 3, 4 and 7), NaCl concentration (0.5, 5, 10, 20, 40 g/dm<sup>3</sup>) as well as the operational form of the ion exchangers were also studied. The results obtained for Lewatit TP 207 and Lewatit MonoPlus MP 64 in the commercial forms are presented in Figs. 1 and 2. Additionally, the results obtained for Lewatit TP 207 and Lewatit TP 208 in the monosodium and disodium forms are presented as Supplementary material (Figs. 1–10S).

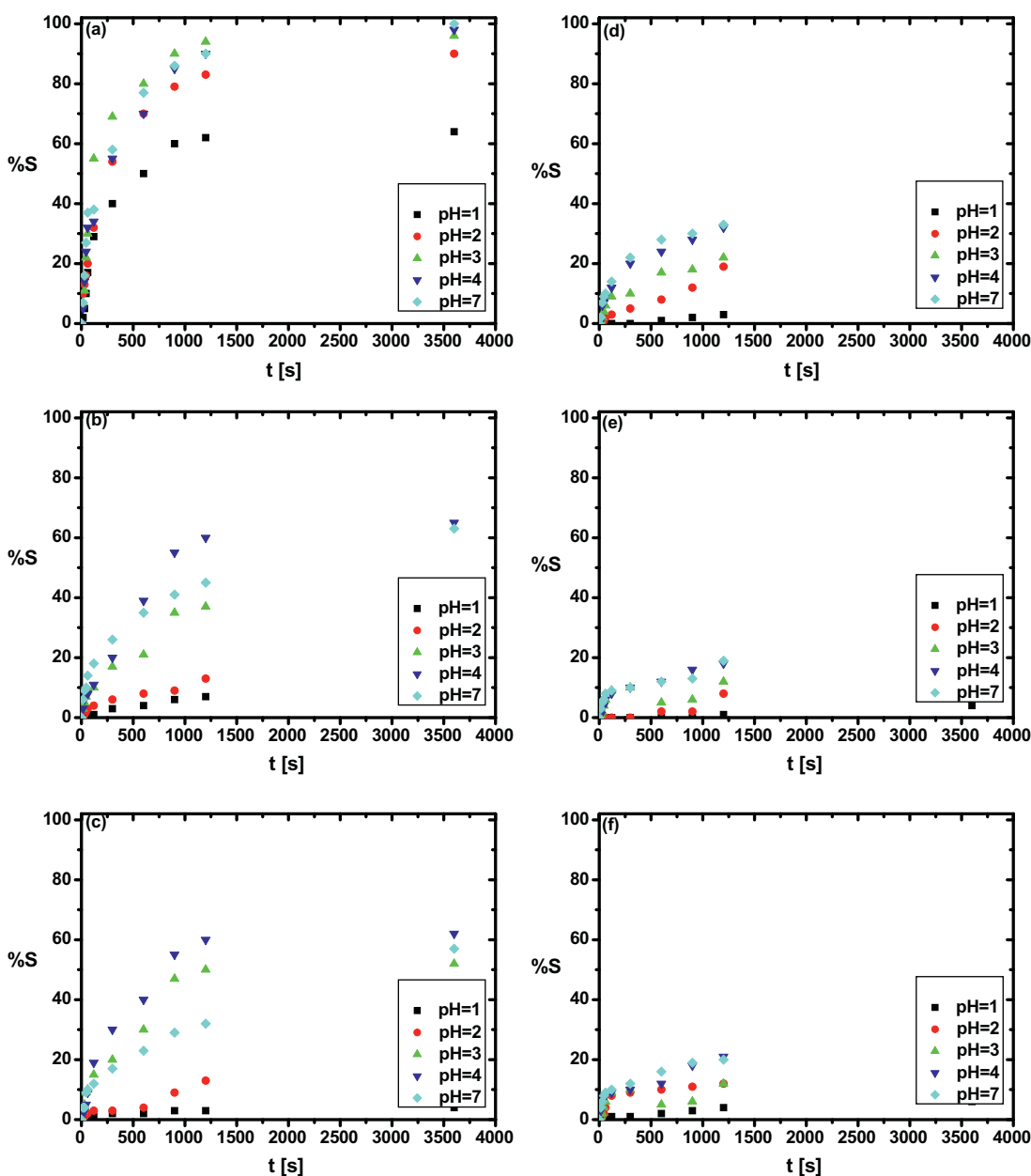


Fig. 2. Comparison of the sorption effectiveness of Cu(II) (a, d), Zn(II) (b, e) and Ni(II) (c, f) in the presence 40 g/dm<sup>3</sup> of NaCl on Lewatit TP 207 in the H<sup>+</sup> form (a–c) and Lewatit MonoPlus MP 64 in the Cl<sup>−</sup>/OH<sup>−</sup> form (d–f) depending on pH.

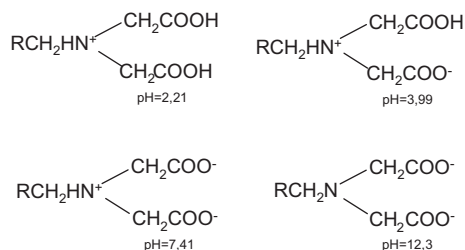


Fig. 3. The form of the iminodiacetate functional groups depending on pH.

It is well known that in the case of metal aqua ions sorption on the ion exchangers no removal by the resin phase can be observed in at pH lower than 2, most likely due to a high  $\text{H}^+$  ion concentration and repulsion of  $\text{M}(\text{II})$  from the positively charged surface of the resin as the result of the protonation of active functional groups [43]. In the range of 2–4 the  $\text{H}^+$  ions compete with the metal ions for the functional groups. However, at pH greater than 5 the precipitation of metal ions can begin, however, this process depends on the solution composition. In the pH range of 6–9, the precipitation is the predominant mechanism of metal ions removal. A different situation was observed in the studied system. Depending on the pH, the iminodiacetate functional groups of the ion exchangers Lewatit TP 207 and Lewatit TP 208 can occur in

different forms, which are presented in Fig. 3. In solutions with the pH value of about 2 (or less) both carboxylic groups as well as the nitrogen atom occur in the protonated form. As a result, the chelating ion exchanger can behave as a weakly basic anion exchanger. At higher pH (~12) both carboxylic groups are deprotonated and the ion exchanger can behave as a typical cation exchanger [44,45]. However, at the intermediate pH values, the resin behaves as an amphoteric one. Under such conditions nitrogen is protonated and at least one of the carboxylic groups is dissociated. For this type of ion exchanger attention should also be paid to the possibility of coordination bonds formed with metal ions from the solutions of high sodium chloride concentration and a wide spectrum of pH values. This is possible due to the presence of a nitrogen donor atom with a lone pair of electrons [46,47].

