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Novel multifunctional ion exchangers for metal ions removal in the presence of citric acid

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Chemosphere

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Ni-MH baterries



2	presence of citric acid
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10 11	Abstract
11	
12	The present study deals with the potential application of Purolite S957 and Diphonix
13	Resin [®] for the removal of rare earth elements from aqueous liquors as a result of the
14	extraction of spent Ni-MH batteries in the presence of citric acid. The effects of the
15	metal ion and the citric acid ratio, pH, ion exchanger dose, contact time, initial
16	concentration and temperature were studied using the batch technique. The
17	Langmuir and Freundlich adsorption isotherm models were used for the description
18	of the adsorption process. The equilibrium adsorption data were fitted using the
19	pseudo first order, pseudo second order, intraparticle diffusion, Boyd, film diffusion
20	and Dumwald-Wagner models. The maximum adsorption capacity q_0 obtained from
21	the Langmuir isotherm was found to be 46.63 mg/g for Ni(II) and 60.75 mg/g for
22	La(III) on Purolite S957 as well as 46.55 mg/g for Ni(II) and 60.12 mg/g for La(III) on
23	Diphonix Resin [®] . The kinetics followed the pseudo second order reaction. Based on
24	the Weber-Morris model the adsorption process proved to proceed in two stages.
25	Based on the Boyd model the rate controlling steps were film and intraparticle
26	diffusions. The adsorption process was spontaneous and endothermic in nature.
27	Reusability of ion exchangers in the desorption studies was also evaluated as a
28	sustainable approach. The physicochemical properties of Purolite S957 and Diphonix

Novel multifunctional ion exchangers for metal ions removal in the

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Journal Pre-proof

Resin[®] were studied using the ASAP analysis, optical and scanning electron
microscopy, potentiometric titration, pH_{ZPC} and FT-IR as well as XPS analysis.

Keywords: La(III); Ni(II); citric acid; Purolite S957; Diphonix Resin[®]; remediation;
 sorption; spent batteries

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37 **1. Introduction**

Several methods can be used to remove rare earth elements (REEs) from the 38 secondary sources such as waste electronic and electrical equipment (WEEEs), mine 39 coal combustion products (CCPs) and acid mine drainages (AMDs) and these are 40 precipitation, ion exchange and extraction. A critical review on secondary wastes has 41 been provided in (Binnemans et al., 2013) including a summary of different 42 components containing REEs and heavy metal ions (HMs). It is well known that using 43 2 M H₂SO₄ it is possible to recover Ni(II) and other metal ions from Ni-MH batteries. 44 After neutralization by NaOH (pH about 1.2) the lanthanides precipitate, however, the 45 highest efficiency for La(III) can be obtained. After leaching, Fe(III) ions are usually 46 the most predominant impurities and can be present at high concentrations (Agarwal 47 et al., 2019). At pH 3.5 it is also possible to remove Fe(III) ions at a temperature 48 higher than 353 K (increasing pH and temperature reduced the solubility of iron 49 hydroxide) (Izadi et al., 2017). As follows from the literature data 2-50 51 ethylhexylphosphonic acid mono 2-ethylhexyl ester (PC88A) and bis(2,4,4trimethylpentyl) phosphinic acid (Cyanex 272) have the potential to remove impurities 52 like Fe(III), Cd(II) and Mn(II) whereas di-2-ethylheyxl phosphoric acid (D2EHPA) can 53 be used for removal of Zn(II), Al(III) and Mn(II) at low pH values from leachates of 54

spent Ni-MH. Typically Ni(II) and Co(II) ions are further separated by Cyanex 272.
However, it should be pointed out that the REEs separation process and mechanism
depend on the state in which REEs occur in the aqueous solutions (Akcil et al.,
2018).

In the ion exchange process the presence of ligands in a solution changes both 59 the mechanism and capacity of sorption due to the modification of metal speciation. 60 In the recovery process, the complexing agents such as ethylenediaminetetraacetic 61 (EDTA) and nitrilotriacetic (NTA) acids are used. However, despite their very good 62 chelating properties these synthetic compounds have some disadvantages such as 63 poor biodegradability. 2-hydroxy-1,2,3-propanotricarboxylic acid also known as 3-64 hydroxy-3-carboxy-pentanodiacetic acid or simply citric acid is a common organic 65 acid containing three carboxyl and one hydroxyl groups. Therefore it is well known for 66 67 its ability to form guite strong complexes with uranium. It is also known to remove metal ions from soils and wastewaters effectively. It is environmentally friendly, 68 exhibits relatively consistent removal efficiency and is cost-effective. Citric acid forms 69 different types of complexes with the transition metals, lanthanides and actinides 70 (Rajan and Martell, 1965; Zabiszak et al., 2018). It has been used to extract 71 plutonium from contaminated soils, to decontaminate the components of nuclear 72 reactors and to extract metals and radionuclides, such as As(III,V), Ba(II), Cd(II), 73 Cs(I), Co(II), Cu(II), Cr(III,V), Pb(II), Ni(II), Zn(II), Sr(II), Th(IV) and U(VI) from 74 contaminated soils, wastes and municipal solid waste ashes. Exemplary, the 75 extraction procedure using citric acid in combination with dithionite followed by the 76 ammonium carbonate extraction allows to decrease U(VI) amounts from 450-540 77 mg/kg to less than 50 mg/kg (Francis et al., 1999). Citrates were used to chelate 78 Fe(III) ions and prevent its precipitation, however, the efficiency is largely dependent 79

on pH. Citric acid has several advantages as an extracting agent; (i) it biodegrades 80 rapidly to carbon dioxide and water, making the treatment and disposal of the effluent 81 more environmentally friendly, (ii) it is inexpensive and can be obtained as an 82 industrial waste product and (iii) it offers a buffered system in contrast to sulphuric 83 acid. One possible solution to obtain citric acid during the biosynthesis, as proposed 84 in the INCOVER project whose aim is to develop innovative and sustainable added-85 value technologies for a resource recovery-based treatment of wastewater, is using 86 smart operation monitoring and control methodologies (Aurich et al., 2017; Förster et 87 al., 2007; Kamzolova et al., 2005). It is important because in the EU the citric acid 88 consumption is 530,000 t/year, the annual import is about 200,000 t and the demand 89 is expected to increase by 5% every year. Citric acid is used in many industrial 90 processes as a cleaner, decalcifier, colour-stabilizer, acidulant and flavour enhancer. 91 92 Citric acid is safe and can be used as food additives (Soccol et al., 2006).

The main objective of this study was to develop the strategy of heavy metals 93 (HMs) and rare earth elements (REEs) removal from liquors obtained from the 94 extraction of spent Ni-MH batteries as WEEEs. As follows form the literature the 95 overall cost to process 1 t of Ni-MH batteries is at maximum US\$ 50.00 and this 96 produces 316 kg of Ni worth at least US\$ 680.00 (Bertuol et al., 2006; Dvořák and 97 Vu, 2015; Tenório and Espinosa, 2002). Obtaining the Ni(II) salts is well described, 98 however, REEs, which can be obtained by the ion exchange separation, are also 99 valuable. The assumption for this was the fact that the strong cation ion exchangers 100 with the sulphonic functional groups were ineffective for selective uptake of useful 101 rare earth metal ions. Therefore, for their preparation the ion exchangers with di- and 102 trifunctional groups were used. The introduction of different functional groups 103 improves the effectiveness of separation, adsorption kinetics and elution processes 104

(Alexandratos, 2007; Smolik et al., 2014). Within this type of ion exchangers there 105 can be distinguished: Purolite S957 which contains the phosphonic and sulphonic 106 functional groups as well as Diphonix Resin[®] with 1,1-diphosphonic, sulphonic and 107 carboxylic ones. The adsorption capacity was investigated by changing different 108 parameters such as the different ratio of metal ions and citric acid solution, pH, ion 109 exchanger dose, contact time as well as the initial concentration and temperature. 110 Moreover, the adsorption mechanisms were examined studying kinetic and isotherm 111 models. The reusability of ion exchangers was also evaluated as a sustainable 112 approach. 113

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115 2. Materials and methods

116 2.1. Materials characterization

Ni(II) and La(III) stock solutions were prepared using Ni(NO₃)₂·6H₂O and La(NO₃)₃·H₂O, respectively by dissolving a suitable amount of salt. The final concentration was estimated by the ICP-OES method. Ni(II) and La(III) working solutions were prepared by diluting stock solutions with deionized water before the use. Citric acid C₆H₈O₇·H₂O was purchased from Chempur Company (Poland).

The chelating ion exchanger Purolite S957 produced by Purolite Ltd (Germany) contains the phosphonic and sulphonic functional groups. Diphonix Resin[®] produced by EiChrom Industries (France) contains geminally substituted diphosphonic, sulphonic and carboxylic acid groups covalently bonded to the polymer matrix (Silva et al., 2018). Both of them were used for the sorption of Ni(II) and La(III). Typical properties of both ion exchangers are collected in Table 1.

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Table 1. Physical and chemical properties of Purolite S957 and Diphonix Resin[®].

Properties Purolite S957 Diphonix Resin [®]	Properties	Purolite S957	Diphonix Resin [®]
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To avoid the changes of acidity during the studies the initial Na⁺ form of the ion exchangers was converted to the H⁺ one (Izadi et al., 2017). The changes of the pH during equilibration in the DI water are presented in Table 1. For both ion exchangers the additional physicochemical properties were determined.

