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Zinc(II) removal from model chloride and chloride-nitrate(V) solutions using various sorbents

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Abstract: Zinc(II) complexes removal from aqueous chloride and chloride-nitrate(V) solutions was realized using different type of sorbents such as an ion exchangers of the chelating type (Lewatit MonoPlus TP220, Purolite S984), strongly basic (Lewatit MonoPlus SR7, Purolite A400TL, Dowex PSR2, Dowex PSR3) and weakly basic (Purolite A830) anion exchangers as well as the adsorbent resin Lewatit AF5. The kinetic and equilibrium studies using the static method were carried out in order to examine the rate of zinc(II) removal as well as to obtain the maximum adsorption capacities. The obtained experimental data were analyzed by means of different kinetic and isotherm models as well as the corresponding parameters were calculated. The desorption and reuse studies (three cycles of sorption/desorption) were also discussed. Lewatit MonoPlus TP220 showed the highest efficiency of zinc(II) removal and the maximum sorption capacity was equal to 620 mg/g. The kinetics of zinc(II) sorption is well described by the pseudo-second order kinetic model. The interactions between the sorbent and zinc ions are strong because no quantitative zinc desorption was observed (40% using nitric(V) and sulfuric(VI) acids for Lewatit MonoPlus TP220).

Keywords: heavy metals, zinc, removal, ion exchanger, Lewatit MonoPlus TP220

1. Introduction

Zinc is one of the most important metals in the world (Nagahashi et al., 2018). In terms of prevalence in the Earth's crust, zinc ranks 23rd (0.013%), but in the worldwide production and consumption of metals it ranks 4th (after iron, copper and aluminium) (Zhang, 1996; Gakwisiri et al., 2012). Zinc is a relatively hard metal, however, soft enough to be rolled, extruded or formed, possessing low melting and boiling points, excellent atmospheric corrosion resistance which makes it useful for versatile application (Gray, 2006). The major categories of zinc application are coating (this area of zinc application uses nearly half of its produced amount), casting, alloys (e.g. brass, tombac, solder etc.), zinc oxides (called zinc white) and chemicals production (Fig. 1). Zinc is widely applied in industries, batteries, smelting, fertilizers and pesticides, pigments, paints, polymer stabilizers, fossil fuel combustion, etc. (Zhang, 1996; Lew, 2008; Nagahashi et al., 2018; Noulas et al., 2018). Zinc enters the environment due to natural processes such as volcanic eruptions, rock weathering, forest fires as well as anthropogenic processes related to human activities. Its content in the surface and groundwater raises mainly from erosion of soil particles containing zinc as well as from mine drainage, industrial and municipal wastes and urban runoff. Zinc may be also leached into groundwater by some mineral fertilizers, old galvanized metal pipes and materials coated with zinc and can be dissolved by acidic waters.

About 300 thousand tons of zinc is discharged every year to the sea and the world average riverine fluxes of zinc to oceans and seas is estimated to be from 20 000 to 200 000 tons per year (Noulas et al., 2018). As was pointed out by the Food and Agricultural Organization (FAO) and the World Health Organization (WHO) drinking water containing above 3 mg/dm³ of zinc (or 4 mg/dm³ in the form of zinc sulfate) has bitter, metallic, astringent taste, tends to opalescence and develops a greasy film when

boiled. Water containing above 5 mg Zn(II)/dm³ can have a milky appearance. The irrigation water should contain up to 2 mg of Zn(II) per dm³ to avoid plant toxic effects. The largest zinc discharge (28%) to the aquatic system in the European Union originates from the manufacturing of basic industrial chemicals (Noulas et al., 2018). In various wastewaters zinc concentration could be in the range from less than 1 mg/dm³ to more than 48 g/dm³ (Abbas et al., 2015).

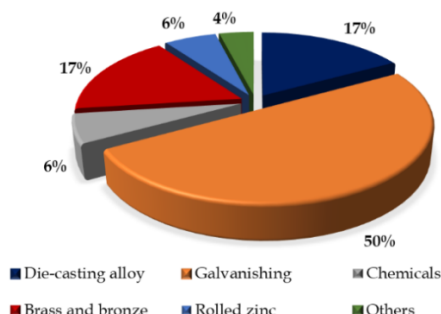


Fig. 1. Zinc application in different areas

Zinc containing wastewaters are a serious environmental problem due to its toxicity, non-biodegradability, possibility to accumulate in living tissues and many negative impacts onto human body such as neurosensory and neuropsychiatric disorders, mental lethargy, skin lesions, hypogonadism, immune dysfunction etc. (Hambidge, 2000; Rink, 2000; Roohani et al., 2013, Nagahashi et al., 2018). Therefore, the development of effective methods of its removal is the subject of many studies nowadays, e.g. papers of Barakat (2011); Gakwisiri et al. (2012); Simonescu et al. (2012) etc. In a wide range of treatment methods chemical precipitation, solvent extraction, membrane filtration, adsorption or ion exchange, reverse osmosis has been employed for toxic zinc ions removal from wastewaters (Regel-Rosocka, 2010; Zwain et al., 2014). Incomplete metal removal, large energy requirements, high reagents consumption, generation of toxic sludge or other waste products containing heavy metals of greater toxicity than that of their parent ones, high costs especially when concentration of heavy metal is very low (10–100 mg/dm³), are main drawbacks of these methods.

However, the adsorption using solid adsorbents shows a potential as one of the most economical and efficient methods for zinc removal from wastewaters due to high sorption capacities of selected sorbents, even when the concentration of zinc is low, e.g. for ion exchangers, simple design, low investment cost are required. On the other site, this method has also disadvantages, such as a very low selectivity and generation of large volumes of diluted solutions after elution (Regel-Rosocka, 2010; Barakat, 2011; Gakwisiri et al., 2012; Rashed, 2013; Babilas and Dydo, 2018).

Zinc could be effectively removed from HCl solutions by strongly and weakly basic anion exchange resins such as Amberlite IRA410, Purolite A103S, Purolite A400MBOH, Purolite NRW700 (Gîlcă et al., 2014; Gîlcă, 2015), 201×7, resin 301, Dowex 2 (Horne et al., 1957; Zhang et al., 2013). The anion exchange resins Amberlite IRA410, Purolite A103S, Purolite NRW700 and Purolite A400MBOH applied for zinc removal in the form of zinc chloride complexes from model aqueous solutions prepared by dissolving ZnCl₂ in 1 mol/dm³ hydrochloric acid, allowed to obtain the maximum percentage removal of 87% for Amberlite IRA410 (5 g of resin, initial concentration 500 mg Zn(II)/dm³, phases contact time 300 min, stirring speed 500 rpm). The Zn(II) ions sorption was strongly dependent on stirring rate and resin quantity (Gîlcă et al., 2014; Gîlcă, 2015). Purolite S985, Purolite A500, AV-17-8 and AM-2B were recommended by Kononova et al. (2011) for zinc(II) ions removal from chloride and chloride-sulfate solutions (HCl concentration was from 0.001 to 4.0 mol/dm³, the chloride-sulfate systems, HCl:H₂SO₄=1:1; 1:2 and 1:4, the acids concentrations was 0.001–2.0 mol/dm³) as a results of good sorption, kinetic properties and quantitative elution by means of 2 mol/dm³ HCl. Nekouei et al. (2019) applied ion-exchange technique for recycling of heavy metals such as Zn(II) as well as Cu(II), Ni(II), Pb(II) and Al(III) from end-of-life printed circuit boards (PCBs) using macroporous ion-exchange resins Amberlite IRA743, Lewatit TP208 and Lewatit TP260 (PCBs were leached by nitric(V) acid, final pH 3.9). Morcali et al. (2014) used macroporous resin Lewatit TP207 to adsorb Zn(II) and Cu(II), whereas Valverde et al. (2002) studied the removal of Zn(II), Cd(II) and Cu(II) ions from industrial wastewaters

on a strong acid resin Amberlite IR120. Strongly basic anion exchange resin Lewatit MonoPlus M500, Lewatit VPOC1071 and weakly basic one Lewatit MonoPlus MP64 were applied for Zn(II) removal from spent hydrochloric acid solutions (exchange capacity, 0.62–0.76 mol/dm³ Zn(II) (Miesiąc, 2005)).

As reported in the literature (Kononova et al., 2011), zinc(II) is usually recovered using cationic or chelating ion exchangers, however, anion exchangers are not so often used for such purpose. The novelty of this paper is application of the ion exchangers (Lewatit MonoPlus TP220, Purolite S984, Lewatit MonoPlus SR7, Purolite A400TL, Dowex PSR2, Dowex PSR3, Purolite A830) and adsorbent resin (Lewatit AF5) for zinc(II) removal from the acidic solutions in order to supplement the knowledge concerning Zn(II) removal by ion exchangers. It should be highlighted that selected sorbents (recommended by manufacturers among other for heavy metal ions removal) have not been studied in the literature yet, not only for Zn(II) recovery but also for some other metal ions. Moreover, Lewatit MonoPlus TP220 is an ion exchanger of new generation containing the bis-picolylamine functional groups similar to those of Dowex M4195, but obtained in another way (Kołodziejńska et al., 2014). Recycling of zinc(II) is very important due to the growing water pollution with zinc, for improving the production efficiency and for complying with ecological safety regulations. Therefore the aim of the paper was to study zinc(II) removal from the HCl and HCl-HNO₃ solutions using the adsorption technique and sorbents mentioned above. The efficiency of zinc(II) removal using various adsorbents was investigated by means of the static method. In addition, the influence of selected parameters on the kinetics of zinc(II) sorption process was investigated and equilibrium tests were carried out to determine the maximum sorption capacity. On the basis of the sorption capacity values the ion exchange resin with the best sorption properties was selected.