Sorption of  $\text{Cu}(\text{II})$ ,  $\text{Zn}(\text{II})$  and  $\text{Ni}(\text{II})$  from the chloride system depends on the pH of the solutions and their concentrations and displays a maximum at pH 4 and 7 (Figs. 1 and 2 and Figs. 1–10S). The degree of  $\text{Cu}(\text{II})$ ,  $\text{Zn}(\text{II})$  and  $\text{Ni}(\text{II})$  sorption from the solutions containing NaCl increased with increasing their concentrations from 0.5 to 40  $\text{mg}/\text{dm}^3$ . Moreover, in the case of the solutions with constant chloride ions concentration (0.5, 5, 10, 20, 40  $\text{g}/\text{dm}^3$ ) the sorption percentage of metal ion increases from 44.8% at pH 1 to reach the maximum at pH 7 (99.0%). Further increase of pH can cause the precipitation of metal ions. It is evident for Lewatit TP 207 in the  $\text{H}^+$  form, where in the range of

Table 2

Kinetic parameters for the  $\text{Cu}(\text{II})$ ,  $\text{Zn}(\text{II})$  and  $\text{Ni}(\text{II})$  on Lewatit TP 207 in the  $\text{H}^+$ ,  $\text{Na}^+$  and  $2\text{Na}^+$  forms (pH 4.0, NaCl concentration 0.5–40  $\text{g}/\text{dm}^3$ ).

$\text{Cu}(\text{II})$					$\text{Zn}(\text{II})$				$\text{Ni}(\text{II})$			
$\text{C}_{\text{NaCl}}$	$q_2$	$k_2$	h	$R^2$	$q_2$	$k_2$	h	$R^2$	$q_2$	$k_2$	h	$R^2$
<i>TP 207 in the <math>\text{H}^+</math> form</i>												
0.5	0.26	1.34	0.086	0.9666	0.12	5.28	0.076	0.9000	0.17	0.56	0.085	0.8351
5	0.26	1.28	0.084	0.9649	0.12	4.01	0.061	0.9287	0.16	0.54	0.084	0.9840
10	0.26	1.25	0.082	0.9622	0.12	4.01	0.060	0.9257	0.15	0.49	0.080	0.9388
20	0.24	1.21	0.083	0.9629	0.12	3.78	0.062	0.9150	0.11	0.56	0.081	0.9072
40	0.24	1.20	0.075	0.9244	0.11	4.09	0.063	0.9610	0.16	0.54	0.083	0.9878
<i>TP 207 in the <math>\text{Na}^+</math> form</i>												
0.5	0.27	1.51	0.104	0.9799	0.28	1.09	0.079	0.9707	0.24	0.40	0.122	0.9721
5	0.27	1.48	0.097	0.9815	0.28	0.99	0.076	0.9784	0.24	0.43	0.126	0.9765
10	0.26	1.44	0.106	0.9795	0.27	1.02	0.074	0.9739	0.24	0.41	0.122	0.9744
20	0.26	1.32	0.100	0.9836	0.27	1.05	0.072	0.9735	0.26	1.13	0.075	0.9769
40	0.27	1.32	0.096	0.9823	0.27	1.04	0.071	0.9755	0.22	0.32	0.137	0.9775
<i>TP 207 in the <math>2\text{Na}^+</math> form</i>												
0.5	0.26	1.61	0.113	0.9752	0.27	1.88	0.113	0.9727	0.24	1.61	0.097	0.9729
5	0.26	1.47	0.101	0.9669	0.26	1.72	0.101	0.9719	0.24	1.53	0.094	0.9685
10	0.25	1.85	0.119	0.9668	0.25	1.67	0.108	0.9728	0.23	1.77	0.086	0.9703
20	0.11	2.96	0.035	0.9452	0.08	1.70	0.012	0.9204	0.25	1.18	0.085	0.9554
40	0.17	1.33	0.040	0.9300	0.12	1.59	0.027	0.9300	0.24	1.13	0.070	0.9697

Table 3

Kinetic parameters for the  $\text{Cu}(\text{II})$ ,  $\text{Zn}(\text{II})$  and  $\text{Ni}(\text{II})$  on Lewatit TP 208 in the  $\text{Na}^+$  and  $2\text{Na}^+$  forms (pH 4.0, NaCl concentration 0.5–40  $\text{g}/\text{dm}^3$ ).

$\text{Cu}(\text{II})$					$\text{Zn}(\text{II})$				$\text{Ni}(\text{II})$			
$\text{C}_{\text{NaCl}}$	$q_2$	$k_2$	h	$R^2$	$q_2$	$k_2$	h	$R^2$	$q_2$	$k_2$	h	$R^2$
<i>TP 208 in the <math>\text{Na}^+</math> form</i>												
0.5	0.27	1.57	0.116	0.9752	0.28	1.28	0.101	0.9828	0.24	1.38	0.080	0.9673
5	0.27	1.56	0.091	0.9854	0.26	1.58	0.107	0.9702	0.24	1.23	0.073	0.9672
10	0.27	1.41	0.112	0.9712	0.28	1.03	0.080	0.9710	0.24	1.36	0.081	0.9705
20	0.27	1.32	0.103	0.9819	0.27	1.11	0.082	0.9718	0.24	1.36	0.078	0.9722
40	0.27	1.22	0.098	0.9828	0.27	1.07	0.080	0.9742	0.24	1.38	0.080	0.9673
<i>TP 208 in the <math>2\text{Na}^+</math> form</i>												
0.5	0.28	1.49	0.113	0.9746	0.27	1.65	0.117	0.9758	0.24	1.71	0.099	0.9690
5	0.26	1.63	0.111	0.9721	0.26	1.58	0.107	0.9702	0.24	1.73	0.096	0.9721
10	0.27	1.56	0.112	0.9712	0.26	1.75	0.115	0.9735	0.24	1.79	0.100	0.9726
20	0.12	2.13	0.030	0.9231	0.08	2.10	0.014	0.9284	0.13	1.88	0.034	0.9275
40	0.16	1.90	0.047	0.9458	0.13	1.68	0.027	0.9432	0.09	5.45	0.048	0.9469



low concentration of sodium chloride the best kinetics was observed for pH 7, but in the case of high concentrations of sodium chloride the best kinetics was for the solutions with the initial pH equal to 4.