Ion exchange capacity (IEC) represents the totality of active sites or functional 135 groups responsible for the ion exchange process which was determined by the 136 titration method (Contescu et al., 1997). The functional groups content was 137 138 determined using the potentiometric titration methods. Purolite S957 and Diphonix Resin[®] were converted to the H⁺ form, i.e. all acid groups obtain H⁺ as counter ions 139 and were titrated with 0.1 M NaOH. The titrations were made at room temperature 140 with the variation ±1℃. For this purpose the 907 T itrando titrator equipped with the 141 800 Dosino type dosing systems, 801 type magnetic stirrer, high performance 142 unitrode and Pt 1000 temperature sensor (Metrohm) were used. 143

Point of zero charge (abbreviated as PZC) of ion exchangers was determined using the pH drift method based on the curve pH₀ vs. Δ pH (pH₁-pH₀) (Lopez-Ramon

et al., 1999). To this end 0.5 g of ion exchanger was added into a flask containing 50 146 cm³ of the pH-adjusted solution of 0.01 M NaCl. The initial pH was adjusted to a 147 value from 2 to 12. The flasks were stoppered and stirred for 24 h. The final pH 148 values were measured (pH₁). The potentiometric titrations in the presence of sodium 149 chloride NaCl at 0.1, 0.01 and 0.001 M were also conducted. 0.5 g of Diphonix 150 Resin[®] or Purolite S957 and 50 cm³ of NaCl solutions were added to the 50 cm³ 151 beaker and stirred. As for potentiometric titrations the standard 0.1 M HCl and 0.1 M 152 NaOH solutions were used. After each addition the suspension pH was measured. 153 As previously the 907 Titrando titrator was used for this purpose. 154

The parameters of the porous structure of Purolite S957 and Diphonix Resin[®] were determined measuring the N₂ adsorption/desorption isotherms at 77 K. The accelerated surface area and porosimetry system, ASAP 2420M (Micromeritics Instrument Corporation, USA) were used to this end. Before measurements the samples were degassed at 378 K. The Brunauer-Emmett-Teller (BET) method was used for the surface area calculation and the Barrett-Joyner-Halenda (BJH) method was applied to determine the pore size distribution.

SEM images of Purolite S957 and Diphonix Resin[®] were also made. To this end
 the Quanta 3D FEG (FEI Corporation) instrument was used.

Purolite S957 and Diphonix Resin[®] were analysed using an attenuated total reflection Fourier transform infrared (ATR-FTIR) spectrometer (Agilent Cary 630, Agilent Technologies) under the ambient conditions. The spectra were recorded from 4000 to 644 cm⁻¹.

168 The X-ray photoelectron spectroscopy (XPS) method was used to study 169 chemical compositions of the samples using the multi chamber ultra-high vapour XPS 170 UVH (Prevac) equipped with the monochromatized AIK_{α} radiation. As for the charge

neutralization of ion exchangers the flood gun source was applied. The bindingenergy scale with the binding energy 285.0 eV was calibrated by means of the
carbon line.

174 2.2. Kinetic and adsorption/desorption tests

The sorption process was studied for the three different metal ion to citric acid ratios 1:1, 1:2 and 2:1. Working solutions were prepared weighing the appropriate amounts of citric acid and stock solutions of Ni(II) and La(III).

Stock solutions of Ni(II) and La(III) ions at the concentration of 1000 mg/dm³ were prepared from NiCl₂·6H₂O and La(NO₃)₃·H₂O (Avantor Performance Materials Poland S.A.) and suitably diluted accordingly to various required initial concentrations. The appropriate amount of citric acid was also added. The concentration of metal ion corresponds to the content of Ni(II) and La(III) ions in the leachates from the spent Ni-MH batteries. The detailed procedure for their extraction by citric acid was not presented due to patent preparation.

Adsorption experiments in the single component systems were performed at 185 293 K using the batch (static) technique. Static sorption experiments were carried out 186 in terms of the invariable solid to solution ratio. 50 cm³ of metal ion solutions with the 187 initial concentration of Ni(II) and La(III) in the presence of citric acid ranging from 25 188 to 200 mg/dm³ were placed in 100 cm³ conical flasks with 0.1 g ion exchanger 189 samples and stirred at 180 rpm, in the time interval from 1 to 360 min using the 190 laboratory shaker type 358A (Elpin Plus, Poland). The experiments were conducted 191 at room temperature (298 K). The initial pHs of the solutions were adjusted to 5.0 192 using the 1 M HNO₃ or 1 M NaOH solution to avoid metal ions precipitation. The pHs 193 of the solution during the sorption studies were not regulated. After stirring the 194 samples were separated by filtration using the filter paper. 195

To determine the adsorption capacity of selected ion exchangers experiments were conducted with the various initial concentrations of metal ions in the presence of citric acid from 25 to 600 mg/dm³. For the desorption process different eluting agents were proposed. The systems were performed as described previously.

The concentrations of Ni(II) and La(III) in the solutions were analysed by the Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) using ICP-OES 720 (Varian, USA) at 216.555 nm for Ni(II) and 333.749 nm for La(III), respectively. The experiments were performed in triplicate and the average values were obtained.

Ni-MH batteries are composed mainly the LaNi₅ and/or MnNi₅ compounds combined with rare earth elements such as La(III), Ce(III), Pr(III) and Nd(III) as well as Fe(III), Ni(II), Co(II), Cu(II) and Zn(II) (Tenório and Espinosa, 2002). Therefore during the selectivity determination these elements were taken into account. Adsorption experiments were performed in the batch mode.

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211 3. Results

3.1. Ion exchangers properties characterization

The ion exchangers can be used for removal of metallic impurities from complex 213 solutions containing chlorides, fluorides, sulphates and phosphates as well as EDTA, 214 citrate and tartrate ligands (Kołodyńska and Hubicki, 2012; Silva et al., 2018; Zhao et 215 al., 2007). The properties of ion exchangers depend on the degree of cross-linking. 216 With the increasing percent of divinylbenzene (%DVB), the resistance to oxidation 217 and the differences in affinity grow, but the operating capacities and rate of kinetics 218 diminish. With the increase of %DVB the water content also decreases. In our 219 experiments it was found that the water content was equal to 53% for Purolite S957 220

and 67% for Diphonix Resin[®]. The pH changes during the equilibration in the DI water are presented in Table 1. Both Purolite S957 and Diphonix Resin[®] are characterized by the spherical shape.

Diphonix Resin[®] is the result of the investigations carried out at the Argonne 224 National Laboratory and University of Tennessee. It was developed primarily for 225 actinide separation in the acidic solutions. However, it also adsorbs strongly divalent 226 transition metal cations at pH 1-2 and trivalent cations at pH 0-2. It is fine-grained as 227 can be seen on the optical microscope scan (Table 1). Another important parameter 228 is the particle size which ranges from 0.55 to 0.75 mm for Purolite S957 and from 229 0.074 to 0.15 mm for Diphonix Resin[®]. The sieve analysis shows that in the case of 230 Diphonix Resin[®] the beads are monodispersive and for Purolite S957 slightly more 231 than 40% mass beads have a coarse grain size 0.40-0.60 mm (Table 1). This is 232 233 relevant taking into account the kinetic process proportional to the inverse of the square of the particle diameter. In the case of Purolite S957 the fraction of beads 234 235 below 0.30 mm and above 0.71 mm which is about 4% by mass is comparable. The ion exchangers being tested have only about 1.5% of the mass fraction with a 236 relatively small size. The analogous results were obtained in (Gargul et al., 2019). 237 Diphonix Resin[®] is characterized by smaller particles and all of them are in the range 238 of 0.1-0.2 mm. In the literature for the other commercial ion exchangers such as 239 Lewatit TP 207 and Chelex 100 the bead size is 0.4-1.250 mm and 0.3-1.20 mm, 240 respectively. 241

Purolite S957 and Diphonix Resin[®] are macroporous and gel types, respectively. Macroporous ion exchangers contain a network of pores within a gel matrix making them appear opaque in contrast to the gel resins with clear glassy beads that are fully translucent to light. As follows from the ASAP analysis for Purolite

S957 (Table 1, Fig.1) the BET total surface area is equal to 14.9 m²/g and the 246 average pore diameter 34.1 nm. For Diphonix Resin[®] these values were 0.2 m²/g 247 and 4.52 nm, respectively (Fila et al., 2019). According to the IUPAC classification 248 the average pore diameter is in the mesoporosity range (2-50 nm). 249



Fig.1. ASAP analysis of Purolite S957.

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The obtained results were confirmed by the SEM analysis at the same 253 magnification (Table 1). The porous structure with large voids and cavities can be 254 seen only in the case of Purolite S957. 255

Another parameter characterizing ion exchangers is the capacity. The content 256 of functional groups by the unit of mass or volume is expressed as the total exchange 257 capacity in millimoles or milliequivalents i.e. mmol/g (meg/g) or mmol/cm³ (meg/cm³) 258 (Nikoloski and Ang, 2014). The IEC value (meq/g) was determined using the 259 following equation: 260

261 IEC =
$$V_{\text{NaOH}} \times C_{\text{NaOH}}/m$$
 (1)

where: V_{NaOH} is the volume of NaOH used for the titration (cm³), *m* is the dry weight 262 of the ion exchanger (g), C_{NaOH} is the NaOH concentration. 263

For Purolite S957 and Diphonix Resin[®] they are equal to 8.0 meq/g and 5.3 264 meq/q, respectively. However, under real operating conditions particularly the 265 dynamic ones, the use of all functional groups is practically impossible. Therefore the 266 working ion exchange capacity is a more useful unit characteristic of ion exchangers. 267 It determines the number of ions that can be exchanged between the solution and 268 the ion exchanger under the given operating conditions. It also determines the 269 sorption mechanism. Based on the potentiometric titration Purolite S957 contains 270 about 60% of sulphone groups. For Diphonix Resin[®] this content is 45% and about 271 5% for the carboxylic groups (titration is characterized by three distinct phases and 272 the total amount of acidic groups can be determined from the second intersection 273 point). The content of the diphosphonic group was determined as a subtraction 274 result. Their presence was confirmed by the XPS analysis (Fig.2). 275



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For Purolite S957 the pH_{PZC} values obtained using the drift and potentiometric titration methods were equal to 1.95 and 1.99, respectively. For Diphonix Resin[®] previously determined by us the value was 2.18 (or 1.85 by the drift method) (Fila etal., 2019).