2. Materials and methods

2.1. Sorbate and sorbents characteristics

The stock and working solutions (solutions used for sorption and desorption) were prepared using chemical compounds of analytical grade purchased from POCh S.A. company (Gliwice, Poland). The working solutions, used for the adsorption tests, containing zinc(II) in the concentration of 100 mg/dm³ were prepared by dilution of the stock solutions prepared from the ZnCl₂ (this solid is a component of electrolyte during the galvanizing process). The required amount of HCl as well as HCl and HNO₃ were also added to obtain their desired concentration. The solutions were as follows: (1) chloride solutions: 0.1; 1; 3; 6 mol/dm³, (2) chloride-nitrate(V) solutions: 0.1 mol/dm³ HCl – 0.9 mol/dm³ HNO₃, 0.2 mol/dm³ HCl – 0.8 mol/dm³ HNO₃, 0.5 mol/dm³ HCl – 0.5 mol/dm³ HNO₃, 0.8 mol/dm³ HCl – 0.2 mol/dm³ HNO₃, 0.9 mol/dm³ HCl – 0.1 mol/dm³ HNO₃. 1 and 2 mol/dm³ HNO₃, HCl, H₂SO₄, NH₃·H₂O, NaOH and NaCl were applied as eluting agents.

Zinc can occur in wastewaters at different levels depending on their type, origin, experimental conditions (Rajoriya and Kaur, 2014). The copper smelter wastewaters contain zinc, arsenic, copper, iron, bismuth, cadmium, nickel, lead and chromium of 1979, 300, 164.48, 88, 85, 76, 12, 4.6 and 2.3 mg/dm³ concentration, respectively (Basha et al., 2008). Wastewaters generated during production processes, the so-called galvanic sewage are classified as particularly dangerous and arduous to the environment due to the high content of heavy metals (10–1000 mg/dm³). The presence of these metals changes the pH of the water, its organoleptic properties, the amount of dissolved oxygen and the process of self-purification of water.

Acid model solutions containing 100 mg Zn(II)/dm³ were used in this study. The composition of the model solutions was selected as to reflect the composition of real wastewaters originated from the galvanizing processes. In this process, there can be distinguish, among others pretreatment, digestion (HCl), post-digestion (HCl) and galvanizing (electrolyte containing ZnCl₂, KCl, H₃BO₃). HNO₃ acid is used for silver passivation and activation. In the hot dip galvanizing process pickling step applied HCl or H₂SO₄ whereas fluxing is in aqueous ZnCl₂/NH₄Cl baths, therefore it generates effluents containing, among other high concentrations of ZnCl₂, FeCl₂ and HCl (Gîlcă et al., 2014). Due to this, as a source of zinc the zinc chloride was applied, and HCl and HNO₃ systems were taken into consideration. As it was shown by Majumdar et al. (2007) concentrations of Zn(II) in galvanizing effluent was higher than 200 and lower than 500 mg/dm³ (Majumdar et al., 2007). Galvanizing wastewaters (GW) and waters collected in the "Kowary" settler (KW), produced during galvanic coating of steel surfaces, contain not

only zinc (4.7–17 g/m³ – GW; 1.7–8.7 g/m³ – KW), but also chromium (0.06–1.1 g/m³ – GW; 0.05–0.63 g/m³ – KW), nickel (10.4–32.7 g/m³ – GW; 5.4–17.7 g/m³ – KW), copper (2–6.4 g/m³ – GW; 3.3–9.3 g/m³ – KW); lead (2.3–6 g/m³ – GW; 0.04 g/m³ – KW) and iron (1.6–7.2 g/m³ – GW; 1.2–4.42 g/m³ – KW) ions (Grabas, 2009).

Zinc(II) removal from acidic streams was carried out using various sorbents such as ion exchange resins of chelating (Lewatit MonoPlus TP220, Purolite S984), strongly basic anion exchangers (Lewatit MonoPlus SR7, Dowex PSR2, Dowex PSR3, Purolite A400TL), weakly basic anion exchange resin (Purolite A830) types as well as the adsorbent resin Lewatit AF5. The physicochemical properties of the applied sorbents are presented in Table 1.

Table 1. Comparison of physicochemical properties of the sorbents (name of sorbent, resin type, matrix, functional groups, total capacity, mean bead size, water retention)

Lewatit MonoPlus TP220	Purolite A400TL
chelating resin	strongly basic
crosslinked polystyrene	polyacrylic crosslinked with divinylbenzene
macroporous	microporous
bis-picolylamine/bis (2-pyridyl-methyl)amine	quaternary ammonium, type 1
2.2 val/dm ³	(Cl): 1.3 val/dm ³
0.62(±0.05) mm	0.425-0.85 mm
48-60%	48-54%
Purolite S984	Dowex PSR2
chelating resin	strongly basic
polyacrylic crosslinked with divinylbenzene	crosslinked polystyrene
macroporous	microporous
polyamine	tri-n-butyl amine type
(FB): 2.7 val/dm ³	0.65 val/dm ³
-	0.3-1.2 mm
44-55%	40-48%
Lewatit MonoPlus SR7	Purolite A830
strongly basic	weakly basic
crosslinked polystyrene	polyacrylic crosslinked with divinylbenzene
macroporous	macroporous
quaternary ammonium, type 3	complex amine
(Cl): 0.6 val/dm ³	(FB): 2.75 val/dm ³
0.57-0.67 mm	0.3-1.2 mm
59-64%	47-53%
Dowex PSR3	Lewatit AF5
strongly basic	adsorbent resin
crosslinked polystyrene	carbonaceous
macroporous	microporous
tri-n-butyl amine type	None
0.60 val/dm ³	-
0.3-1.2 mm	0.4-0.8 mm
50-65%	48-60%

2.2. Kinetic studies

Adsorption experiments were performed in the mechanical shaker Elphin+ type 357 (Lubawa, Poland) at 180 rpm (amplitude A=8) using 100 cm³ Erlenmeyer flasks containing 0.5±0.0005 g of sorbents and 50 cm³ of zinc(II) containing solutions (100 mg/dm³): 0.1–6 mol/dm³ HCl – 100 mg Zn(II)/dm³ or 0.1–0.9 mol/dm³ HCl – 0.9–0.1 mol/dm³ HNO₃ – 100 mg Zn(II)/dm³. After the appropriate phases contact time (1 min to 4 h) the phases were separated by filtration with Whatman filter paper. The zinc(II) content in the solution after filtration was determined using Atomic Absorption Spectrophotometer Varian AA240FS (Varian, Australia) (see Fig. 2). The amount of adsorbed metal, q_t (mg/g) by various sorbents, was calculated from the differences between the zinc(II) quantity added to the sorbent and the zinc(II) content in the solutions after sorption, as well as percentage removal efficiency of zinc(II), $R(\%)$ were obtained using the following equations:

$$q_t = (C_0 - C_t) \times \frac{V}{M} \quad (1)$$

$$R = \frac{(C_0 - C_e)}{C_0} \times 100\% \quad (2)$$

where C_0 and C_t are the initial and after time t zinc(II) concentrations in the solution (mg/dm³), respectively; V is the volume of solutions before and after adsorption (dm³); M is the mass of the sorbent (g). In Eq. 1 q_t and C_t could be replaced by q_e and C_e when the system reached equilibrium (q_e (mg/g) is the sorption capacity, and C_e is the equilibrium zinc(II) concentrations in the solution (mg/dm³)). Zn(II) adsorption using the static method was performed in triplicate and the plots show the arithmetic mean. The standard deviation was calculated and did not exceed 4% in all cases.