Sorption of metal ions onto ion exchange particles involves the following steps: (i) bulk diffusion, (ii) external mass transfer of metal ions across the external liquid film around the resin bed, (iii) binding of metal ion on the active functional group distributed on the outer surface of the resin, (iv) intraparticle diffusion of molecules into macro, meso and micropores of ion exchanger and (v) sorption of metal ions onto active sites distributed within the sorbent particles. The steps (iii) and (v) are very rapid and hence they

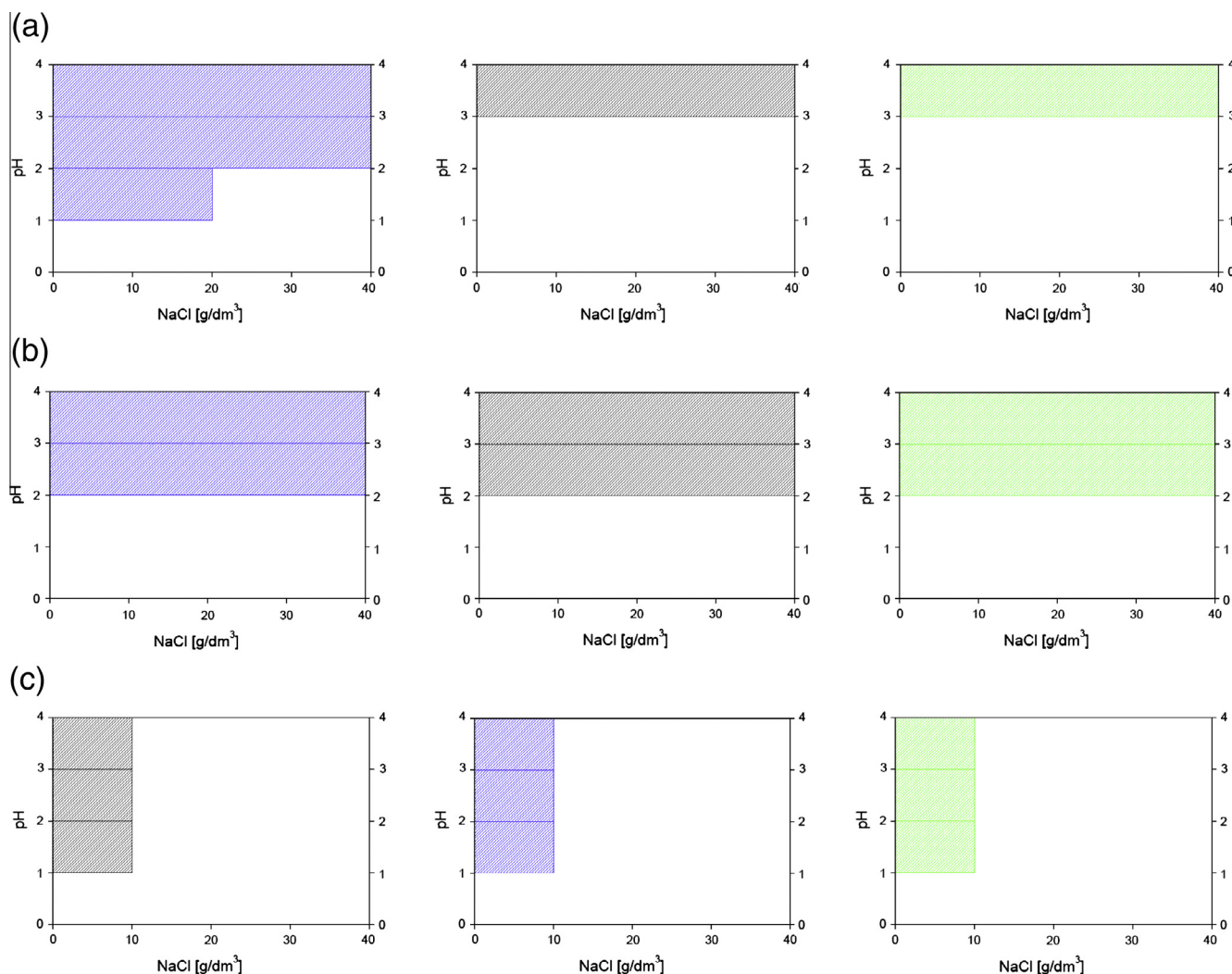
do not play a great role in determination of the rate of sorption process. Thus, only external mass transfer and intraparticle diffusion play an important role in rate determination. In order to evaluate the relative importance of these two processes, metal sorption data in the different phase contact times were processed using the intraparticle diffusion and the external mass transfer models [48,49].

From the literature data it is well-known that the pseudo first order equation (PFO) is used for sorption modelling. In this case the occupation of active sites of the functional groups is proportional to the number of unoccupied sites of the resin and assumes that the reaction rate is limited by only one process or mechanism

**Table 4**

Kinetic parameters for the Cu(II), Zn(II) and Ni(II) on Lewatit MonoPlus MP64 in the  $\text{Cl}^-/\text{OH}^-$  form (pH 4.0, NaCl concentration 0.5–40 g/dm<sup>3</sup>).

Cu(II)					Zn(II)					Ni(II)				
$C_{\text{NaCl}}$	$q_2$	$k_2$	h	$R^2$	$q_2$	$k_2$	h	$R^2$		$q_2$	$k_2$	h	$R^2$	
<i>MP64 in the <math>\text{Cl}^-/\text{OH}^-</math> form</i>														
0.5	0.11	1.57	0.116	0.9752	0.08	1.28	0.101	0.9828		0.08	1.38	0.080	0.9673	
5	0.11	1.21	0.091	0.9854	0.09	1.58	0.107	0.9702		0.08	1.23	0.073	0.9672	
10	0.11	1.56	0.112	0.9712	0.08	1.03	0.080	0.9710		0.08	1.36	0.081	0.9705	
20	0.11	1.41	0.103	0.9819	0.07	1.11	0.082	0.9718		0.08	1.36	0.078	0.9722	
40	0.11	1.32	0.098	0.9828	0.07	1.07	0.080	0.9742		0.08	1.38	0.080	0.9673	



**Fig. 4.** The useful operating range of Lewatit TP 207 in the case of the Cu(II) ions sorption (blue), Zn(II) (black) and Ni(II) (green) in the  $\text{H}^+$  (a),  $\text{Na}^+$  (b) and  $2\text{Na}^+$  (c) forms. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