The Fourier transform infrared spectra with the ATR mode for Purolite S957 and Diphonix Resin[®] before and after Ni(II) and La(III) ions adsorption in the presence of citric acid are shown in Fig.3.



Fig.3. FTIR spectra for a) Purolite S957and b) Diphonix Resin[®] before and after the
 adsorption of Ni(II) and La(III) ions in the presence of citric acid.

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The hydroxyl –OH stretching vibration broad band occurred at 3412 and 3436 291 cm⁻¹ for Purolite S957 and Diphonix Resin[®], respectively. After the sorption of Ni(II) 292 and La(III) ions in the presence of citric acid its maximum is at 3420 and 3426 cm⁻¹. 293 This band is characterized by not only the residual hydration water but also the 294 presence of the sulphonic groups. A weak band at 1440-1395 cm⁻¹ refers to the O-H 295 deformation in the plane. The absorption band at 875-960 cm⁻¹ has been ascribed to 296 the OH-O out- of-plane deformation. The bands in the range from 2800 to 3000 cm⁻¹ 297 are characteristic of the polystyrene structure (Lazar et al., 2014; Zagorodni et al., 298 2002). The gel and macroporous styrene-divinylbenzene (ST-DVB) copolymer 299 matrices correspond to the vibrations of the asymmetric v_{as} and symmetric v_{s} 300

stretching vibrations of aliphatic -CH chains at 2960 cm⁻¹ and 2920 cm⁻¹ (double 301 peaks). After the sorption of La(III) and Ni(II) ions in the presence of citric acid they 302 are at 2968, 2931 as well as 2973 and 2929 cm⁻¹, respectively. The next are C-H 303 bending vibrations in the side chain at 669, 703, 830 and 1029 cm⁻¹, -CH₂ scissoring 304 at 1411 and 1449 cm⁻¹ as well as δ_s CH₂ 1470 cm⁻¹ scissoring bands (Bogoczek and 305 Surowiec, 1986; Ghosh et al., 2015). Additionally, the absorption peaks at 1627 and 306 1656 cm⁻¹ correspond to the simple C=C bonds in the ST-DVB structure. For both 307 ion exchangers the absorption bands in the 1200-900 cm⁻¹ region are attributed to 308 the S=O stretching vibrations in the $-SO_3$ groups i.e. at 1230 cm⁻¹ asymmetric v_{as} 309 stretching, 1220 cm⁻¹ symmetric v_s stretching, 985 cm⁻¹ stretching v vibrations of 310 single S–OH as well as P=O stretching vibrations in the $-PO_3^{2-}$ groups (Zagorodni et 311 al., 2002). The absorption band of carbonyl C=O stretching and hydroxyl -OH 312 deformation vibrations of the carboxylic groups is at about 1740 cm⁻¹ and 1644 cm⁻¹, 313 respectively. A peak around 1450 cm⁻¹ is characterized of the symmetric C=O 314 stretching vibrations. After metal ions sorption the stretching frequency of the 315 carboxylate carbonyl is shifted to the lower wavelength of 1560 cm⁻¹. These 316 functional groups can coordinate metal ions by the unidentate, bidentate and bridging 317 complexes. The presence of the phosphonic group in Purolite S957 and Diphonix 318 Resin[®] is confirmed by the bands at 2280 cm⁻¹ which corresponds to the stretching 319 vibrations of the P-OH groups. The bands at 1132 and 989 cm⁻¹ correspond to the 320 stretching vibrations of the P=O and P-O groups. 321

322 3.2. Physicochemical properties of citric acid and its complexes with metal ions

The main objective of this study was to develop the removal strategy of heavy metal ions and rare earth elements represented by the Ni(II) and La(III) ions from the aqueous solutions containing citric acid based on the extraction of spent Ni-MH

batteries. Technological progress with the increased demand for REEs resulted in the 326 need to develop new methods of recovery of these elements from the secondary 327 sources such as WEEEs, CCPs and AMDs. One of the solutions can be the use of 328 non-toxic and biodegradable citric acid. It is obtained from many sources, 329 commercially through the fermentation of waste potatoes after the starch extraction 330 by mycological fermentation using *Candida spp.* or by the solvent extraction process 331 from the Aspergillus niger fermentation solution (Huang et al., 2011). It occurs in 332 living organisms playing a very important role in metabolism as a transitional product 333 in the Krebs cycle in which it is isomerized to isocitric acid. It is generally recognized 334 as safe approved by the Joint Food and Agriculture Organization and World Health 335 Organization Expert Committee on Food Additives (Soccol et al., 2006). Citric acid 336 has also been classified by the U.S. Food and Drug Administration as a nontoxic 337 338 compound and approved for the general use as a food additive. In the EU it is designated by the E numbers: E330 (citric acid), E331-E333 (citrates). In the food 339 industry it plays a variety of roles, for example, prevents spoilage of food caused by 340 the presence of microorganisms, acts as an antioxidant, prevents changes in colour 341 or taste and is used as a pH control agent and acidulant. In addition, iron ammonium 342 citrate acts as an anti-caking agent added to loose products and prevents the 343 absorption of moisture. Besides the food industry, citric acid is also used in the 344 cosmetics, pharmaceutical, textile and many other industries (Dhillon et al., 2011; 345 Soccol et al., 2006). 346

Citric acid (CA) is commonly considered to be a tribasic moderately strong organic acid, with the pK_a values extrapolated to the zero ionic strength of 2.92, 4.28 and 5.21 at 298 K (Apelblat 978-3-319-11233-6). The percentage contents of the citric acid forms as a function of pH are presented in Table 2. The successive pK_a

values for citric acid deprotonation at 293 K are pK_{a1}=3.15, pK_{a2}=4.77 and pK_{a3}=6.39 351 (Aurich et al., 2017). The pK_a of the hydroxyl group has been found to be 14.4 by 352 means of ¹³C NMR spectroscopy. The speciation diagram shows that the citric acid 353 solution is the buffer between the pH about 2 and 8 (or in the pH range 2.5-6.5 354 according to (Aurich et al., 2017)). In the biological systems at the pH about 7 the two 355 species are the citrate ion and the monohydrogen citrate ion. At the zero ionic 356 strength, the enthalpy change associated with two ionizations was reported to be 357 0.28 and -0.71 kcal/mol. The presence of active carboxyl and hydroxyl groups in the 358 molecule makes citric acid a chelating agent of great complexation affinities not only 359 for REEs but also for other elements. The comparison of the stability constants of 360 REE complexes with various chelating agents is presented in Table 2. 361

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Table 2. Comparison of the percentage contents of the citric acid forms as a function of pH, the stability constants of REE complexes with various chelating agents of [LnL] type (μ =0.1; T=293 K) and pH of REE precipitation from different solutions.



The percentage contents of the citric acid forms as a function of pH

СН2СООН НО — С — СООН СН2СООН	H ₂ 0000 H ₂ 0000CCH	с он 2 H ₂ CCOO-	M00C CH ₂ CH ₂ CCCCH ₂ CCCCC	о н ₂ с -оосн ₂ с-с- н	0 0 c 0 0 002 H 0 0 - C - CH ₂ COO 0 0 - C - CH ₂ COO
Citric acid	Bidentate com	plex	H Tridentate complex	O	
REE(III)			loaK[LnL]	220	
	СА	EDTA	PDTA	HEDTA	DTPA
La	7.10	15.50	16.42	13.82	19.96
Ce	7.40	15.98	16.79	14.45	20.90
Pr	7.60	16.40	17.17	14.96	21.85
Nd	7.70	16.61	17.54	15.16	22.24
Pm	7.71	16.90	17.80	15.40	22.50
Sm	7.80	17.14	17.97	15.64	22.84
Eu	7.80	17.35	18.26	15.62	22.91
Gd	7.72	17.37	18.21	15.44	23.01
Tb	7.74	17.93	18.64	15.55	23.21
Dy	7.79	18.30	19.05	15.51	23.46
Ho	7.84	18.60	19.30	15.55	23.30
Er	7.86	18.85	19.61	15.61	23.18
Tm	8.00	19.32	20.08	16.00	22.97
Yb	8.05	19.51	20.25	16.17	23.01
Lu	8.07	19.83	20.56	16.25	23.00
	pH of R	EEs precipitat	ion from differen	t solution	
	SO4 ²⁻	Cľ	NO ₃	CH₃COO ⁻	CIO4
La	7.41/7.61	8.03	7.83/8.35/8.7 [,]	7.93	8.76/8.10
Ce	7.35/7.07	7.41	76/8.1	7.77	n.a.
Pr	7.17/6.98	7.05	7.35	7.66	7.40
Nd	6.95/6.73	7.02/7.40	7.00/7.31	7.59	7.6/7.3
Sm	6.70	6.83	6.92	7.40	7.57/7.13
Eu	6.68	n.a.	6.82	7.18	6.91
Gd	6.75	n.a.	6.83	7.10	7.45/6.81
Y	6.83	6.78	7.95/7.39	6.83	7.57/6.81
Er	6.50	n.a.	6.76	6.59	n.a.
Tm	6.21	n.a.	6.40	6.53	n.a.
Yb	6.18/6.16	n.a.	6.30	6.50	7.30/6.45
Lu	6.18	n.a.	6.30	6.46	6.45
Sc	n.a.	4.8	n.a.	6.1	n.a.