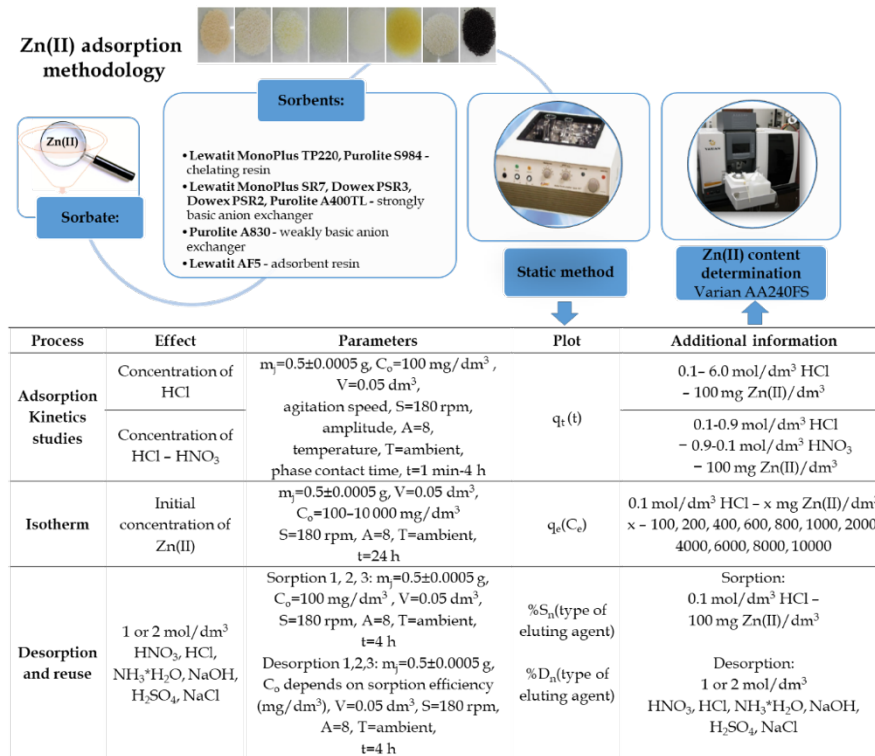


Fig. 2. Zinc(II) adsorption methodology

The obtained results were analysed using the kinetic models such as the pseudo-first order (PFO), pseudo-second order (PSO) kinetic equations and intraparticle diffusion (IPD) one (Table 2) (Lagergren, 1898; Ho and McKay, 1999; Qiu et al., 2009, Syafiuddin et al., 2018).

Table 2. Kinetic models used in the experiments

Model	Equation	Plot
Pseudo-first order kinetic equation PFO	$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t$ (3)	$\log(q_e - q_t)$ vs t
Parameters:	k_1 (1/min) - the rate constant of PFO equation $k_1 = -2.303 \times \text{slope}$ q_e (mg/g) - the adsorption capacity $q_e = 10^{\text{intercept}}$	
Pseudo-second order kinetic equation PSO	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$ (4)	t/q_t vs t
Parameters:	k_2 (g/mg*min) - the rate constant of PSO equation $k_2 = \text{slope}^2 / \text{intercept}$ q_e (mg/g) - the adsorption capacity $q_e = 1 / \text{slope}$ h (mg/g*min) - the initial sorption rate $h = k_2 q_e^2$ (5)	

2.3. Equilibrium studies

Equilibrium experiments were performed by contacting 0.5 ± 0.0005 g of sorbents with 50 cm³ of zinc(II) solution of different initial concentration 100–10000 mg/dm³. The procedure was similar to that applied in the kinetic studies. The phases were placed in 100 cm³ conical flasks and mechanically shaken using a water-bath shaker at a constant agitation speed of 180 rpm. The agitation was made for 24 h, which is

more than the time needed to reach equilibrium. The Langmuir and Freundlich isotherm models were applied to analyze the equilibrium data (Table 3).

Table 3. Isotherm models

Model	Equation	Plot
Langmuir	$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0}$	(6) C_e/q_e vs C_e
Symbols:	Q_0 – the Langmuir monolayer sorption capacity (mg/g) $Q_0 = 1/\text{slope}$ (mg/g) b – the Langmuir constant related to the free energy of sorption (dm ³ /mg) $b = \text{slope}/\text{intercept}$ (dm ³ /mg) R_L – the separation factor or equilibrium parameter $R_L = 1/(1 + b \times C_0)$ (7)	
Freundlich	$\log q_e = \log k_F + \frac{1}{n} \log C_e$	(8) $\log q_e$ vs $\log C_e$
Symbols:	k_F – the Freundlich adsorption capacity (mg/g) $k_F = 10^{\text{intercept}}$ (mg/g) $1/n$ – the Freundlich constant related to the surface heterogeneity $1/n = \text{slope}$	

2.4. Desorption and reuse studies

Based on the kinetic and equilibrium studies the best ion exchanger was found for zinc(II) removal from acidic streams. Therefore the next step was an attempt to remove the loaded zinc(II) from the anion exchangers (0.5±0.0005 g). The desorption experiments were performed using 50 cm³ of the following eluting agents: 1 or 2 mol/dm³ HNO₃, 1 or 2 mol/dm³ HCl, 1 or 2 mol/dm³ NH₃*H₂O, 1 or 2 mol/dm³ NaOH and 1 or 2 mol/dm³ NaCl. The desorption time was equal to 4 h and elution was made just after the zinc(II) adsorption (4 h, 0.1 mol/dm³ HCl – 100 mg Zn(II)/dm³) at 180 rpm and amplitude 8. Three cycles of sorption/desorption were performed to examine the resin reuse possibility and the sorption (%S1, %S2, %S3) as well as desorption (%D1, %D2, %D3) yield were calculated (1, 2, 3 indicated number of cycle) using the following formulas:

$$\%S_n = \frac{C_{\text{sorb } n}}{C_0} \times 100\%, \quad n = 1, 2, 3 \quad (9)$$

$$\%D_n = \frac{C_{\text{des } n}}{C_{\text{sorb } n}} \times 100\%, \quad n = 1, 2, 3 \quad (10)$$

where $C_{\text{sorb } n}$ (mg/dm³) is the concentration of metal ions sorbed on sorbent at first ($C_{\text{sorb } 1}$), second ($C_{\text{sorb } 2}$) and third ($C_{\text{sorb } 3}$) cycle (calculated as a difference between the initial and after time t zinc(II) concentration in the solution (mg/dm³), ($C_0 - C_{t,n}$)), C_{des} (mg/dm³) is the concentration of metal ions in the solutions after desorption at first ($C_{\text{des } 1}$), second ($C_{\text{des } 2}$) and third ($C_{\text{des } 3}$) cycle.

3. Results and discussion

Zinc(II) removal from acidic solutions using various sorbents was performed by the static method. The effect of phase contact time and the concentration of hydrochloric acid were studied. The kinetic results of zinc(II) sorption from the chloride solutions (0.1–6.0 mol/dm³ HCl) obtained previously applying Lewatit MonoPlus TP220 (Wołowicz and Hubicki, 2012), Purolite S984 (Wołowicz and Hubicki, 2014), Dowex PSR2 and Dowex PSR3 (Wołowicz and Hubicki, 2016a), Lewatit AF5 (Wołowicz and Hubicki, 2016b) were compared with those found using Lewatit MonoPlus SR7, Purolite A400TL and Purolite A830 as sorbents (the results are presented in Fig. 3).

The amount of zinc(II) sorbed on the sorbents under discussion increases with increasing phase contact time. This tendency holds for all examined systems (0.1–6.0 mol/dm³ HCl) except for the results obtained by Lewatit AF5 using 0.1 mol/dm³ HCl. In this case the q_t values remain at the same level; 4.3–4.5 mg/g. In diluted hydrochloric acid solutions (0.1 mol/dm³ HCl) the q_t values increase is negligible whereas for Lewatit MonoPlus TP220 they increase more significantly than for the other sorbents. Comparing the q_t values, e.g. after 1 and 15 min of phase contact time, this value increases from 2.9 to

6.3 mg/g for Lewatit MonoPlus TP220 (0.1 mol/dm³ HCl) (Wołowicz and Hubicki, 2012), from 1.7 to 2.0 mg/g for Dowex PSR2 (0.1 mol/dm³ HCl) and from 2.3 to 3.2 mg/g for Dowex PSR3 (0.1 mol/dm³ HCl) (Wołowicz and Hubicki, 2016a).