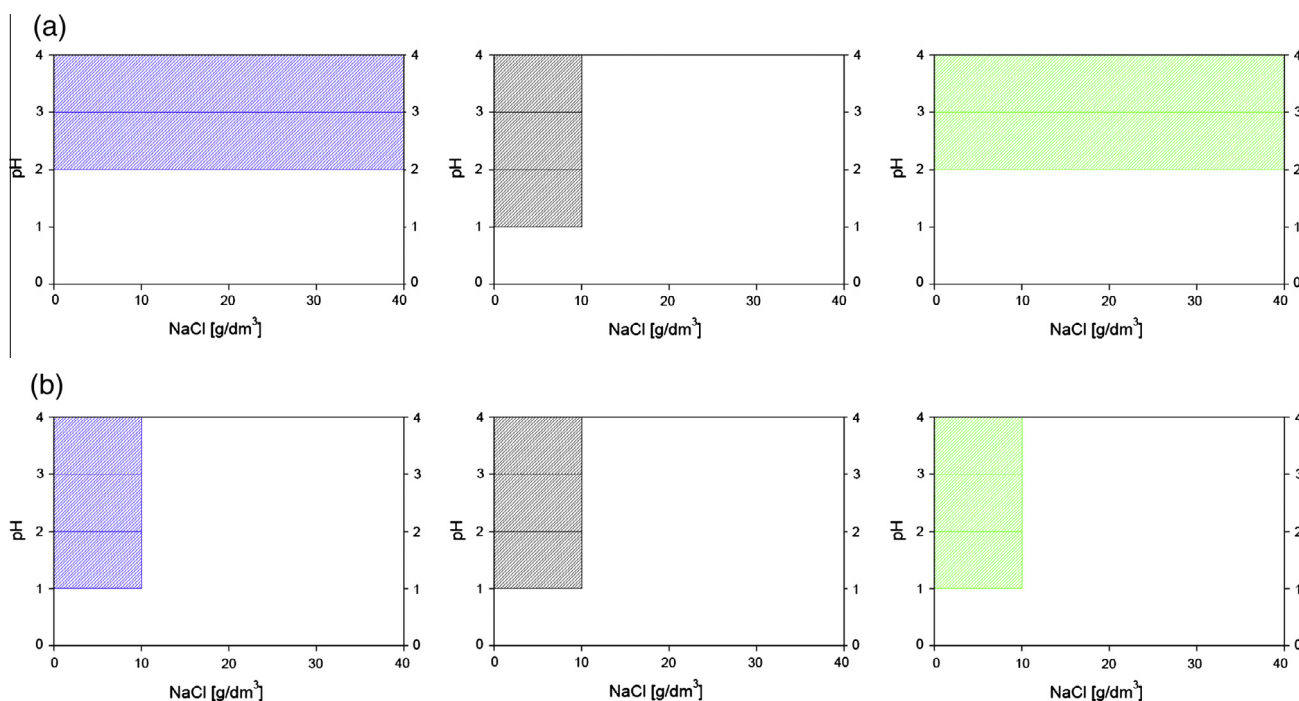
on a single class of sorbing sites and that all sites are of the time dependent type [50,51]. The parameters  $q_e$  and  $k_1$  are determined by applying the linear regression procedure for Eq. (4). On the other hand, the pseudo second order equation (PSO) can be used when the rate of occupation of active sites is proportional to the square number of unoccupied sites and the process is connected with chemisorption involving valence forces through sharing or exchanging of electrons between the adsorbent and the adsorbate. Additionally, the initial sorption rate constant ( $h$ ) is proportional to the second order rate constant ( $k_2$ ).

It was found that the estimated kinetic parameters of PFO equation for the sorption of Cu(II), Zn(II) and Ni(II) and the theoretical  $q_{e,cal}$  values found did not give reasonable values (data not presented). The  $R^2$  values for sorption in the presented systems were very low, also in the case of the fitting the experimental data within the first 1200 s. This indicates that the sorption process within this time cannot proceed by diffusion through the boundary layer and this suggests that this is not the PFO reaction. Using Eq. (5) the pseudo second order sorption rate constant ( $k_2$ ) and  $q_{e,cal}$  values were determined from the slope and intercept of the plots. The values of the parameters  $k_2$  and  $q_{e,cal}$  as well as the correlation coefficients  $R^2$  are also presented in Tables 2–4. The  $R^2$  (0.9257–0.9878) and almost equal values of  $q_{e,exp}$  and  $q_{e,cal}$  show that the data fit the pseudo second order model well. For example, for Lewatit TP 207 in the  $H^+$ ,  $Na^+$  and  $2Na^+$  forms, the pseudo second order rate constant ( $k_2$ ) decreased from 1.34 to 1.20; 1.51 to 1.32 and 1.61 to 1.32 g/mg min for Cu(II) in the case when the initial concentration of NaCl increased from 0.5 g/dm<sup>3</sup> to 40 g/dm<sup>3</sup>. This finding confirms the chemisorption of Cu(II), Zn(II) and Ni(II) onto Lewatit TP 207 and Lewatit TP 208 in the commercial form. The initial sorption rate ( $h$ ) was also observed to decrease with the increased initial NaCl concentrations. However, the amount of the metal ions sorbed on the ion exchangers is slightly affected by the NaCl addition.

As for Lewatit MonoPlus MP 64 in the  $Cl^-/OH^-$  form, a negligible sorption was observed and therefore the studies were not continued. It is well-known that in the case of Lewatit MonoPlus MP

64 metal ions should bond to the free electron pair of the nitrogen atom of the functional group of the neutral pH values. To maintain electroneutrality, equivalent amounts of anions should be co-adsorbed. Thus, there is a competition between metal ions and hydrogen ions which renders the entire adsorption strongly pH dependent. The process is also selective for Cu(II), Zn(II), Cd(II), Ni(II), Hg(II) and Pb(II). The competition and the strong preference for  $H^+$  ions is used for regeneration, which proceed at low pH values. Then the functional groups have to be neutralized by contact with alkaline solutions.