The types of metal complexes with citric acid

 367 CA – citric acid, EDTA – ethylenediaminetetraacetate, PDTA – 3-propanediamine-tetraacetate, HEDTA – N-(2-368 hydroxyethyl)ethylenediaminetriacetate, DTPA – diethylenetriaminepentaacetate
 369

370

The ability to coordinate metal ions for citric acid is not as high as for EDTA or DTPA but its undoubtful advantage is its biodegradability, particularly when more and more attention is paid to the environmental protection and the principles of green chemistry are widely used (Römkens et al., 2002).

The chelating properties of citric acid against heavy metals, e.g. Fe(III) and Cu(II) have also contributed to its use as a stabilizer of oils and fats as well as for

cleaning of power station boilers. Mg(II) and Ca(II) ions complexation is used in the
 process of water softening (Begum et al., 2012; Kirimura et al., 2011).

The types of complexes formed by citric acid depend on the metal ions (Table 2). They can be mononuclear, binuclear or polynuclear as well as bi-, tri- and multidentate. For example with Ni(II) or Fe(II) it forms bidentate, mononuclear complexes with two carboxyl acid groups of the citric acid molecule and with Cu(II) and Cd(II) tridentatate, mononuclear complexes with two carboxyl acid groups and the hydroxyl group (Bassi et al., 2000; Huang et al., 2011). The general reaction of complex formation is as follows:

$$386 \qquad M^{2+} + \operatorname{cit}^{3-} \rightleftharpoons [M(\operatorname{cit})]^{-} \tag{2}$$

(3)

387 M^{3+} + cit³⁻ \rightleftharpoons [M(cit)]

The citrate ligand binds tridentately with α -hydroxy or α -alkoxy, α -carboxy and 388 one of β -carboxy groups. This is the most common coordination mode found for the 389 390 transition metal citrates such as those with Ni(II) (Chen et al., 2012). Biodegradation of these complexes by Pseudomonas fluorescens revealed that this process is 391 influenced by the type of the formed complex. According to (Francis et al., 1998) 392 bidentate Ca(II), Fe(II), Ni(II), Zn(II) citrate complexes are readily degraded. 393 Tridentate Cd(II), Cu(II), binuclear U(VI) and polynuclear U(VI) species are 394 recalcitrants. Several metals such as Cr(III) with In(III), Cd(II) with Ni(II), Mn(II) or 395 Zn(II), and U(VI) with Al(III), Cu(II), Fe(III) and In(III) formed mixed-metal complexes 396 with citric acid. 397

In the paper (Ohyoshi et al., 1972) it was found that different lanthanide complexes are formed depending on pH of the solution. They can be as follows: $[Ln(Hcit]]^+$, [Ln(cit)], $[Ln(cit)_2]^3$, $[Ln(OH)(cit)]^-$ (Svoronos et al., 1981). The mole fraction of La(III) species vs. pH for the solution with citric acid can be calculated from the stability constant logarithms according to the reactions:

(6).

403	Ln ³⁺ + cit ³⁻	(4)
404	Ln ³⁺ + Hcit ²⁻ ≓ [Ln(Hcit)] ⁺	(5)

405
$$\operatorname{Ln}^{3+} + \operatorname{H}_2\operatorname{cit}^{-} \rightleftharpoons [\operatorname{Ln}(\operatorname{H}_2\operatorname{cit})]^{2+}$$

In the pH range 7-8, the precipitation of neutral complex of the Ln:cit=1:1 system was observed. A small amount of $[Ln(H_2cit)]^{2+}$ of low stability is likely to form near pH 3 (Zhou et al., 2008). For Hcit²⁻ the complexes are as follows:

409
$$\operatorname{Ln}^{3+} + \operatorname{Hcit}^{2-} \rightleftharpoons [\operatorname{Ln}(\operatorname{cit})] + \operatorname{H}^{+}$$
 (7)

410 3.3. Effect of the citric acid to metal ion ratio

In the preliminary studies the sorption process was examined for the three different metal ion to citric acid ratios 1:1, 1:2 and 2:1. The adsorption capacity (q_t) at time t, adsorption percentage (S%) as well as the partition coefficient of metal ions between the ion exchangers and solution (K_d) were calculated according to Eqs.8-10:

415
$$q_t = (c_0 - c_t) \times \frac{V}{m}$$
 (8)

416
$$S\% = \frac{(c_0 - c_t)}{c_t} \times 100$$
 (9)

417
$$K_d = \frac{(c_0 - c_e)}{c_e} \times \frac{V}{m}$$
(10)

where: q_t is the adsorption amount of Ni(II) or La(III) ions in the presence of citric acid at time t (mg/g), c_0 is the initial concentration of Ni(II) or La(III) in the solution in the presence of citric acid (mg/dm³), c_t is the concentration of Ni(II) or La(III) in the presence of citric acid at time t (mg/dm³), V is the volume of solution (dm³), m is the mass of dry ion exchange sample (g), *S*% is the adsorption percentage (%). All the experiments were performed in triplicate and the general agreement of the obtained values was within 5%. For *t* equal to the equilibrium contact time when c_t is equal to c_e and q_t is equal to q_e , the amount of M(II/III) adsorbed at equilibrium, q_e , can be calculated using Eq.11:

428
$$q_e = (c_o - c_e) \times \frac{V}{m}$$
 (11)

The research results show that the optimal citric acid to metal(II/III) ion ratio in the sorption of Ni(II) and La(III) ions from the citrate solutions is 1:1 due the largest values of q_t (Fig.4a). Therefore, subsequent studies were carried out for this ratio. For La(III) the neutral complexes with citric acid are supposed.





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Fig.4. The effect of a) the citric acid:metal ion ratio and b) the mass on the sorption of
Ni(II) and La(III) ions in the presence of citric acid on Purolite S957 and Diphonix
Resin[®] (the initial concentration of La(III) and Ni(II) 50 mg/dm³).

439

435

440 3.4. Ion exchangers mass effect

As for the ion exchanger mass effect, different quantities of Purolite S957 and 441 Diphonix Resin[®] varying from 0.05, 0.1, 0.5 and 1 g were used. The results showed 442 that the amount of La(III) ions sorbed on Diphonix Resin[®] decreased from 5.63 to 443 2.75 mg/g increasing the ion exchange amount (Fig.4b). The analogous results for 444 Ni(II) are as follows 4.92 and 2.60 mg/g. With decreasing the ion exchange amount, 445 the number of ion exchange functional groups also decreases. However, increasing 446 the amount of resin the La(III) and Ni(II) removal efficiency (%S) increased from 55 to 447 99.9%. This is due to the fact that there are no available functional groups for 448 449 complete removal of the metal ions/complexes from the solution. At a higher adsorbent dose the solution ion concentration drops to lower values and the system 450 reaches equilibrium at lower values of q_t which indicates that the adsorption sites 451 remain unsaturated. In addition, this phenomenon may be caused by the aggregation 452 of sorbent particles at a larger mass which will reduce the chemically active sites. 453

454

455 3.5. pH effect

As for pH effects it was found that SACs such as these containing sulphonic groups and SBA with the quaternary ammonium can dissociate over the entire pH range. The sulphonic groups, which ionise even under strongly acidic conditions (pK_a ~1), are not characterized by good selectivity towards metal ions. WACs are ionized at the solutions pH higher than the acid dissociation constant i.e. pK_a of the

functional groups, so they operate when the solution pH is higher than the pKa and 461 the ion exchangers with higher pK_a are preferred. Therefore the ion exchangers 462 containing carboxylic groups operate at pH higher than 4, whereas the ion 463 exchangers with the amino groups operate at pH lower than 11. The phosphonic ion 464 exchangers are characterized by intermediate acidity which results in greater 465 selectivity than that of the sulphonic ion exchangers as well as much higher capacity 466 than the carboxylic ones at low pH (both studied ion exchangers contain the 467 phosphonic groups). The influence of pH on the sorption of HMs and REEs has been 468 extensively studied by many authors. The sorption of metal ions is low at very acidic 469 pH and increases with the increasing pH to a certain value. This phenomenon can be 470 explained by the surface charge of the adsorbent. At low pH the cations compete with 471 the H⁺ ions in the solution for the active sites which causes low adsorption. At high 472 473 pH the adsorbent surface has a negative charge as a result of the complete dissociation of the functional groups, whereby it is easy for the positively charged 474 475 ions to be adsorbed resulting in the higher adsorption. A very high pH value makes the adsorption process impossible due to formation of metal hydroxides and 476 precipitation. 477

It can be assumed that basicity of rare earth elements increases successively from Sc(III) to La(III). Of all the elements with the III oxidation degree, lanthanides form the most basic hydroxides. This is confirmed by (i) the ease of hydroxides to dissolve in acids or ammonium salts solutions and (ii) their absorption of CO_2 from the atmosphere as well as (iii) great electrode potentials, tendency towards hydrogen removal from water and large heat of their oxides dissolution in acids.