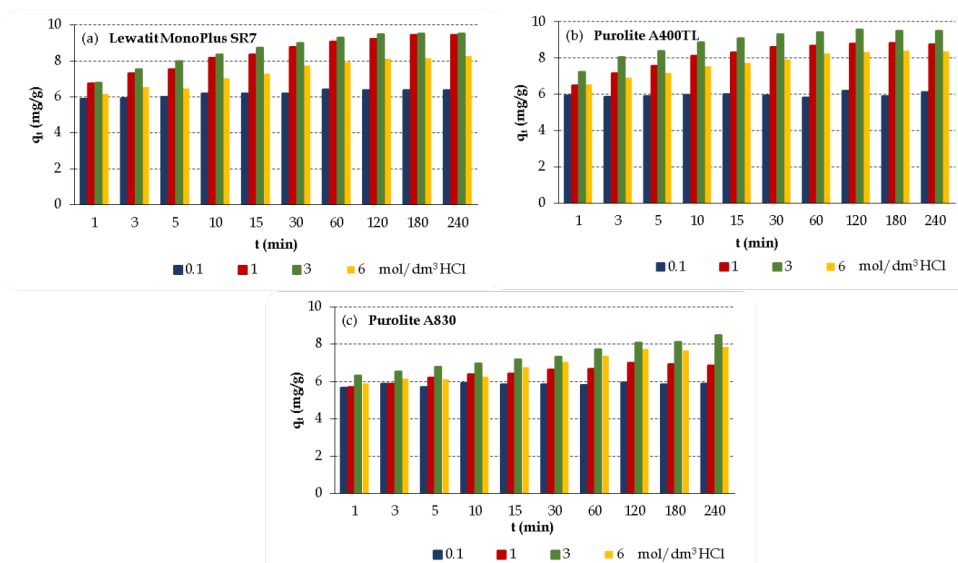


Fig. 3. Effect of the phases contact time and the concentration of hydrochloric acid on removal of zinc(II) using: (a) Lewatit MonoPlus SR7, (b) Purolite A400TL and (c) Purolite A830

Moreover, the q_t values change with increasing HCl concentration. As it can be seen in Fig. 3. the q_t values increase with increasing concentration of hydrochloric acid up to 3 mol/dm³ and then decrease. This tendency was observed for all examined systems. The sorption capacities achieved the highest values in 3 mol/dm³ HCl (see Table 4). Different sorption capacity values result from different physicochemical properties of sorbents as well as depend strictly on the form in which zinc(II) is present in the solutions. The stability constants of the aqueous chloro complexes of zinc(II) were obtained previously by solvent extraction (Sato and Nakamura, 1980; Gloe et al., 1993). With an increase of HCl concentration, the charge of zinc form changed e.g. from positive, through null to negative charge. As was pointed out by Maeda et al. (1996) the zinc(II) chloro complex of the highest charge is $[\text{ZnCl}_4]^{2-}$ of tetrahedral structure with the Zn-Cl bond length of 2.294(4) Å, which is dominant in the solution of higher Cl⁻ concentration (14.1, 14.8 mol/dm³; different chloride ions to zinc ratios, e.g. 4.81 or 7.18 mol/dm³ result in $[\text{ZnCl}_4]^{2-} = 2.08$ or 2.01 mol/dm³). The lower chloro complexes could be also formed in the chloride solutions, e.g. trichloro complex $[\text{ZnCl}_3]^-$ of pyramidal structure with the Zn-Cl bond length of 2.282(4) Å or $[\text{ZnCl}_2]$ and $[\text{ZnCl}]^+$ which could not be separated by Raman spectra. The tetrachlorozincate $[\text{ZnCl}_4]^{2-}$ complex is formed in strong acidic HCl solutions in concentration of 1–6 mol/dm³ concentration. Decrease of solutions acidity to 10⁻²–10⁻³ mol/dm³ results in increasing concentration of anionic and cationic forms of aquacomplexes $[\text{ZnCl}_4(\text{H}_2\text{O})_2]^{2-}$ and $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$ (Kononova et al., 2011). Despite many examples of zinc(II) removal by different sorbents the interaction between the ion exchangers and the chloride complexes of zinc(II) is not discussed in details. As it was summarized by Skorokhodov et al. (2004), the prevailing opinion is that in the chloride solutions zinc(II) exists in the anionic forms $[\text{ZnCl}_4]^{2-}$, $[\text{ZnCl}_3]^-$ and such species interact with anion exchangers (sorbed by anion exchangers). Moreover, the adsorption of neutral species $[\text{ZnCl}_2]$ could not be excluded (non-exchangeable mechanism) either (Helfferich, 1959) and could proceed due to weak hydration. The other authors suggest that the counter ions fixed with the anion exchange resins taking part in the zinc(II) sorption (completion of the coordination sphere) or “electroselectivity” phenomena could affect zinc chloride complexes sorption (Skorokhodov et al., 2004).

Taking into account the type of sorbents under discussion and Zn species in the HCl solutions, Zn(II) sorption efficiency is different due to physicochemical properties of sorbents used as well as due to other mechanism of sorption. In the case of strongly basic anion exchange resins, e.g. Lewatit MonoPlus SR7 the anion exchange mechanism take place (see Fig. 4).

Zinc sorption on strongly basic anion exchanger, from the strong acidic HCl solutions, proceeds as follows:



As was mentioned before, in the solutions of lower acidity (10^{-2} – 10^{-3} mol/dm³), aquacomplexes are present and the Zn sorption mechanism is as follows:

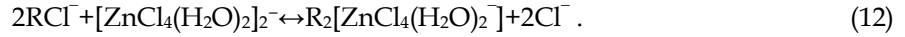
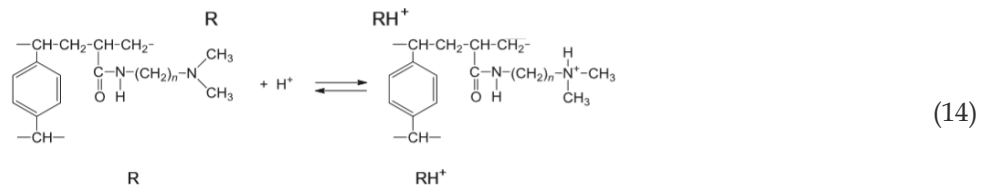
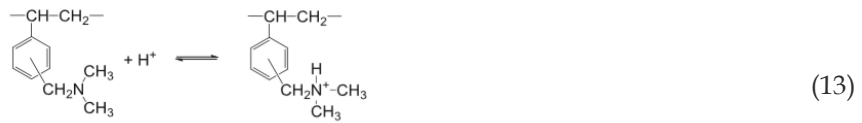


Table 4. Comparison of sorption capacity values obtained during zinc(II) sorption from the chloride solutions 0.1–6 mol/dm³ HCl – 100 mg Zn(II)/dm³

Sorbent	Concentration of HCl (mol/dm ³)			
	0.1	1	3	6
	Sorption capacity (mg/g)			
Dowex PSR2	2.4±0.012	8.5±0.009	8.6±0.022	4.5±0.020
Dowex PSR3	4.1±0.025	8.9±0.014	9.1±0.024	6.6±0.019
Lewatit MonoPlus SR7	6.4±0.015	9.4±0.015	9.5±0.023	8.3±0.021
Purolite A830	5.9±0.011	6.9±0.021	8.5±0.011	7.9±0.020
Lewatit MonoPlus TP220	9.1±0.002	8.7±0.006	9.5±0.009	9.2±0.008
Purolite S984	2.8±0.022	3.8±0.017	6.3±0.014	5.8±0.022
Lewatit AF5	1.5±0.009	3.0±0.014	3.3±0.016	2.0±0.002
Purolite A400TL	6.1±0.008	8.8±0.010	9.5±0.009	8.4±0.014

In the case of weakly basic anion exchange resins (polystyrenic or polyacrylic matrix) their functional groups, e.g. tertiary amine, in HCl solution are protonated (Miyazaki and Nakai, 2011):



and then the anion exchange mechanism take place.

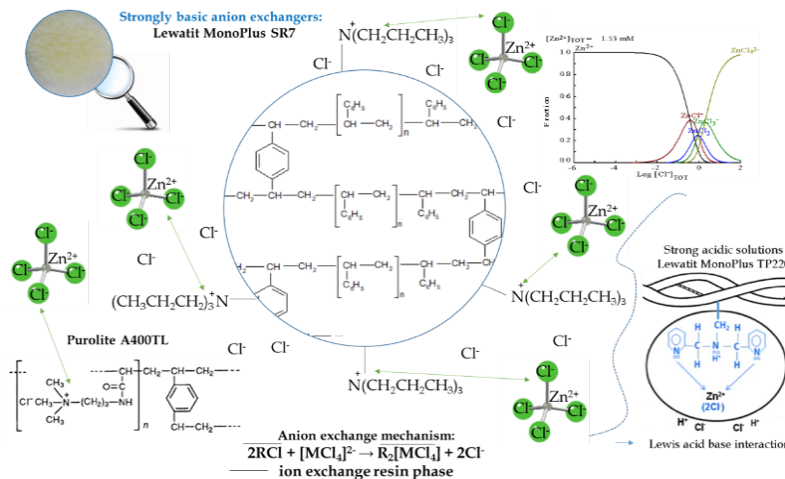
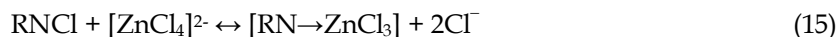


Fig. 4. Mechanism of Zn(II) sorption on Lewatit MonoPlus SR7, Lewatit MonoPlus TP220 and Purolite A400TL

The ion exchange resins with chelating functional groups can act also as a weakly basic anion exchange resin (anion exchange mechanism) or coordinate mechanism take place (proceeds between metal ions and nitrogen atoms belonging to the ion exchange resin functional groups):



In the case of Lewatit MonoPlus TP220 it possesses three donor N atoms (aliphatic as well as aromatic ones) and thus anion exchange as well as complexing reaction could proceed (Chatterjee and SenGupta, 2011). As was pointed out by Miyazaki and Nakai (2011) the acrylic-type weak base anion-exchange resins could produce protons as the results of functional group tautomerism, from the amide form to the imide one at high pH, therefore such resins could act as cation-exchangers.