To evaluate the contribution of Cu(II), Zn(II) and Ni(II) diffusion within the resin pores, the diffusion kinetics was modelled using the Weber–Morris intraparticle diffusion. It was found that the diffusion kinetic curves exhibit two parts of the studied concentration range. The first was at 0–1200 s, which reflects the easy diffusion onto the macropores of chelating ion exchangers, and the second one above this value. The initial portion is connected with the surface sorption and rapid external diffusion (boundary layer diffusion). The second linear portion is a high and gradual sorption stage where the intraparticle diffusion is the controlling mechanism [52]. The existence of the gradual portion (that does not pass through the origin) indicates that there is some degree of boundary layer control and suggests that the intraparticle diffusion is not the only controlling mechanism. By increasing initial NaCl concentration, the boundary layer thickness value ( $C$ ) was increased which indicated the enhancement of mass transfer resistance through the boundary layer. The first linear portion with a short sorption period of 0–1200 s indicates that the outer diffusion was involved at the early stage of sorption. The values of the boundary layer thickness in the first stage were in the range: 0.0206–0.0251 for Cu(II), 0.0233–0.0292 for Zn(II) and 0.019–0.022 for Ni(II) sorption on Lewatit TP 207 in the  $H^+$  form. For the  $Na^+$  and  $2Na^+$  form of this ion exchanger they are as follows: 0.024–0.027 for Cu(II), 0.019–0.026 for Zn(II) and 0.024–0.026 for Ni(II) and 0.0228–0.0298 for Cu(II), 0.0202–0.0301 for Zn(II) and 0.023–0.0251 for Ni(II), respectively. It was also shown that the intercept increases with the increasing NaCl concentration which suggests that for the larger



**Fig. 5.** The useful operating range of Lewatit TP 208 in the case of the Cu(II) ions sorption (blue), Zn(II) (black) and Ni(II) (green) in the  $Na^+$  (a) and  $2Na^+$  (b) forms. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



values of concentration, the boundary layer effect will be larger. Moreover, for both chelating resins Lewatit TP 207 and Lewatit TP 208, the intraparticle diffusion constant  $k_i$  values for Cu(II), Zn(II) and Ni(II) decrease with the increase of NaCl concentration from 0.066 mg/g min<sup>1/2</sup> to 0.023 mg/g min<sup>1/2</sup>, 0.058 mg/g min<sup>1/2</sup> to 0.019 mg/g min<sup>1/2</sup> and 0.054 mg/g min<sup>1/2</sup> to 0.012 mg/g min<sup>1/2</sup>, respectively.

However, the Weber–Morris intraparticle diffusion model was determined to be not quite a suitable diffusion model with the medium values of  $R^2$ . Moreover, with an increase in the initial concentration of NaCl they better fit the second portion of the curve (>1200 s).

Taking into account the effect of the form of the ion exchanger, no significant change of sorption kinetics was found for the ion exchanger Lewatit TP 207 in the H<sup>+</sup> form in the case of Cu(II) ions sorption for the pH range 2–7. Also, no significant negative effect of NaCl concentration increase on the process kinetics was observed, which is confirmed by the obtained  $q_{e,cal}$  values. As mentioned earlier, a significant decrease in the kinetics of Cu(II) ions sorption for extremely low values (pH 1) and the NaCl concentration 20 g/dm<sup>3</sup> and 40 g/dm<sup>3</sup> was found. Insignificant kinetics of sorption capacity of Zn(II) and Ni(II) ions with the low pH values 1–2 was found in the whole range of sodium chloride concentration. The obtained results indicate the possibility of applying the ion exchange TP 207 in the H<sup>+</sup> form for removal of Cu(II) ions from the acid brine solutions of pH 2. Moreover, application of the H<sup>+</sup> form enables separation of Cu(II) ions from Ni(II) and Zn(II) ions at low pH values (Fig. 4a).

For the same ion exchanger but in the monosodium (Na<sup>+</sup>) form no significant change in the kinetics of Cu(II) ions sorption was found in the pH range of 2–7. Also no significant negative effect of NaCl concentration increase on the process kinetics was observed. For pH 1 a slight decrease of the kinetics of Cu(II) ions sorption was observed in the whole range of the NaCl concentrations studied. For Zn(II) and Ni(II) ions as well as pH value equal to 1, low kinetics of sorption capacity was found in the whole range of NaCl concentrations (Fig. 4b). Increase of sodium chloride concentration up to 40 g/dm<sup>3</sup> did not cause a noticeable change in the kinetics of the sorption of metal ions under investigations.

Application of the ion exchanger Lewatit TP 207 in the monosodium (Na<sup>+</sup>) form enables removal of heavy metal ions from acid solutions containing sodium chloride of high concentration and pH > 2. However, the obtained results indicate that it is possible to carry out sorption of the metal ions in question on the ion exchanger Lewatit TP 207 in the disodium (2Na<sup>+</sup>) form in the entire range of pH to the value of 10 g/dm<sup>3</sup> of sodium chloride concentration (Fig. 4c). Deterioration of sorption kinetics, particularly for Ni(II) and Zn(II) ions, was found from the concentration 20 g/dm<sup>3</sup>. Application of the ion exchanger in the disodium form does not make it possible to separate individual ions, but it works at very low pH values.

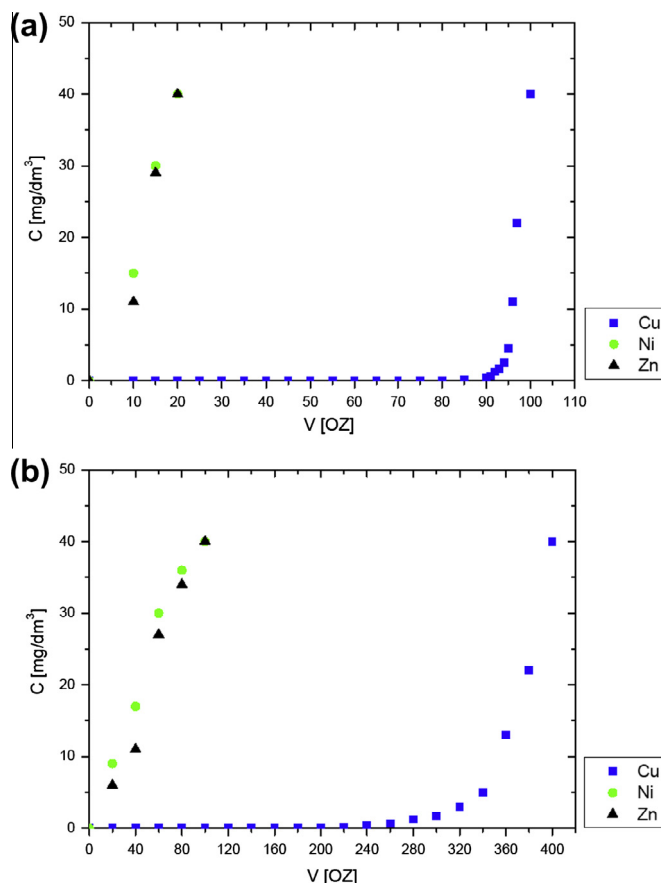


Fig. 7. The breakthrough curves of Cu(II), Zn(II) and Ni(II) ions at pH = 2 (a) and pH = 4 (b) on chelating ion exchanger Lewatit TP 207 in the H<sup>+</sup> form (NaCl concentration 40 g/dm<sup>3</sup>).