484 The change of rare earth elements basicity, decreasing with the order number 485 often constituted the basis for various methods of their separation. Another method of

fractionation precipitation is the basic precipitation of hydroxides and basic salts 486 based on precipitation in the order of increasing basic properties of lanthanides with 487 the decrease of hydrogen ions concentration in the solution. The hitherto 488 investigations show that precipitation of hydroxides of all lanthanides proceeds in a 489 narrow range of pH values. The pH values, at which precipitation of lanthanide salts 490 solutions begins, are presented in Table 2. Therefore further studies on the La(III) 491 ions sorption on the ion exchangers Purolite S957 and Diphonix Resin® were carried 492 out for the pH value 6.0. The discrepancies in the pH values of the precipitation 493 threshold given by various authors are a result of different precipitation process 494 conditions. 495

496 3.6. Kinetic studies

The kinetic parameters of La(III) or Ni(II) ions in the presence of citric acid on the ion exchange samples were compared and calculated based on the following models (Eqs.12-18) (Ho and Mckay, 1999; Ho and McKay, 1998):

a) the pseudo first order (PFO)

501 $\frac{dq_t}{dt} = k_1(q_e - q_t)$ and the applying boundary conditions t=0 to t=t and q_t=0 to q_t=q_t,

502
$$\log(q_e - q_t) = \log(q_e) - \frac{k_1 t}{2.303}$$
 (12)

- b) the pseudo second order (PSO)
- 504 $\frac{dq_t}{dt} = k_2(q_e q_t)^2$ and the applying boundary conditions t=0 to t=t and q_t=0 to q_t=q_t

505
$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} - \frac{t}{q_e}$$
 (13)

- 506 with the initial sorption rate for $q_t/t \rightarrow 0$
- 507 $h = k_2 q_e^2$

508	c) the Weber-Morris model also known as the intraparticle diffusion model (IPD)
509	$q_t = k_i t^{0.5} + C$
510	(14)
511	d) the Boyd model (BM)
512	$Bt = -0.497 - \ln(1 - F) \tag{15}$
513	e) the film diffusion model (FD)
514	$ln(1-F) = k_f t \tag{16}$
515	f) the Dumwald-Wagner model (DW)
516	$\log(1 - F^2) = -\frac{k_{DW}}{2.303t} $ (17)
517	as well as
518	g) the pore and film diffusion coefficients:
519	$D_p = 0.03 \frac{r^2}{t_{1/2}}$ and $D_f = 0.23 \frac{r\delta q_e}{t_{1/2} c_0}$ (18)
520	where: q_e , q_t were defined as previously, k_1 is the pseudo first order rate constant
521	(dm ³ /min), k_2 is the pseudo second order rate constant (g/mg·min), k_i is the
522	intraparticle diffusion rate constant (mg/g·min ^{0.5}), C is the intercept called the Weber-
523	Morris diffusion constant, F is the fraction of solute adsorbed at any time (fractional
524	attainment of equilibrium at time t equal to $F=q_t/q_e$), for F>.85 B is the diffusion
525	constant, k_f is the film diffusion model rate constant (1/min), k_{DW} is the Dumwald-
526	Wagner model rate constant (1/min), r is the mean radius of the sorbent (cm), δ is the
527	film thickness equal to 1×10^{-3} cm, $t_{1/2}$ is the time at which the half of the maximal
528	sorption was achieved (s), c_0 is the initial concentration of Ni(II) or La(III) ions in the
529	presence of citric acid (mg/dm ³).

It was found that the removal of Ni(II) and La(III) increased rapidly during the 530 first 10-15 min caused by the strong forces of Ni(II) and La(III) and the ion 531 exchangers and then more slowly until the equilibrium. The %sorption increased from 532 10% to 100%. However, when the initial concentration of metal ions increased from 533 25 to 200 mg/dm³ it decreased. The results showed that the removal efficiency 534 increased rapidly from 40% to 100% and thereafter it remained almost constant at a 535 lower concentration particularly in the case of Diphonix Resin[®]. This is due to the fact 536 that the removal efficiency depends more upon the concentration of the solution and 537 less upon the dose larger than the optimal. Moreover, the greater the concentration 538 of the ion in the solution, the greater is the ion exchange process. It is obvious that 539 for the ion exchanger with a low percentage of cross-linking, the solution passes 540 quickly through the matrix and the kinetics is fast. With the increase of the cross-541 542 linking diffusion of the exchangeable ions is hindered by the dense matrix and the kinetics is slow. However, those with the low cross-linking are characterized by the 543 544 tendency towards swelling which confines their physical strength. For the applied ion exchangers %DVB was equal to 10. 545

In the case of the ion exchange process metal ions transfer is usually characterized by either external mass transfer (boundary layer diffusion) or intraparticle diffusion or both. The most commonly used technique to identify the sorption mechanism and to predict the rate controlling step is fitting the experimental data in an intraparticle diffusion plot. Therefore the obtained results were analyzed by different kinetic models. The kinetic parameters and other values were estimated based on Figs.5a-b and they are listed in Table 3.





Fig.5. a-b) Effect of the phase contact time, c-d) the pseudo-second-order kinetic plots, e-f) the intraparticle kinetic plots and g-h) the Dumwald-Wagner kinetic plots for the sorption of Ni(II) and La(III) complexes with citric acid on Purolite S957 and Diphonix Resin[®].

561

Practically all kinetic theories (except for the PSO equation) lead to dependence 562 of the exponential type $F = 1 - exp(-k_1 t)$ described by the Boyd model. In the PFO the 563 parameter $k_1(q_e-q_t)$ does not represent the number of available sites. The expression 564 of q_e - q_t represents the fraction of available functional groups at time t. Additionally, 565 $log(q_e)$ is an adjustable parameter and often not equal to the intercept of a plot of 566 $log(q_e-q_t)$ vs. t (Douven et al., 2015; Ho and McKay, 1998). Moreover, the PFO 567 equation does not adjust the whole range of contact time and generally is applicable 568 over the initial 10-20 min of the sorption process (Figs.5c-d). During the kinetic 569 experiments in which adsorption phenomena are important in addition to the 570 intramolecular diffusion, a gradual shift in the impact of individual phenomena from 571 pure diffusion (*c*=0, high constant K_d) to pure adsorption (high c, low K_d) is evidently 572 observed. Therefore, the nature of kinetic phenomena can be indirectly identified 573 using the empirical Weber-Morris equation. However, it should be remembered that 574

in this case this equation can be treated as only a comparative tool. If the diffusion is rate controlling, the slope of the plots based on the PFO will vary inversely with the particle size, the film thickness and the distribution coefficient k_1 . If the sorption rate controlling step is chemical exchange, the slope is independent of particle diameter and depends only on the concentration of the sorbate in solution and the temperature.

According to (Płaziński and Rudziński, 2011) for PFO the difference (q_e-q_t) 581 becomes smaller and the value $ln(q_e-q_t)$ greater and greater. The effect of random 582 errors will grow proportionally to the reverse of the factor (q_e-q_t) . As for PSO the plot 583 of t/q_t vs. t should give a linear relationship, based on which q_2 , k_2 and h can be 584 determined from the slope and intercept of the plot. The PSO equation can be used 585 for extrapolation of the kinetic data q_t and estimation of the value q_e corresponding to 586 587 them. It should be mentioned that extrapolation confinement to the points measured for the states close to equilibrium is $q_t > 80\% q_e$. 588

In our studies the better R^2 values were observed for the PSO kinetic model 589 which indicates that this model fits the adsorption kinetic data best. The kinetic data 590 of Ni(II) and La(III) were plotted with the excellent correlation coefficients 0.999 for 591 Ni(II) and 1.000 for La(III). It was found that the equilibrium adsorbed amounts 592 calculated from the PSO kinetics $(q_{e,cal})$ are also close to the experimental amounts 593 adsorbed at equilibrium $(q_{e,exp})$. The PSO constant k_2 decreased with the increase of 594 Ni(II) and La(III) concentration. It also increased with the decrease in the particle size 595 of Diphonix Resin[®] compared to Purolite S957. The values of the rate constant were 596 found to decrease from 0.564, 0.632, 0.175, 0.026 to 0.017 g/mg min for Ni(II) on 597 Purolite S957 as well as from 20.918, 14.419, 10.334, 9,693 to 8.804 g/mg·min for 598 Ni(II) on Diphonix Resin[®]. For La(III) on Purolite S957 they were as follows from: 599

600 0.782; 0.437; 0.359; 0.247 to 0.239 g/mg·min as well as on Diphonix Resin[®] from 601 14.462, 13.206, 10.344, 9,668 to 4.705 g/mg·min with the increase of the initial 602 concentration from 25 to 200 mg/dm³. As for *h* these values were as follows: 1.09, 603 1.19, 2.75, 3.63 and 5.72 mg/g·min for Ni(II) on Purolite S957 and 35.25, 54.27, 604 63.69, 74.58, and 93.66 mg/g·min for Ni(II) on Diphonix Resin[®], for La(III) on Purolite 605 S957 4,91, 11.00, 38.37, 50.15 and 94.42 mg/g·min as well as 100.99, 103.75, 606 116.52, 129.66, 132.92 mg/g·min on Diphonix Resin[®].