During the studies of zinc(II) adsorption on the polycondensation ion exchangers such as SB-1 and AN-31 (epoxyamine resins) and the polymerization ones (AV-17, AN-18, ANKB-35, VP-1aP, AN-31, SN-3) based on the copolymer of styrene with divinylbenzene (AV-17, AN-18, ANKB-35) or of vinylpyridine with divinylbenzene (VP-1aP, AN-31, SN-3), Skorokhodov et al. (2004) concluded that sorption of zinc complexes on the ion exchangers proceeds not by the anion exchange mechanism but by the solvation one (at $[\text{Cl}^-]=2\text{--}3 \text{ mol/dm}^3$ the dominant species is the neutral complex $[\text{ZnCl}_2]$ with 70%). 20% of zinc(II) exists as cationic species (Zn^{2+} , ZnCl^+ - such forms are not sorbed by anion exchange resins) and 10% as the negatively charged species $[\text{ZnCl}_4]^{2-}$ and $[\text{ZnCl}_3]^-$. The amino groups are surrounded by solvation shell (HCl and H_2O molecules). Moreover, neutral $[\text{ZnCl}_2]$ species interact with the amino functional groups resulting in HCl, H_2O molecules substitution. Zn(II) sorption on anion exchangers from the chloride solutions proceeds due to competition of neutral molecules for solvation of functional groups (Skorokhodov et al., 2004). Additionally, authors stated that Zn(II) sorption from the chloride solutions is mainly affected by the amount and basicity of amino functional groups of anion exchangers whereas the synthesis procedure, type of matrix and structure as well as the degree of monofunctionality and position of nitrogen atoms in the chain of ionogenic groups affect the zinc(II) sorption insignificantly. A similar observation, that the presence of functional groups and their basicity affect the zinc(II) removal efficiency, was also made in presented studies. In the case of Lewatit AF5, which does not possess the functional groups, the sorption capacity is the lowest, e.g. 1.5 mg/g (0.1 mol/dm^3 HCl) whereas for the ion exchangers with the functional groups the sorption capacity is higher, e.g. Purolite S984 - 2.8 mg/g (0.1 mol/dm^3 HCl) or much higher, e.g. Lewatit MonoPlus TP220 - 9.1 mg/g (0.1 mol/dm^3 HCl). Moreover, in the case of 6 mol/dm^3 HCl solution slightly lower sorption capacities than for the 3 mol/dm^3 HCl solution could be caused by the competition effect of zinc(II) complexes with chloride anions for the adsorption sites. Horne et al. (1957), Zhang et al. (2013) and Gilcă et al. (2014) found out that zinc(II) removal from the HCl solutions by the strongly and weakly basic anion exchange resins, such as Amberlite IRA410, Purolite A103S, Purolite A400MBOH, Purolite NRW700, 201×7, 301, Dowex 2, is pH dependent and is affected by the chloride ions concentration. The time required to reach equilibrium is different and depends on the sorbent type and concentration of the hydrochloric acid. This time usually increases with the increasing hydrochloric acid concentration, e.g. from 60 min (0.1 mol/dm^3) to 180 min (6 mol/dm^3) for Lewatit AF5 (Wołowicz and Hubicki 2016b), from 60 min (0.1 mol/dm^3) to >240 min (6 mol/dm^3) for Lewatit MonoPlus SR7, from 1 min (0.1 mol/dm^3) to 180 min (6 mol/dm^3) for Purolite A400TL or from 1 min (0.1 mol/dm^3) to 240 min (6 mol/dm^3) for Purolite A830. The polyacrylic matrix of ion exchangers ensures better kinetic properties of Purolite A400TL and Purolite A830 as compared to the ion exchangers of polystyrenic matrix. The percentage removal of zinc(II) was in the range from 29.1% to 94.9% for Lewatit MonoPlus TP220, from 16.9% to 85.9% for Dowex PSR2, from 23.2% to 90.6% for Dowex PSR3, from 9% to 38% for Lewatit AF5, from 58.8% to 95.2% for Lewatit MonoPlus SR7, from 56.8% to 84.4% for Purolite A830, from 90.4% to 94.2% for Purolite A400TL and from 24.5% to 63% for Purolite S984.

Zinc(II) removal from the chloride-nitrate(V) solutions was also analyzed (see Fig. 5 - the chosen examples). In such solutions it was observed that Lewatit AF5 - a sorbent without functional groups - exhibits the smallest sorption affinity towards zinc(II) (q_t values from 0 to 1.4 mg/g) (Wołowicz and Hubicki, 2016b) whereas the sorption capacities for the other ion exchangers were much higher, e.g. the q_e values obtained using 0.9 mol/dm^3 HCl - 0.1 mol/dm^3 HNO_3 solutions were equal to 7.9 mg/g for Purolite A400TL, 6.5 mg/g for Purolite A830, 7.1 mg/g for Lewatit MonoPlus TP220. Moreover, the sorption capacities increase with increasing concentration of HCl and decreasing concentration of HNO_3 .

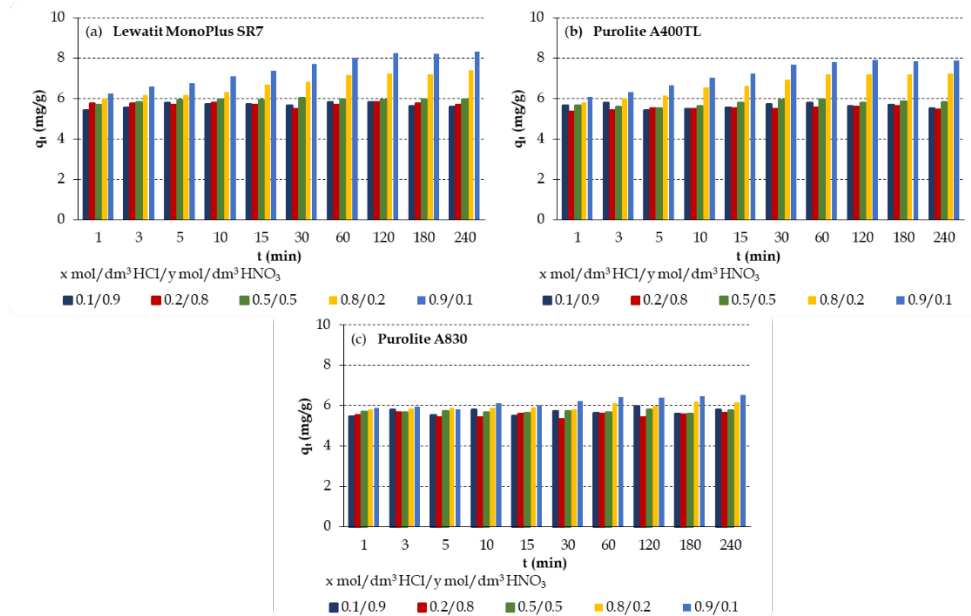


Fig. 5. Effect of the phase contact time and the HCl and HNO₃ concentration on zinc(II) removal using: (a) Lewatit MonoPlus SR7, (b) Purolite A400TL and (c) Purolite A830

e.g. the q_e values increase from 5.5 mg/g (0.1 mol/dm³ HCl – 0.9 mol/dm³ HNO₃; 0.2 mol/dm³ HCl – 0.8 mol/dm³ HNO₃) through 5.8 mg/g (0.5 mol/dm³ HCl – 0.5 mol/dm³ HNO₃), 7.2 mg/g (0.8 mol/dm³ HCl – 0.2 mol/dm³ HNO₃) to 7.9 mg/g (0.9 mol/dm³ HCl – 0.1 mol/dm³ HNO₃) for Purolite A400TL. Additionally, the time required to reach equilibrium increases with increasing concentration of HCl and decreasing concentration of HNO₃ e.g. from 30 min (0.1 mol/dm³ HCl – 0.9 mol/dm³ HNO₃) to 120 min (0.9 mol/dm³ HCl – 0.1 mol/dm³ HNO₃) for Purolite A400TL. Based on the kinetic studies and the obtained sorption capacities it was concluded that zinc(II) removal from the chloride solutions is more effective than from the chloride–nitrate(V) systems. In such a type of solutions the formation of mixed complexes could not be excluded and the lower sorption capacities could result from changes of such form diffusivity and competitive effect, therefore at the same phases contact time the q_e parameter is shorter. Based on the obtained results Lewatit MonoPlus TP220 was selected as the best sorbent for zinc(II) removal from the chloride solutions due to fast kinetics and high Zn(II) sorption ability. As it was found in literature, different type of resins (type of functional groups) affect the zinc removal efficiency (Valverde et al., 2002, Kononova et al., 2011, Zhang et al., 2013; Gilcă et al., 2014, Morcali et al., 2014; Nekouei et al., 2019) (see Table 5).