For the ion exchanger Lewatit TP 208, regardless of the fact that this is the ion exchanger of analogous functional groups, no significant change of sorption kinetics was found for its Na<sup>+</sup> form in the Cu(II) ions sorption in the pH range of 2–7. Also no significant negative effect of NaCl concentration increase on the process kinetics was observed, whereas a slight decrease in sorption kinetics was found at pH 1 in the entire range of sodium chloride concentrations. For Zn(II) and Ni(II) ions and pH 1, lower kinetics of sorption capacity was found in the range of studied NaCl concentrations. The increase in sodium chloride concentration up to 40 g/dm<sup>3</sup> did not induce a noticeable change in kinetics of the sorption process of metal ions (Fig. 5a and b). The results obtained for the disodium (2Na<sup>+</sup>) for Lewatit TP 208, analogously to those obtained on Lewatit TP 207, suggest a possibility of sorption in the entire pH range up to the NaCl concentration of 10 g/dm<sup>3</sup>.

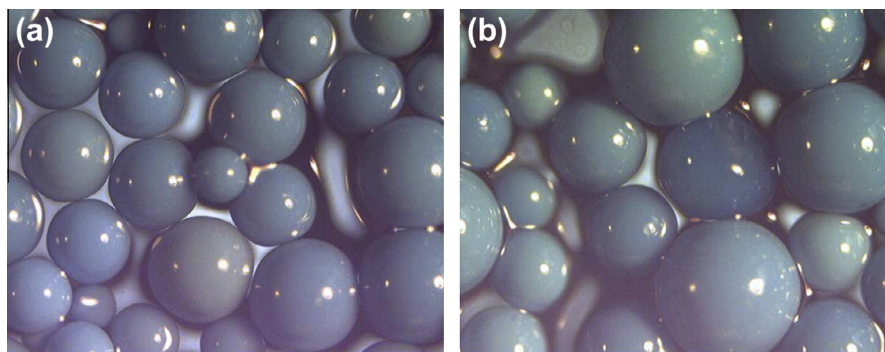


Fig. 6. Lewatit TP 207 (a) and Lewatit TP 208 (b) after 50 cycles of Cu(II) ions sorption–desorption process (magnification 40×).

Deterioration of sorption kinetics, particularly for Ni(II) and Zn(II) ions, was found from the concentration  $20 \text{ g/dm}^3$ . The behaviour of the chelating ion exchanger Lewatit TP 208 towards Cu(II), Zn(II) and Ni(II) ions was similar to that of Lewatit TP 207. However, these ion exchangers differ in the type of matrix and degree of cross-linking, which is evidenced in different physicochemical properties (Table 1). The different structure did not affect sorption capacities towards the above-mentioned heavy metal ions. These ion exchangers are also characterized by good resistance to osmotic shocks and offer 50 loading sorption–desorption cycles without any mechanical damage connected with the acid base cycle regeneration (Fig. 6a and b). However, due to a little higher market price, the use of the ion exchanger Lewatit TP 207 is justified.

### 3.3. Column studies

Column experiments were conducted to understand the sorption behaviour in bed columns and to determine the total ion exchange capacity of Lewatit TP 207 and Lewatit TP 208 in different operational forms. The exemplary breakthrough curves for Cu(II), Zn(II) and Ni(II) ions adsorption onto Lewatit TP 207 in the  $\text{H}^+$ ,  $\text{Na}^+$  and  $2\text{Na}^+$  forms are shown in Figs. 7–9 a and b. Typical 'S' shaped curves were obtained for all experiments. As follows from the obtained results, Cu(II) ions exhibit a higher affinity compared to Zn(II) and Ni(II) ions for the chelating ion exchangers in the operational forms. The obtained results were also confirmed by the calculated mass ( $D_g$ ) and volume ( $D_v$ ) distribution coefficients as well as the sorption capacities ( $C_w$ ,  $C_t$ ) of ion exchangers (Table 5). As follows from the research, the chelating ion

exchangers, according to their applicability in the sorption of Cu(II), Zn(II) and Ni(II) ions by the dynamic method can be put in the order:

#### 3.3.1. At pH 2.0

**Cu(II):** Lewatit TP 208  $\text{Na}^+$  > Lewatit TP 208  $2\text{Na}^+$  > Lewatit TP 207  $\text{Na}^+$  > Lewatit TP 207  $2\text{Na}^+$  > Lewatit TP 207  $\text{H}^+$ .

**Zn(II):** Lewatit TP 208  $2\text{Na}^+$  > Lewatit TP 208  $\text{Na}^+$  > Lewatit TP 207  $\text{Na}^+$  > Lewatit TP 207  $2\text{Na}^+$  > Lewatit TP 207  $\text{H}^+$ .

**Ni(II):** Lewatit TP 208  $2\text{Na}^+$  > Lewatit TP 208  $\text{Na}^+$  > Lewatit TP 207  $\text{Na}^+$  > Lewatit TP 207  $2\text{Na}^+$  > Lewatit TP 207  $\text{H}^+$ .