607 As for the Weber-Morris model (Figs.5 e-f) it is known that the intraparticle diffusion is the only rate limiting step when the plot q_t vs. $t^{0.5}$ is linear and passes 608 through the origin. If the plot does not pass through the origin, this indicates that the 609 adsorption processes do not follow only the intraparticle diffusion but also the film 610 diffusion (connected with the thickness of the boundary layer). The external mass 611 transfer is significant, particularly in the initial reaction phase. The IPD plots can be 612 sometimes divided into steps. The initial stages of sorption are connected with the 613 boundary layer diffusion effect (diffusion/convection in the bulk solution and boundary 614 layer diffusion) and the later stages (linear portion of the curve) due to the 615 616 intraparticle diffusion (diffusion into pores) and approaching the equilibrium state. This kind of multilinearity was also reported in the recent studies (Fila et al., 2019). 617 The intercept of the plot reflects the boundary layer effect. The larger is the intercept, 618 the greater is the surface sorption contribution in the rate controlling step. In our 619 studies the slope of the first and second portions is defined as the intraparticle 620 diffusion parameter k_i displayed in Table 3. The values of C_i and R^2 are also listed in 621 this table. For the C_i parameter there was found the following relation: $C_1 > C_2$. They 622 indicate that the resistance to the external mass transfer decreases as the intercept 623 decreases. Additionally, the intraparticle diffusion parameter k_i (mg/g·min^{0.5}) is 624

625 proportional to the initial concentration due to the greater deriving force with the 626 increasing initial concentration.

After determination of q_e value, the fractional attainment of equilibrium at time t 627 (min) equal to $F=q_t/q_e$ can be used for the identification of the slowest step of sorption 628 process according to the Boyd model. If the plots Bt (where Bt is a function of F) vs. t 629 (t < 120 min) are linear and pass through the origin, the slowest step in the 630 adsorption process is the internal diffusion. The plot of Bt vs. t is linear with the 631 distribution coefficients 0.885-0.994 indicating that sorption is controlled by the film 632 diffusion connected with the external mass transfer. The values of B, D_i and R^2 are 633 listed in Table 3. In the case of Purolite S957 the calculated values of the effective 634 diffusion coefficients D_i for Ni(II) were found to be 1.09×10^{-7} , 1.37×10^{-7} , 2.41×10^{-7} , 635 6.56×10^{-8} and 7.05×10^{-8} m²/min for the initial concentration of 25, 50, 100, 150 and 636 200 mg/dm³, respectively. The analogous values for Diphonix Resin[®] are as follows: 637 1.64×10⁻⁷, 1.85×10⁻⁷, 3.19×10⁻⁷, 3.27×10⁻⁷ and 4.29×10⁻⁷ m²/min. For La(III) they 638 are equal to: 1.40×10^{-7} , 1.43×10^{-7} , 1.47×10^{-7} , 1.56×10^{-7} and 1.67×10^{-7} m²/min for 639 Purolite S957 and 3.24×10^{-7} , 3.33×10^{-7} , 3.65×10^{-7} , 3.89×10^{-7} and 3.96×10^{-7} m²/min 640 for Diphonix Resin[®]. 641

As for the film diffusion (FD) model it was found that the k_f parameters were as follows for Ni(II): 0.072, 0.241, 0.276, 0.330 and 0.322 1/min on Purolite S957 and 0.148, 0.247, 0.298, 0.381 and 0.392 1/min on Diphonix Resin[®]. For La(III) they are equal to: 0.268, 0.209, 0.272, 0.304 and 0.314 1/min on Purolite S957 as well as 0.259, 0.264, 0.276, 0.302 and 0.321 1/min on Diphonix Resin[®].

The Dumwald-Wagner model assumes that for the linearity the plots do not intersect the origin, the rate limiting step is an intraparticle diffusion process, otherwise that is a film diffusion. Furthermore, the higher intercept indicates that the

650 film diffusion rate control step has greater influence on the rate limiting step (Figs.5g-651 h).

It should be concluded that the rate limiting step is not a sole intraparticle diffusion process and there can be also the film diffusion. The adsorption of Ni(II) and La(III) ions proceeds in the presence of citric acid on Purolite S957 and Diphonix Resin[®] by a complex mechanism consisting of both film adsorption and intraparticle transport. Some limitations could be also due to the structure of the applied ion exchangers. The macroporous ion exchanger Purolite S957 is characterized by the much more heterogeneity than Diphonix Resin[®].

659

Table 3. The kinetic parameters for the sorption of Ni(II) and La(III) on Purolite S957
 and Diphonix Resin[®] for the selected models.

	Purolite	S957	Diphonix	
Parameter/Model	Ni(II)	La(III)	Ni(II)	La(III)
q _{e.exp} (mg/g)	18.32	19.04	18.33	19.04
PFO				
q _{e,cal} (mg/g)	0.42	0.46	0.01	0.02
k ₁	0.04	0.04	0.03	0.03
R ²	0.955	0.984	0.803	0.979
PSO model				
q _{e,cal} (mg/g)	18.34	19.06	18.33	19.04
k ₂	0.017	0.239	8.808	4.705
h	5.72	94.42	93.66	132.92
R ²	0.999	1.000	1.000	1.000
IPD model				
k _{i1}	6.38	2.98	6.02	4.41
C_1	2.403	10.710	18.280	18.068
R ²	0.910	0.971	0.970	0.756
k _{i2}	0.27	0.11	0.00	0.00
R ²	0.958	0.964	0.992	0.947
Boyd model				
B	7.05×10 ^{−8}	1.67×10 ⁻⁷	4.29×10 ⁻⁷	3.96×10⁻′
R ²	0.855	0.984	0.926	0.979
FD model				
k _f	0.322	0.314	0.392	0.321
R ²	0.955	0.984	0.911	0.979
DW model				
k _{DW}	0.027	0.059	0.079	0.085
R ²	0.9645	0.9863	0.9031	0.980
log K _d				
Fe(III)	3.7	5	5.8	88
Ni(II)	3.9	4	5.	96

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Co(II)	3.20	5.65
Cu(II)	3.18	5.51
Zn(II)	3.04	5.23
La(III)	4.35	6.66
Ce(III)	3. 74	6.31
Pr(ÌII)	3.62	5.90
Nd(III)	3.60	5.78
)		

In the presented studies the adsorption kinetics is mainly connected with the film diffusion as well as the internal diffusion. Both these steps can take considerable time. The external mass transfer is several times as important as the migration of the metal species through the pore volume. The obtained results confirm that the film diffusion is the rate controlling step because the film diffusion coefficients D_f are in the range $10^{-6}-10^{-8}$ cm²/s. If pore diffusion is to be rate controlling, the pore diffusion coefficient D_p should be in the range $10^{-11}-10^{-13}$ cm²/s.

670 3.7. Partition coefficient determination

In the separation processes the partition between two phases is described by 671 the partition coefficient (K_d). As metal ions occur in different forms, the more 672 appropriate is the use of the distribution ratio (D). K_d and D are identical if the solute 673 has only one chemical form in each phase. If the solute exists in more than one 674 chemical form in both the solution and solid phase, then K_d and D have usually 675 different values, however, D changes depending on the operating conditions (Fryxell 676 et al., 2004; Shaibu et al., 2006). The high values of K_d indicate that the majority of 677 the metal ions are adsorbed on the ion exchangers, however, this does not indicate 678 the strength of the process. It should be noted that it provides only indirect 679 information on the type of surface interactions taking place. Often these values are 680 681 determined over a range of concentrations at a constant temperature. Plotting of $logK_d$ as a function of pH (or acid concentration) provides some information about the 682 mechanism involved in the ion exchange process i.e. the number of protons 683 exchanged during the process referring to the chemical equation. Taking into account 684

their values in our studies it was established that they increase with the increasing 685 concentration of the complexes. In Table 3 the comparison of the distribution 686 coefficients ($logK_d$) for the sorption of metal ion complexes with citric acid on Purolite 687 S957 and Diphonix Resin[®] is presented. The highest values were obtained for La(III) 688 and the smallest in the case of Zn(II) complexes with citric acid. These values were 689 referred to those reported in the literature. Even at low concentrations the majority of 690 REEs reported are in the III oxidation state in the acid leaching solutions. Therefore 691 compared to Fe(III) the selective sorption is a challenging task. 692

Strong cationic ion exchangers with the sulphonic functional groups sorb Fe(III) 693 and other HMs quickly (Silva et al., 2018) due to fast diffusion/convection in the 694 solution bulk. As presented in (Canner et al., 2018a) U(VI), Cu(II), Ni(II) and Co(II) 695 follow the chelating mechanism with respect to the iminodiacetate functional groups. 696 697 For Fe(III) partial hydrolysis occurs. However, the pure anion exchange mechanism was observed for REEs. In malic acid buffer the ion exchanger Purolite S910 shows 698 a preference towards the medium REEs. Unlike Purolite S910, Amberlite IRC86 with 699 the carboxylic functional group exhibits a definite selectivity towards the light REEs 700 with La(III) and Ce(III) showing the highest adsorption (Bezzina et al., 2018). It was 701 found that the ion exchange process involves the ion exchange with a slight 702 difference between La(III) and Gd(III), increase in the case of Tb(III) and constant 703 value for Lu(III). An unusual behaviour of Y(III) is observed. The slope gradient from 704 this plot for the Y(III) ion indicates a process involving the transfer of another proton. 705

3.8. Adsorption isotherm determination

The influence of the concentration of selected metal ions on the sorption capacity was analysed. The adsorption data of La(III) or Ni(II) in the presence of citric

acid on Purolite S957 and Diphonix Resin[®] were analysed using the Langmuir
 (Eq.19) and Freundlich (Eq.20) isotherm models:

711
$$q_{\rm e} = \frac{q_0 K_L c_{\rm e}}{1 + K_L c_{\rm e}}$$
(19)

712
$$q_e = K_F c_e^{1/n}$$
 (20)

where: q_e , c_e were defined as previously, q_0 is the maximum amount of metal 713 complexes sorbed per unit mass of adsorbent to form a complete monolayer on the 714 surface of ion exchanger (mg/g), K_L is the Langmuir constant related to the affinity of 715 the binding sites (dm³/mg), $K_{\rm F}$ is the Freundlich adsorption capacity (mg/g), 1/n is the 716 Freundlich constant related to the surface heterogeneity. The above mentioned 717 parameters can be calculated from the linearized plots of c_e/q_e vs. c_e and $\log q_e$ vs. 718 logce, respectively. Moreover, the obtained results can be described with the 719 separation factor R_L as well as 1/n. R_L and 1/n are dimensionless and R_L is defined 720 as follows: 721

722
$$R_L = \frac{1}{1 + K_L c_0}$$
 (21)

The Langmuir and Freundlich models are two isotherm models generally used for quantitative description of the adsorption equilibrium between the ion exchanger and the solution phase (Nikoloski and Ang, 2014). The shape of the obtained isotherm is indicative of adsorption processes.