Kinetic studies provide important information about adsorption mechanisms. The kinetic data were fitted to two kinetic models: pseudo-first-order (PFO) (Lagergren, 1898), pseudo-second-order (PSO) (Ho and McKay, 1999) (description of kinetic models is presented in Table 2). The plots of $\log(q_e - q_t)$ vs. time for the PFO and t/q_t vs. time for PSO concerning zinc(II) adsorption onto the studied sorbents were estimated (not presented). The calculated values of k_1 , k_2 , h , $q_{e,exp}$ and their corresponding determination coefficients (R^2) are presented in Table 6, whereas the PSO fitting of the experimental results is depicted in Fig. 6.

As can be seen in Table 6 the values of determination coefficients obtained from the PFO and PSO models are much higher for the PSO model as compared to R^2 obtained from the PFO one. This indicates that the zinc(II) removal by all examined sorbents is better fitted by the PSO model (determination coefficients are close to 1). Moreover, comparing the values of sorption capacity obtained experimentally ($q_{e,exp}$) and those calculated (q_1 and q_2) from the pseudo-first- and pseudo-second order kinetics, it can be concluded that the experimental sorption capacity values ($q_{e,exp}$) are similar in the case of PSO model (q_2), e.g. the $q_{e,exp}$ value is equal to 9.15 mg/g whereas q_2 is equal to 9.24 mg/g for Lewatit MonoPlus TP220 (6 mol/dm³ HCl). The differences between the $q_{e,exp}$ and q_1 values are much higher for all the examined sorbents. As can be found in the literature, zinc sorption on the other ion exchangers and sorbents also follows the pseudo-second order kinetic model, e.g. zinc sorption on Amberlite

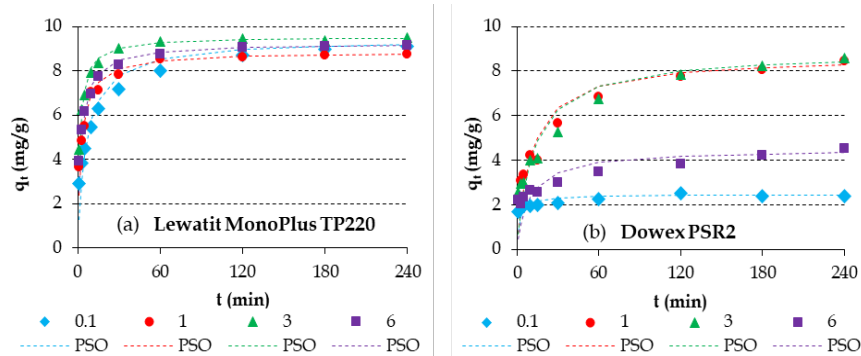


Fig. 6. Fitting of the experimental and calculated data concerning Zn(II) adsorption on the selected sorbents based on the PSO kinetic model (0.1–6 mol/dm³ HCl – 100 mg Zn(II)/dm³) using: (a) Lewatit MonoPlus TP220 and (b) Dowex PSR2

IRA410 (Zhang et al., 2013), zinc(II) removal from strongly acidic solutions by Amberlite IRA410 (Gilcă et al., 2014), zinc removal by low cost adsorbents (Mishra and Patel 2009), zinc removal from synthetic electroplating rinse water by the cationic exchange resin of the commercial name Ceralite IR120 (Revathi et al., 2012) etc. This indicates chemisorption during the adsorption process.

3.1. Equilibrium studies – maximum sorption capacities determination

The equilibrium studies were carried out to verify the sorption mechanism. The effect of initial zinc(II) concentration on zinc(II) uptake was analysed. Zinc(II) sorption capacities for eight sorbents vs. the equilibrium Zn(II) concentration are presented in Fig. 7. Comparing the sorption capacity values, the Zn(II) ion affinity towards analysed adsorbents is as follows: Lewatit MonoPlus TP220 (620±0.8 mg/g) > Dowex PSR2 (594±0.5 mg/g) > Lewatit MonoPlus SR7 (592±0.4 mg/g) > Prurilite S984 (584 ±0.4 mg/g) ≈ Dowex PSR3 (584±0.1 mg/g) > Lewatit AF5 (582±0.2 mg/g) > Purolite A830 (566±0.3 mg/g) > Purolite A400TL (520±0.2 mg/g). The highest sorption capacity of 620 mg/g was obtained in the case of Lewatit MonoPlus TP220 of the bis-picolylamine functional groups. The sorption capacities for all of the examined sorbents were in the range from 520±0.2 to 620±0.8 mg/g.

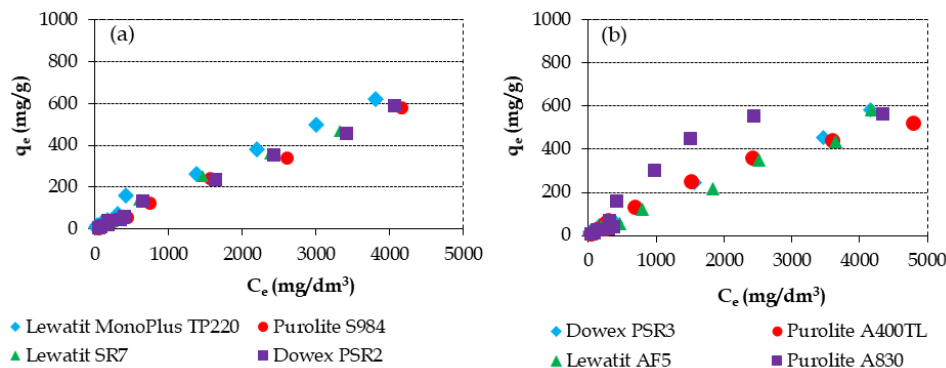


Fig. 7. Isotherms of zinc(II) adsorption (initial concentration 100–10000 mg/dm³, mass of a sorbent 0.5±0.0005 g, volume of solutions 0.05 dm³, agitation speed 180 rpm, amplitude A=8, phases contact time 24 h)

Based on the Langmuir and Freundlich isotherm models (Table 7), equilibrium parameters concerning zinc(II) sorption using sorbents under discussion, were obtained. As it was found the determination coefficient was higher in the case of the Freundlich model and was in the range from 0.942 to 0.986, whereas this value for the Langmuir model was lower than 0.637. The other, obtained parameters were: the adsorbate affinity for the adsorbent k_f from 0.115 to 0.945 mg/g and the adsorption intensity or surface heterogeneity, $1/n$ from 0.774 to 0.994 (obtained using the Freundlich model). The R_L parameters were in the range from 0.971 to 0.997 (obtained from the Langmuir model). The surface heterogeneity, $1/n$, and the values of an equilibrium constant, R_L , were found to be less than one ($R_L > 1$