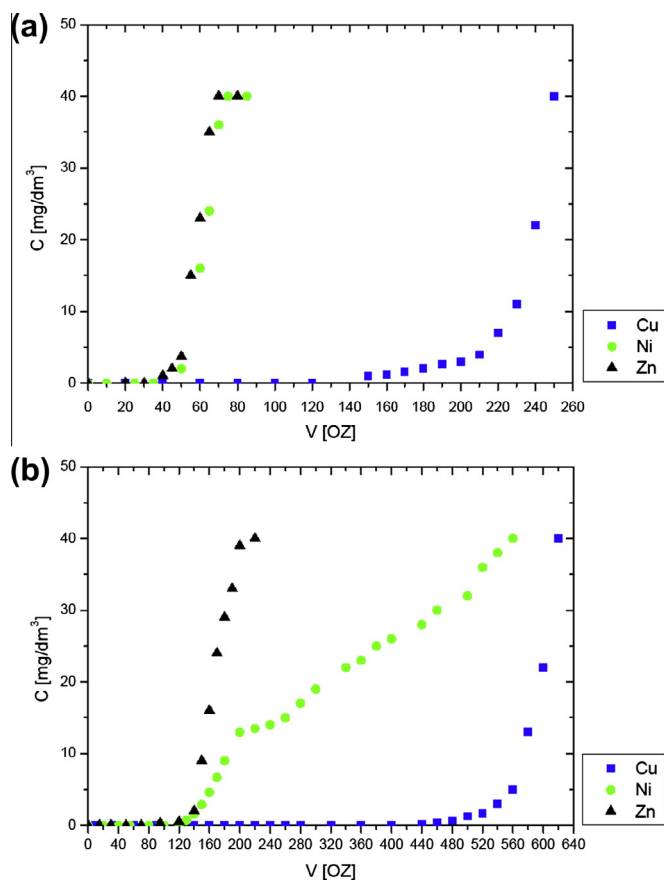
#### 3.3.2. At pH 4.0

**Cu(II):** Lewatit TP 208  $2\text{Na}^+$  > Lewatit TP 207  $\text{Na}^+$  > Lewatit TP 207  $2\text{Na}^+$  > Lewatit TP 208  $\text{Na}^+$  > Lewatit TP 207  $\text{H}^+$ .

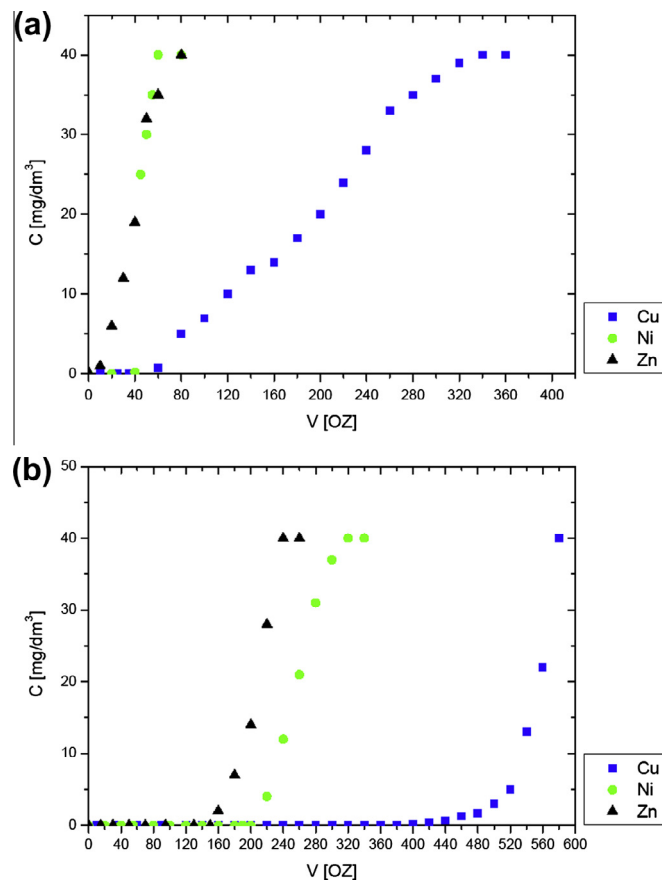
**Zn(II):** Lewatit TP 208  $2\text{Na}^+$  > Lewatit TP 207  $2\text{Na}^+$  > Lewatit TP 208  $\text{Na}^+$  > Lewatit TP 207  $\text{Na}^+$  > Lewatit TP 207  $\text{H}^+$ .

**Ni(II):** Lewatit TP 208  $2\text{Na}^+$  > Lewatit TP 207  $\text{Na}^+$  > Lewatit TP 208  $2\text{Na}^+$  > Lewatit TP 207  $2\text{Na}^+$  > Lewatit TP 207  $\text{H}^+$ .

It was also found that both forms of the ion exchangers for pH 2 were characterized by a similar total capacity, but for pH 4 the disodium form possessed an increased total capacity compared with the monosodium form. Though the ion exchanger Lewatit TP 208 possesses the same functional groups as the Lewatit TP 207 in the NaCl concentrations and pH range studied, it does not give as distinct and sharp breakthrough profiles as Lewatit TP



**Fig. 8.** The breakthrough curves of Cu(II), Zn(II) and Ni(II) ions at pH = 2 (a) and pH = 4 (b) on chelating ion exchanger Lewatit TP 207 in the  $\text{Na}^+$  form (NaCl concentration  $40 \text{ g/dm}^3$ ).



**Fig. 9.** The breakthrough curves of Cu(II), Zn(II) and Ni(II) ions at pH = 2 (a) and pH = 4 (b) on chelating ion exchanger Lewatit TP 208 in the  $2\text{Na}^+$  form (NaCl concentration  $40 \text{ g/dm}^3$ ).

**Table 5**

The mass ( $D_g$ ), 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 207 and Lewatit TP 208 in the  $H^+$ ,  $Na^+$  and  $2Na^+$  forms.

pH	Cu(II)				Zn(II)				Ni(II)			
	$D_g$	$D_v$	$C_w$	$C_t$	$D_g$	$D_v$	$C_w$	$C_t$	$D_g$	$D_v$	$C_w$	$C_t$
<i>TP 207 in the <math>H^+</math> form</i>												
2	235.6	97.1	0.006	0.0045	34.8	14.4	0.001	0.0007	27.6	11.2	0.001	0.0006
4	930.1	384.4	0.018	0.0049	95.3	39.1	0.001	0.0013	95.3	39.4	0.002	0.0013
<i>TP 207 in the <math>Na^+</math> form</i>												
2	579.3	239.2	0.007	0.0044	143.7	59.2	0.003	0.0013	155.8	64.9	0.001	0.0011
4	1450.3	599.3	0.025	0.0045	409.9	169.5	0.009	0.0019	918.0	379.7	0.007	0.0020
<i>TP 207 in the <math>2Na^+</math> form</i>												
2	530.8	219.8	0.004	0.0025	105.0	43.3	0.001	0.0007	100.2	41.2	0.001	0.0005
4	1353.6	559.1	0.028	0.0046	526.5	217.7	0.009	0.0019	639.7	264.1	0.012	0.0021
<i>TP 208 in the <math>Na^+</math> form</i>												
2	773.5	309.3	0.013	0.0039	178.3	71.8	0.003	0.0012	211.0	84.2	0.002	0.0010
4	1323.5	529.7	0.027	0.0040	498.4	199.2	0.008	0.0016	698.5	279.3	0.009	0.0019
<i>TP 208 in the <math>2Na^+</math> form</i>												
2	598.5	239.4	0.007	0.0038	273.2	109.1	0.005	0.0023	348.5	139.5	0.005	0.0025
4	1548.5	619.3	0.031	0.0044	798.5	319.9	0.014	0.0035	1061.0	424.4	0.012	0.0028