The Langmuir isotherm can be used for quantitative determination and comparison of different sorbents (Deepatana et al., 2006; Escudero et al., 2008). At first it was elaborated for description of adsorption of gases on active carbon. Its application was extended to the empirical description of the equilibrium between the liquid and solid phases. The model is based on the assumptions: (i) the adsorbent

possesses active sites on its surface called active centres (these may be lattice 732 defects or interfaces), (ii) the adsorption process proceeds on the active centres, (iii) 733 each centre can adsorb only one molecule, thus a monomolecular layer is formed on 734 the adsorbent surface, (iv) the adsorbed molecules in the active sites do not interact 735 and the adsorption process is characterized by the dynamic equilibrium between the 736 sorption and desorption. This equation describes particularly well the chemical 737 adsorption when the adsorbed substance forms a monomolecular layer on the solid 738 phase surface. 739

The Freundlich isotherm is the earliest known relationship describing the 740 sorption equation. This fairly satisfactory empirical isotherm can be used for non-ideal 741 sorption that involves heterogeneous surface energy systems. In general, as the K_F 742 value increases the adsorption capacity of adsorbent for a given adsorbate 743 744 increases. Additionally, n is indicative of adsorption preference. The value of 1/n below one indicates the Langmuir isotherm while 1/n above one is indicative of 745 cooperative adsorption. The plot of *logq_e* vs. *logc_e* gives a straight line with the slope 746 of 1/n and the intercept of the values of K_F . The evaluated constants are given in 747 Table 4. Comparing the parameters of isotherms (Figs.6a-d, Table 4) it can be stated 748 that the value of R^2 from the Langmuir isotherm is the highest indicating a good fit to 749 the experimental data. In addition, the values of R_l from 0 to 1 indicate favourable 750 adsorption nature. The results also showed that the adsorption was enhanced upon 751 752 increasing temperature, suggesting that the adsorption process could be more likely chemical adsorption rather than physical one. 753

754



Table 4. Adsorption isotherm parameters for the sorption of Ni(II) and La(III)
 complexes with citric acid on Purolite S957 and Diphonix Resin[®].

Parameter	Purolite S957		Diphoni	x Resin [®]
	Ni(II)	La(III)	Ni(II)	La(III)
		293	3 K	
q _{e,exp} (mg/g)	41.29	58.29	41.83	58.59
Langmuir isotherm				
q ₀ (mg/g)	40.14	60.35	41.81	60.15
K _L (dm³/mg)	1.121	5.623	1.206	9.121
R ²	0.9968	0.9941	0.9937	0.9944

		A		
Freundlich isotherm				
K _F (dm ³ /mg)	17.24	45.25	15.97	102.35
n	3.979	2.375	2.929	1.716
R^2	0.9191	0.6893	0.6911	0.6536
		313	K	
q _{e,exp} (mg/g)	43.26	58.33	43.22	59.07
Langmuir isotherm				
q₀ (mg/g)	45.11	62.29	45.30	63.00
K _L (dm³/mg)	0.951	5.465	0.899	0.911
R ²	0.9899	0.9962	0.9996	0.9999
Freundlich isotherm				
K _F (dm ³ /mg)	16.29	46.99	16.12	38.32
n	2.334	2.137	2.266	2.227
R^2	0.7485	0.8903	0.7178	0.8899
		333	К	
q _{e,exp} (mg/g)	44.09	58.35	44.14	60.01
Langmuir isotherm				
q₀ (mg/g)	46.63	60.75	46.55	60.12
K _L (dm ³ /mg)	0.896	4.648	0.856	3.789
R ²	0.9979	0.9943	0.9968	0.9999
Freundlich isotherm				
K _F (dm³/mg)	17.18	45.59	16.76	35.55
n	2.146	2.078	2.119	2.011
R^2	0.7485	0.8813	0.7507	0.8898
Thermodynamic parameters				
∆G°at 293	-16.96	-23.31	-17.35	-26.53
∆G°at 313	-20.06	-25.13	-19.99	-33.11
∆G°at 333	-22.92	-26.91	-23.06	-38.46
ΔH°(kJ/mol)	26.77	23.06	24.43	61.01
ΔS°(J/mol K)	91.9	32.6	84.9	24.0

764

765 3.9. Temperature effect

The nature of the sorption process can be estimated by thermodynamic parameters such as the change in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°). These parameters can be estimated considering the equilibrium constants at different temperatures. Thermodynamic parameters of the adsorption were calculated from the variations of the thermodynamic equilibrium constant K_d determined by plotting ln(q_e/c_e) vs. q_e and extrapolating to zero q_e . The standard free energy change ΔG° can be calculated using Eqs.22-24:

772	$\Delta S^{\circ} \Delta H^{\circ}$	(22)
//5	$InK_d = \frac{1}{R} - \frac{1}{RT}$	(22)

774
$$\Delta G^{\circ} = -RT \ln K_{d}$$
(23)

$$\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ}$$
 (24)

where: ΔG° is the standard free energy change of the ion exchange (kJ/mol), *R* is the universal gas constant (8.314 J/mol K), *T* is the absolute temperature (K), ΔH° is the enthalpy (kJ/mol), ΔS° is the entropy (J/mol K).

The values of enthalpy ΔH° and entropy ΔS° were obtained from the slope and 779 intercept of InK_d vs. 1/T plots. The Gibbs free energy ΔG° was calculated using the 780 K_d value. The values of the thermodynamic parameters for the sorption of Ni(II) and 781 La(III) ions on Purolite S957 and Diphonix Resin[®] are given in Table 4. The positive 782 value of enthalpy change ΔH° shows that the adsorption of Ni(II) and La(III) ions is of 783 784 an endothermic nature. An adsorption process is generally considered as physical if ΔH° 20 kJ/mol and as chemical when ΔH° > 40 kJ/mol. The negative value of ΔG° 785 decreases with an increase in temperature, indicating that the reaction is 786 spontaneous and demonstrating that the higher temperatures facilitate the 787 adsorption. The obtained positive values of ΔS° showed the affinity of Purolite S957 788 and Diphonix Resin[®] for Ni(II) and La(III) and the increasing randomness. The 789 positive value of ΔH° indicated the endothermic nature of adsorption p rocess. On the 790 other hand, either change in the pore size of the ion exchangers causing intraparticle 791 diffusion within the pores or enhancement in the chemical affinity of Ni(II) and La(III) 792 ions for the functional groups leading to some chemical interactions takes place 793 during the adsorption process. 794

The Arrhenius equation was applied to evaluate the activation energy of adsorption representing the minimum energy that reactants must have for the reaction to proceed, as shown by the following relationship:

798
$$\ln k_2 = \ln A - \frac{E_a}{RT}$$
 (25)

where: k_2 (g/mg min) is the rate constant obtained from the pseudo second-order kinetic model, E_a (kJ/mol) is the Arrhenius activation energy of adsorption and A is

the Arrhenius factor (g/mg min). When $\ln k_2$ is plotted against 1/*T*, a straight line with the slope of $-E_a/R$ is obtained.

The activation energy values were found to be: 0.47 kJ/mol for Ni(II) on Purolite 803 S957, 0.83 kJ/mol for La(III) on Purolite S957 as well as 68.1 kJ/mol for Ni(II) on 804 Diphonix Resin[®], 76.5 kJ/mol for La(III) on Diphonix Resin[®]. It is evident that there is 805 an apparent relationship between the E_a and the relevant structural parameters of the 806 ion exchangers (gel and macroporous). It is also known that the value < 50 kJ/mol 807 generally indicates a film and particle diffusion controlled process, whereas higher 808 values represent chemical reaction processes. In similar studies, Ea values for 809 810 Amberlite IRA-743 and XSC-800 ion exchangers were reported to be 4.952 kJ/mol (Ohyoshi et al., 1972) and 20.38 kJ/mol (Canner et al., 2018b), respectively. 811

The comparison of the obtained results with those by other researchers is 812 813 presented in Table 5. In our studies the obtained results were not compared to those of the ion exchangers with the sulphonic functional groups although they are mainly 814 used in metal separation processes without specific adsorption requirements. This 815 group of resins shows the strongest adsorption capacity of the cation exchangers but 816 poor metal selectivity and difficulties of the adsorbed metal ions elution. Additionally, 817 it depends on the ion exchanger form. For example in the wastewater treatment from 818 inorganic industrial streams such ion exchanger as Dowex 50Wx8 in the Na⁺ form 819 shows a 10% higher metal loading capacity than in the H^+ form. 820

821

Table 5. Comparison of the obtained results with those by other researchers for theNi(II) and La(III) sorption.