Table 5. Comparison of Zn(II) sorption/removal efficiency from aqueous solutions

Ion exchanger	Additional information	Solutions, metal removal	Experimental conditions	Sorption capacity (q_e), Percentage removal (%R)	Ref.
Lewatit TP260	WAC, matrix - ST-DVB, structure - MP, FG - amino methyl phosphonic acid groups	Zn(II), Al(III), Cu(II), Ni(II), Pb(II) removal; digestion of crushed waste PCBs (<1mm) in 2.7 mol/dm ³ HNO ₃ , 60 min leaching time, 25 °C temperature and 0.05 solid to liquid ratio	M=100 g/dm ³ T=25 °C	q_e : Al(III)=0.77 mg/g; Cu(II)=64.76 mg/g; Ni(II)=0.47 mg/g; Pb(II)=1.75 mg/g; Zn(II)=3.25 mg/g	Nekouei et al., 2019
Lewatit TP208	WAC, matrix - ST-DVB, structure - MP, FG - iminodiacetic acid groups		M=100 g/dm ³ T=25 °C	q_e : Al(III)=0.73 mg/g; Cu(II)=66.66 mg/g; Ni(II)=0.56 mg/g; Pb(II)=1.68 mg/g; Zn(II)=2.74 mg/g	
Amberlite IRA743	WBA, matrix - ST-DVB, structure - MP, FG - N - methylglucamine acid groups		M= 90 g/dm ³ T=25 °C	q_e : Al(III)=0.55 mg/g; Cu(II)=35.5 mg/g; Ni(II)=0.16 mg/g; Pb(II)=1.34 mg/g; Zn(II)= 1.18 mg/g	
Lewatit TP207	WAC, matrix - ST-DVB, structure - MP, FG - iminodiacetic acid groups	Zn(II) and Cu(II) adsorption; sulfate solutions	T=25 °C, 100 rpm, pH 6, V=10 cm ³ , C ₀ =300 mg/dm ³	q_e Zn max=73 mg/g, q_e Cu max=68.5 mg/g (25 °C) q_e Zn max=87.7 mg/g, q_e Cu max=78.7 mg/g (35 °C) q_e Zn max=111.1 mg/g, q_e Cu max=84.6 mg/g (45 °C)	Morcali et al., 2014
Amberlite IR120	SAC, matrix - ST-DVB, structure - G, FG - sulfonic acid groups	Zn(II), Cu(II), Cd(II) adsorption; industrial solutions	V=0.1 dm ³ , c=0.05 mol/dm ³ , t=24 h, T=10, 30 °C	Amberlite IR-120 exhibits different orders of selectivity at 10 and 30 °C, Cu(II) > Zn(II) > Cd(II) > Ca(II) at 10 °C, Zn(II) > Cu(II) > Cd(II) > Ca(II) at 30 °C	Valverde et al., 2002
Amberlite IRA410	SBA, type 2, matrix - ST-DVB, structure - G, FG - N - dimethyl ethanol ammonium	Zn(II) removal; model solutions, ZnCl ₂ in 1 mol/dm ³ HCl	M=5 g, V=100 cm ³ , C ₀ =500 mg/dm ³ , room temperature, stirring rate 500 rpm t=300 min	%R max= 87% for Amberlite IRA410 %R min=79% for Purolite A400MBOH. The following series was depicted based on removal efficiencies: Amberlite IRA410 > Purolite A103S > Purolite NRW700 > Purolite A400MBOH. q_e : 8.34 mg/g for Amberlite IRA410; 7.83 mg/g for Purolite A400MBOH.	Gilcă et al., 2014
Purolite A400MBOH	SBA, type 1, matrix - ST-DVB, structure - MP, FG - quaternary ammonium				
Purolite NRW700	WBA, matrix - ST-DVB, structure - MP, FG - tertiary amine				
Purolite A103S	WBA, FG - tertiary amine				
301	WBA, FG - tertiary amine	Zn(II) removal; cyanide effluents, C ₀ =636.5 mg/cm ³ , pH 12	L/S mass ratios is 60 T=20 °C; pH 12.	q_e Zn(II) =25.78 mg/cm ³	Zhang et al., 2013
Purolite S985	WBA, matrix - PA-DVB, structure - MP, FG - polyamine	Zn(II) removal; chloride and chloride-sulfate solutions (HCl concentration was from 0.001 to 4.0 mol/dm ³ , the chloride-sulfate systems, HCl:H ₂ SO ₄ =1:1; 1:2 and 1:4, the HCl acids concentrations 0.001-2.0 mol/dm ³	C ₀ Zn(II)=1 mmol/dm ³ , M=0.2 g, V=0.2 dm ³ , T=20±1 °C, t=24 h	HCl solutions: 0.01-4 mol/dm ³ %R S985=60-80%; %R A500=69-83%; %R AV-17-8=54-74%; %R AM-2B=68-75%	Kononova et al., 2011
Purolite A500	SBA, matrix - ST-DVB, structure - MP, FG - quaternary ammonium			HCl-H ₂ SO ₄ solutions: 2 mol/dm ³ -2 mol/dm ³ HCl:H ₂ SO ₄ =1:1; 1:2 and 1:4 %R S985=55-60%, %R A500=58-71%, %R AM-2B=68-69%	
AM-2B	IMA, matrix - ST-DVB, structure - MP, FG - secondary and tertiary amine, quaternary ammonium				
AV-17-8	SBA, matrix - ST-DVB, structure - G, FG - quaternary ammonium				

FG - functional groups, WAC - weakly acidic cation exchange resin, WBA - weakly basic anion exchange resin, SAC - strongly acidic cation exchange resin, SBA - strongly basic anion exchange resin, IMA - intermediate anion exchange resin, ST-DVB - styrene-divinylbenzene, PA-DVB - polyacrylic -divinylbenzene, MP - macroporous, G - gel

Table 6. Comparison of the kinetic parameters from the PFO and PSO models, concerning adsorption of Zn(II) using the sorbents under discussion

System	q_{exp} (mg/g)	PFO			PSO			
		q_1 (mg/g)	k_1 (1/min)	R^2	q_2 (mg/g)	k_2 (g/mg*min)	h (mg/g*min)	R^2
Lewatit MonoPlus TP220								
HCl, (mol/dm ³)								
0.1	9.1±0.24	4.7	0.021	0.981	9.3	0.017	1.49	0.999
1	8.7±0.14	2.8	0.028	0.925	8.8	0.042	3.25	1.000
3	9.5±0.04	2.0	0.023	0.733	9.5	0.061	5.56	1.000
6	9.2±0.15	2.8	0.025	0.914	9.2	0.041	3.48	1.000
Dowex PSR2								
0.1	2.4±0.27	0.5	0.023	0.948	2.4	0.214	1.25	0.999
1	8.5±0.13	5.2	0.015	0.972	8.6	0.011	0.80	0.996
3	8.6±0.24	5.6	0.016	0.991	8.9	0.009	0.72	0.995
6	4.5±0.11	2.3	0.011	0.983	4.5	0.024	0.49	0.992
Dowex PSR3								
0.1	4.1±0.20	1.1	0.010	0.704	4.1	0.069	1.15	0.998
1	8.9±0.14	3.7	0.019	0.939	9.0	0.023	1.85	0.999
3	9.1±0.15	3.1	0.015	0.570	9.0	0.029	2.30	0.997
6	6.6±0.09	2.2	0.022	0.795	6.7	0.036	1.62	0.999
Lewatit MonoPlus SR7								
0.1	6.4±0.08	0.4	0.040	0.624	6.4	0.592	24.01	1.000
1	9.4±0.13	1.8	0.021	0.886	9.5	0.064	5.75	1.000
3	9.5±0.11	1.8	0.033	0.967	9.6	0.086	7.89	1.000
6	8.3±0.17	1.4	0.017	0.897	8.3	0.076	5.23	1.000
Purolite A830								
0.1	5.9±0.24	0.1	0.006	0.264	5.9	2.964	102.40	1.000
1	6.9±0.04	0.8	0.029	0.799	6.9	0.203	9.70	1.000
3	8.5±0.14	1.7	0.010	0.919	8.4	0.047	3.29	0.999
6	7.9±0.15	1.6	0.016	0.856	7.9	0.062	3.80	1.000
Purolite S984								
0.1	2.8±0.05	0.1	0.001	0.002	2.9	0.623	5.14	0.996
1	3.8±0.07	0.8	0.057	0.970	3.8	0.350	5.13	1.000
3	6.3±0.10	2.5	0.018	0.968	6.4	0.035	1.40	0.999
6	5.8±0.11	3.0	0.015	0.817	5.8	0.017	0.58	0.981
Lewatit AF5								
0.1	1.5±0.04	-	-	-	-	-	-	-
1	3.0±0.04	0.8	0.011	0.450	3.0	0.120	1.09	0.993
3	3.3±0.03	1.7	0.056	0.826	3.5	0.071	0.87	0.993
6	2.0±0.01	0.7	0.005	0.520	1.9	0.066	0.24	0.985
Purolite A400TL								
0.1	6.1±0.05	0.2	0.000	0.075	6.1	0.365	13.42	0.999
1	8.8±0.14	1.5	0.060	0.921	8.8	0.172	13.38	1.000
3	9.5±0.24	1.5	0.065	0.950	9.5	0.213	19.25	1.000
6	8.4±0.17	1.3	0.031	0.948	8.4	0.119	8.39	1.000

- indicates that the kinetic parameters were not obtained due to the fact that the q_t values were very similar (1.5–2.0 mg/g)

(unfavourable), $0 < R_L < 1$ (favourable), $R_L = 0$ (irreversible) and $R_L = 1$ (linear)) indicating that the zinc(II) adsorption onto analysed sorbents is favourable. Comparing the determination coefficients obtained using the Langmuir and Freundlich models it could be stated that zinc(II) sorption is rather not monolayer and proceeds on the heterogeneous sites. As it was found in the literature (Dada et al., 2012; Revathi et al., 2012; Gilcă et al., 2014) the zinc(II) sorption follows different isotherm models. Zinc(II) and copper(II) removal from aqueous solutions using chelating ion exchangers Chelex 100 and Amberlite IRC748, containing iminodiacetic functional groups, was carried out by Lin and Juang (2005) (percentage removal of metal ions were 68% – Cu(II), 84% – Zn(II) for Chelex 100; and 65% – Cu(II), 82% – Zn(II) for Amberlite IRC748). The Langmuir equation gave a better fitting of the equilibrium data (correlation coefficient, $R^2 > 0.992$) than the Freundlich one. Strongly basic anion exchange resin such as Amberlite IRA402 and Amberlite IRA458, in the presence of the complexing agent of a new generation, were applied in Zn(II) and Cu(II) removal from aqueous solutions and the equilibrium studies were fitted using the Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherm models. Obtained results shows that Langmuir isotherm model fit well the experimental data (the maximum sorption capacities were 56.41 mg Cu(II)/g and 44.05 mg Zn(II)/g for Amberlite IRA402 and 50.91 mg Cu(II)/g and 46.51 mg Zn(II)/g for Amberlite IRA458) (Kołodźńska, 2011). Zinc(II) sorption from the model electroplating rinse water by the cationic exchange resin Ceralite IR120 follows the Langmuir, Redlich–Peterson, and Toth isotherms. In this case the sorption capacity was much lower (105.1 mg/g) than that obtained due to another type of interaction (Revathi et al., 2012). Zinc(II) sorption performed from 1 mol/dm³ HCl solutions onto Amberlite IRA410 reveals physical sorption (results confirmed by the Dubinin–Radushkevich and Temkin isotherm models as well as by the obtained mean free energy (7.45 kJ/mol) and heat of sorption 1×10^{-4} kJ/mol) (Gilcă et al., 2014). Zinc(II) sorption by the modified rice husk using the phosphoric acid follows the Langmuir isotherm model (Dada et al., 2012).