**Table 6**

The total ion exchange capacities (meq/cm<sup>3</sup>) for Lewatit TP 207 in the  $H^+$ ,  $Na^+$  and  $2Na^+$  forms at the NaCl concentration 20 g/dm<sup>3</sup> and 40 g/dm<sup>3</sup>.

pH	Cu(II)	Zn(II)	Ni(II)	$\Sigma$
<i>TP 207 in the <math>H^+</math> form, 20 g/dm<sup>3</sup> of NaCl</i>				
2	0.29	0.04	0.05	0.38
4	0.79	0.07	0.07	0.93
<i>TP 207 in the <math>Na^+</math> form, 20 g/dm<sup>3</sup> of NaCl</i>				
2	0.52	0.10	0.11	0.73
4	0.86	0.26	0.29	1.41
<i>TP 207 in the <math>2Na^+</math> form, 20 g/dm<sup>3</sup> of NaCl</i>				
2	0.24	0.05	0.06	0.35
4	0.76	0.36	0.54	1.66
<i>TP 207 in the <math>H^+</math> form, 40 g/dm<sup>3</sup> of NaCl</i>				
2	0.12	0.01	0.01	0.14
4	0.46	0.06	0.06	0.58
<i>TP 207 in the <math>Na^+</math> form, 40 g/dm<sup>3</sup> of NaCl</i>				
2	0.29	0.06	0.08	0.43
4	0.74	0.20	0.45	1.39
<i>TP 207 in the <math>2Na^+</math> form, 40 g/dm<sup>3</sup> of NaCl</i>				
2	0.21	0.05	0.04	0.30
4	0.69	0.23	0.32	1.24

207. This fact may result from the different matrix structure of the ion exchangers or the use of a different cross-linking agent. However, these data are not available as they are the producer's trade secret. Therefore analysing the values of the total ion exchange capacity for Lewatit TP 207 and Lewatit TP 208 in the  $H^+$ ,  $Na^+$  and  $2Na^+$  forms, it was found that only Lewatit TP 207 in the  $H^+$  form can be used for Cu(II) ions sorption from the acidic brine solutions (Tables 6 and 7). Application of the hydrogen form allows separation of Cu(II) from Zn(II) and Ni(II) ions. The increase of sodium concentration from 20 g/dm<sup>3</sup> to 40 g/dm<sup>3</sup> in the studied pH range decreases twice the total capacity of the ion exchanger in the  $H^+$  form towards Cu(II) ions. However, Lewatit TP 207 in the  $Na^+$  form at pH 2 shows a twice smaller total capacity for 40 g/dm<sup>3</sup> NaCl concentration compared to that of 20 g/dm<sup>3</sup>. No significant decrease in the total capacity at pH 4 was found when sodium chloride concentration increased. The monosodium form of Lewatit TP 207 does not enable separation of the studied ions compared to the disodium form of Lewatit TP 207 at low pH values. The disodium form at low pH values does not reveal decrease in total capacity with the increasing NaCl concentration. However,

**Table 7**

The total ion exchange capacities (meq/cm<sup>3</sup>) for Lewatit TP 208 in the  $Na^+$  and  $2Na^+$  forms at the NaCl concentration 40 g/dm<sup>3</sup>.

pH	Cu(II)	Zn(II)	Ni(II)	$\Sigma$
<i>TP 208 in the <math>Na^+</math> form</i>				
2	0.37	0.08	0.09	0.54
4	0.63	0.22	0.32	1.17
<i>TP 208 in the <math>2Na^+</math> form</i>				
2	0.29	0.12	0.17	0.57
4	0.76	0.37	0.51	1.64

at pH 4 about 25% decrease in the total capacity of Lewatit TP 207 was observed with the increasing NaCl concentration (Table 6). For Lewatit TP 208 (Table 7) at pH 2, both forms ( $Na^+$  and  $2Na^+$ ) showed similar values of total capacity but at pH 4 the disodium form was characterized by an increased total capacity compared to the monosodium one. Under the same conditions Lewatit TP 208 does not give such evident and sharp breakthrough profiles as Lewatit TP 207. The different shape of breakthrough curves may result from different matrix structure of these ion exchangers.

Taking into account the effect of form of ion exchangers, it was found that Lewatit TP 208 in the  $2Na^+$  form is more effective in the sorption of Cu(II), Zn(II) and Ni(II) than in the  $Na^+$  form. In this part of research the effect of a regenerating agent was also investigated. The exhausted chelating ion exchangers can be completely regenerated by the 1 M  $H_2SO_4$  and 1 M HCl mixture.

#### 4. Conclusions

Prevention of metal loss and the necessity to ensure proper process economy connected with the elimination of one of the stages in the current technologies (bringing solution to the defined pH) required thorough kinetic and static studies, choice of suitably durable ion exchangers, checking their resistance to osmotic shocks and examining separation selectivity for various metal ions (Cu(II), Zn(II) and Ni(II)). The kinetic and dynamic studies indicate the possibility of applying the commercially available ion exchangers in question for the removal of the above-mentioned heavy metal ions from waste acidic streams. Combination of the results obtained from static and dynamic studies for various operational forms of Lewatit TP 207 and Lewatit TP 208 allows selection of the systems satisfying the processes conducted on the commercial

scale for heavy metals removal, taking into account their selectivity and effectiveness. The medium basic anion exchanger Lewatit MonoPlus MP 64 did not satisfy any of the above requirements. The total capacities determined for the selected ion exchangers indicate a significant effect of both waste water composition (different concentrations of NaCl) and functional groups (iminodiacetate, weakly basic) as well as functional group forms ( $H^+$ ,  $Na^+$  and  $2Na^+$ ) on heavy metal ions removal. By choosing a proper functional group form of the ion exchanger, metal ions sorption was achieved in the whole range of NaCl concentration and pH.

## Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.cej.2014.04.035>.

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