Metal ion	Adsorbent	q _{e,max} (mg/g)	Ref.
	Purolite S957	44.09	This work
NG/11)	Diphonix Resin [®]	44.14	This work
INI(11)	Purolite S930	10.43	(Deepatana et al.,
	Purolite S950	18.42	2006)

Journal Pre-proof				
	Coffee wastes	7.25	(Escudero et al.,	
	Grape stalk	38.31	2008)	
	Lignin	5.99	(Guo et al., 2008)	
	Brewer's spent grain	1.64	(Wierzba and Kłos, 2019)	
	Magnetic peptide resins with glycine (MGLY)	391.00	(Hamza and Abdel- Rahman, 2015)	
	Purolite S957	58.35	This work	
	Diphonix Resin [®]	60.01	This work	
	Amberlite IRC86	40.60	(Bezzina et al., 2018)	
	Lewatit TP 207	114.70	(Esma et al., 2014)	
	Lewatit TP 260	106.70		
La(III)	polyaminophosphonic acid sorbent (PPA-PGMA)	109.59	(Galhoum et al., 2019)	
	Iron oxide loaded Ca-alginate beads	123.50	(Wu et al., 2010)	
	Fe ₃ O ₄ @DTPA	62.00	(Almeida and Toma,	
	superparamagnetic		2016)	
	nanoparticles			

824

825 3.10. Desorption and mechanism description

As for desorption studies two eluents were applied e.g. hydrochloric and nitric

acids at a concentration 0.5, 1.0 and 2.0 mol/dm³ (Fig.7).



828

Fig.7. The effect of desorbing agents for the desorption of Ni(II) and La(III) from
 Purolite S957 and Diphonix Resin[®].

Since using 2.0 mol/dm³ nitric acid resulted in the highest leaching of 832 lanthanide ions, it was proposed for desorption. Generally, the HMs ions such Ni(II) 833 are more readily desorbed than REEs such as La(III). As follows from the literature 834 data there is the strict relationship between the functional groups and their metal ions 835 removal. The presence of sulphonic functional groups determines better hydrophilic 836 properties of Purolite S957 and Diphonix Resin[®] compared to the traditional ion 837 exchangers such as Lewatit SP112 (Kołodyńska, 2010). The sulphonic acid groups 838 increase the hydrophilicity of ion exchanger, metal accessibility and ensures fast 839 kinetics: 840

841
$$2R-SO_3H + M^{2+} \Rightarrow (R-SO_3)_2^{2-} \rightarrow M^{2+} + 2H^+$$
 (26)

For M^{3+} this reaction should be analogous.

Moreover, the diphosphonic acid groups determine selectivity of the resin with $pK_1 = 1.27$, $pK_2 = 2.41$, $pK_3 = 6.67$ and pK4 = 10.04. They also ensure high selectivity and low desorption for Fe(III) over the divalent cations M(II) in the acid solutions as well as high affinity for lanthanides, actinides and polyvalent cations over a wide range of acid concentrations. The complexation reaction can be as follows:

848
$$R-(PO_3H_2)_2^{2-}+2H^++M^{2+} \approx R-(PO_3H_2)_2^{2-} \rightarrow M^{2+}+2H^+$$
 (27).

In the case of metal ions with the additional charge (M³⁺), it can be neutralized by the sulphonate functional groups. It was found that phosphoryl oxygen and acidic oxygen cannot be simultaneously coordinated to the metal ion. In acidic solutions, for example the neutral metal-nitrate(V) species may be bound to the phosphoryl groups of diphosphonic acid.

However, in the case of the carboxylic groups, the resin has strong affinity for protons (above a low acid concentration, ion exchangers are completely converted to

ourn	Ð	nr	
oun			

the free acid and do not react with neutral salts) (Höll, 1984). WAC sorbs metal ionsonly when protons are neutralized by co-ions of the solution:

858 R-COOH + NaOH
$$\Rightarrow$$
 R-COONa + H₂O (28)

859
$$2R$$
-COONa + $M^{2+} \rightleftharpoons 2(R$ -COO⁻) $\rightarrow M^{2+} + 2Na^+$ (29).

860 Such groups have a great ability to remove REEs from solution due to their 861 ability to form the strongest complexes with O-donor ligands (Bezzina et al., 2018).

In the case of Purolite S957 containing only sulphonic and phosphonic 862 functional groups the selectivity series at low pH follows the order of Fe(III) > AI(III) > 863 Mn(II) = Cu(II) = Zn(II) = Co(II) = Ni(II), therefore it preferentially extracts trivalent 864 metal cations below pH 1. It should be added that the sulfonic acid resin Bio-Rad[™] 865 AG MP-50 displayed much lower selectivity at these higher proton concentrations. 866 These combined properties provide high selectivity for Fe(III) and other transitional 867 metals in the acidic solutions (Canner et al., 2018b). To describe the mechanism of 868 metal ion sorption it should be known that according to the Pearson Hard and Soft 869 Acids and Bases (HSAB) theory, the ligands of the functional groups in ion 870 exchangers behave as electron donors (bases) and the metal ions as electron 871 acceptors (acids) following the Lewis theory. Hard acids are ions with low 872 electronegativity, non-polarizable, have the high charge to ionic radius ratio and are 873 attracted to hard bases of high electronegativity. On the other hand, soft acids are 874 polarizable ions with the low charge to ionic radius ratio and with relatively high 875 876 electronegativity that matches the relatively low electronegativity of soft bases. Thus ion exchangers with the phosphonic, phosphinic, phosphonic, carboxylic groups 877 (hard base) can interact with hard acids like Fe(III), Al(III), Sc(III) and Ln(III). When 878 high selectivity between two hard or soft acids (i.e., metal ions) is required a base 879 group containing the number of donor atoms similar to the oxidation state of the 880

target acid ion is preferred e.g. carboxylic groups with two electron donor atoms
favour the interactions with metal ions with II over III the oxidation state.

The characterization of selected ion exchangers requires the determination of 883 both their equilibrium and kinetic properties. Acidity of a solution has two effects on 884 metal sorption. Under the acidic conditions protonation of the binding chelating 885 functional groups is observed, however, hydroxide ions in the basic solution 886 complexed and precipitated metal ions. Therefore, pH of a solution is the first 887 parameter which should be optimized. At pH of the solution equal to pH_{PZC}, the 888 surface charge of the ion exchangers is neutral and therefore the negligible sorption 889 of La(III) and Ni(II) or their complexes with citric acid is observed. When pH is lower 890 than pH_{PZC}, the surface charge of the ion exchangers is positive. There is an 891 electrostatic repulsion between La(III) and Ni(II) and low sorption efficiency. In the 892 893 case of negative metal ions complexes with citric acid they are supposed to be adsorbed, however, in this pH region they do not exist. At pH greater than pH_{PZC} this 894 value is negative which produces the attraction of metal ions. Generally, the lower 895 pH_{PZC} is, the more metal ions are attracted. Maximum sorption is likely to occur at pH 896 values greater than PZC when adsorbents have a net negative charge. In the case of 897 the citric acid in the solution, the carboxylic groups act with La(III) and Ni(II) to form 898 complexes by releasing protons. This indicates that the ion exchange reaction 899 increases acidity of solution as described in (Lu et al., 2009). The negligible effect of 900 the increased ionic strength on the REEs cation extraction suggests chelating 901 interactions of the phosphonic acid functionality with La(III) and not strong 902 interactions with Ni(II) ions. However, this mechanism is rather complicated. 903

904

905 4. Conclusions

The use of ion exchange resins is constantly evolving and new areas are 906 emerging. In this study, the removal of Ni(II) and La(III) ions from the citrate solutions 907 onto the ion exchangers Diphonix Resin[®] and Purolite S957 was investigated under 908 different experimental conditions varying such parameters as solution pH, contact 909 time, ion exchanger dose, different ratio of ion exchanger and the initial concentration 910 of metal ions. The optimal sorption process conditions were determined. The 911 adsorption mechanisms were examined studying kinetic and isotherm models. Based 912 on the obtained results, it can be concluded that the phase contact time, 913 concentration and citric acid to metal ion ratio affect the sorption process. The results 914 show that the sorption of Ni(II) and La(III) ions on the tested ion exchangers is very 915 fast. The equilibrium is determined after 10-20 min. for Diphonix Resin[®] and Purolite 916 S957. Moreover, the adsorbents exhibit excellent adsorption of Ni(II) and La(III) ions 917 918 from the citric solutions achieving removal of almost 100%. The suitability of the pseudo first order, pseudo second order, intraparticle diffusion, Boyd, film diffusion 919 920 and Dumwald-Wagner kinetic models for the adsorption is also discussed. The pseudo second order kinetic model agrees very well with the adsorption behaviour 921 over the studied range of metal ions concentration. The Langmuir model was found 922 to provide the best fit to the data, as evidenced by the highest correlation coefficient. 923 The obtained results have practical significance in the process of removing heavy 924 metal ions and lanthanide ions from the solutions after the extraction of the Ni-MH 925 batteries. The experimental results of this study demonstrate that Purolite S957 and 926 Diphonix Resin[®] are suitable for adsorption of Ni(II) and La(III) ions from solutions. 927 Moreover, citric acid can be proposed as an alternative chelating agent to EDTA, 928 having the advantage of low price and high biodegradability. Both ion exchangers 929

can be used for pretreatment of the acidic liquors to remove less valuable iron and to maximize further stages of exchange columns usage.

932

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Highlights

Citric acid for NiMH recycling was proposed.

A ion exchange process was developed for removal of REEs and HMs ions from battery leaching solution.

Journal Proposi

Declaration of interests

⊠The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

□The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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