Table 7. Comparison of Langmuir and Freundlich isotherm parameters concerning zinc(II) adsorption onto various sorbents

q_e (mg/g)	Langmuir isotherm				Freundlich isotherm		
	Q_0 (mg/g)	b (dm ³ /mg)	R^2	R_L	k_f (mg/g)	$1/n$	R^2
Lewatit MonoPlus TP220							
620±0.8	1053.8	0.0003	0.637	0.971	0.945	0.780	0.975
Purolite S984							
584±0.4	2082.4	0.0001	0.192	0.992	0.369	0.870	0.959
Lewatit MonoPlus SR7							
592±0.4	1662.0	0.0001	0.280	0.988	0.528	0.833	0.942
Dowex PSR2							
594±0.5	2763.7	0.0001	0.230	0.994	0.223	0.949	0.986
Dowex PSR3							
584±0.1	980.6	0.0002	0.593	0.977	0.763	0.774	0.965
Purolite A400TL							
520±0.2	1348.7	0.0001	0.497	0.986	0.270	0.920	0.971
Lewatit AF5							
582±0.2	1502.9	0.0001	0.279	0.988	0.386	0.860	0.967
Purolit A830							
566±0.3	6182.9	0.00003	0.0120	0.997	0.115	0.994	0.948

3.2. Desorption and reuse studies

As the kinetic studies results indicated that Lewatit MonoPlus TP220, Lewatit MonoPlus SR7 and Purolite A400TL show high sorption capacity for zinc(II), therefore these sorbents were applied in the desorption studies. By using 50 cm³ of 1 or 2 mol/dm³ HNO₃, 1 or 2 mol/dm³ HCl, 1 or 2 mol/dm³ NH₃*H₂O, 1 or 2 mol/dm³ NaOH and 1 or 2 mol/dm³ NaCl as eluting agents (mass of loaded Zn(II) ion exchanger was equal to 0.5 g, V/M=0.1), desorption yields (%D1, 1 indicates the first cycle) were obtained and presented in Table 8. Sorption yield (%S1, 1 indicates the first cycle) was in the range from 93.41% (Purolite A400TL) through 94.04% (Lewatit MonoPlus SR7) to 96.7% (Lewatit MonoPlus TP220).

Despite the highest adsorption yield in the case of Zn(II) on Lewatit MonoPlus TP220 (8.2–9.5 mg/g) the desorption yield was not much higher as compared to Purolite A400TL and Lewatit MonoPlus SR7. The interaction of Zn(II) with functional groups of chelating ion exchanger are usually strong (coordinating mechanism), therefore the desorption yield are slightly lower or similar to another sorbents. As was pointed out by the other authors, e.g. Kononova et al. (2011), common mineral acids are applied for zinc(II) desorption, therefore they applied hydrochloric acid solution 2 mol/dm³ in concentration for zinc(II) removal from Purolite S985, Purolite A500 and AM-2B ion exchangers and desorption was practically complete (%D=93±5 (Purolite S985), 94±5 (Purolite A500) and 95±5 (AM-2B)). In presented study the desorption yield was the highest using nitric(V) acid, sodium hydroxide and sulfuric(VI) acid and the concentration of the eluting agent affected %D yield. The highest %D1 was obtained for Lewatit MonoPlus TP220 using 1 mol/dm³ HNO₃ and 2 mol/dm³ H₂SO₄ (%D1=40%), for Lewatit MonoPlus SR7 using 2 mol/dm³ NaOH (%D1=48.41%) and for Purolite A400TL using 2 mol/dm³ HNO₃ (%D1=42.18%). Three cycles of sorption/desorption were performed using the best eluting agents (HNO₃, H₂SO₄ and NaOH). The yields of sorption and desorption, in the three cycles, for Lewatit MonoPlus TP220 are presented in Fig. 8.

Table 8. Comparison of desorption yield (%D1) of zinc(II) from the anion exchangers Lewatit MonoPlus TP220, Lewatit MonoPlus SR7, Purolite A400TL

Eluting agent	Lewatit MonoPlus TP220	Lewatit MonoPlus SR7	Purolite A400TL	Eluting agent	Lewatit MonoPlus TP220	Lewatit MonoPlus SR7	Purolite A400TL
Desorption yield, %D1							
1 mol/dm ³ HNO ₃	40.00	40.20	40.04	1 mol/dm ³ NaOH	20.90	41.26	41.75
2 mol/dm ³ HNO ₃	38.50	45.94	42.18	2 mol/dm ³ NaOH	37.10	48.49	36.61
1 mol/dm ³ HCl	6.30	6.59	12.20	1 mol/dm ³ H ₂ SO ₄	37.30	48.28	41.11
2 mol/dm ³ HCl	2.70	3.83	5.78	2 mol/dm ³ H ₂ SO ₄	40.00	34.67	41.75
1 mol/dm ³ NH ₃ *OH	24.20	24.46	24.20	1 mol/dm ³ NaCl	3.80	6.38	11.56
2 mol/dm ³ NH ₃ *OH	35.40	31.05	31.26	2 mol/dm ³ NaCl	2.90	3.19	4.92

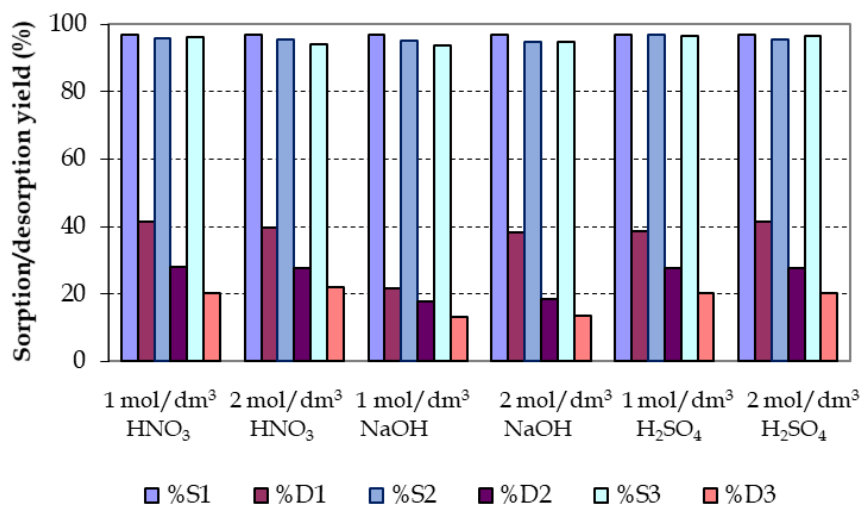


Fig. 8. Zinc(II) sorption and desorption efficiency using Lewatit MonoPlus TP220 (three cycles of sorption-desorption)

4. Conclusions

The effectiveness of Zn(II) sorption depends on the phase contact time, HCl concentration and physicochemical properties of the sorbents. With increasing time, there is usually an increase in the amount of adsorbed zinc(II) on the tested sorbents. The time required to achieve the equilibrium is different and depends on the sorbent type and concentration of hydrochloric acid. This time usually increases with increasing hydrochloric acid concentration. The highest sorption capacity values were obtained for the 3 mol/dm³ HCl based systems, due to high fractions of the anionic, chloride complexes of Zn(II) and possible interaction of sorbate with resin's functional groups. Based on the sorption capacities, the Zn(II) affinity towards analysed adsorbents is as follows: Lewatit MonoPlus TP220 > Dowex PSR2 > Lewatit MonoPlus SR7 > PruroLite S984 ≈ Dowex PSR3 > Lewatit AF5 > Purolite A830 > Purolite A400TL. Lewatit MonoPlus TP220 of bis-picolylamine functional groups as chelating resin (in acidic solutions works similar to weakly basic anion exchanger) of three donor N atoms (soft Lewis base) shows high affinity for soft Lewis acid like Zn(II) complexes and form coordinate bonds. The maximum sorption capacity was estimated as 620 mg/g for Lewatit MonoPlus TP220. Lower sorption capacities were observed for the strongly basic ion exchangers of polystyrenic type with the quaternary ammonium functional groups, whereas lack of functional groups shows additional reduction of sorption yield. Anion exchangers of polyacrylic type shows the lowest sorption capacities. High sorption capacity connected with the presence of bis-picolylamine functional groups, fast sorption kinetics and good sorption behavior even in strongly acidic solutions, make this ion exchange resin very promising in the practical applications. Zinc(II) adsorption kinetics is better described by the pseudo-second order kinetic model, indicated that chemisorption could proceed, but to prove this fact the diffusion models should be also analysed. Zn(II) desorption from the Lewatit TP220 ion exchanger is not effective enough – this indicate strong interactions between zinc(II) and ion exchanger. After 3 cycles of sorption-desorption, there is no rapid reduction in the sorption capacity of analysed ion exchangers.

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