Recovery of metals from waste nickel-metal hydride batteries using multifunctional Diphonix resin

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Abstract

In this study, Diphonix resin containing sulfonic, diphosphonic and carboxylic groups was used to evaluate the adsorption capacity of metal ions contained in the nickel-metal hydride batteries (Ni-MH). This type of ion exchanger can be considered as the multifunctional material having great affinity to many metal ions. Using Diphonix resin adsorption process was carried out for La(III) and Ni(II) ions to characterize kinetic, adsorption and thermodynamic parameters. Preliminary studies of the Nd(III), Ce(III), La(III), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) metal ions mixture were also performed. The best results of adsorption studies were obtained using 0.2 M HNO₃. Diphonix resin exhibits especially good adsorptive properties with respect to rare earth element ions (adsorption efficiency of about 100%) in comparison with the heavy metal ions in the second oxidation state (about 50% or below). The series of affinity of the resin for the studied ions can be presented as follows: La(III) > Fe(III) > Nd(III) > Ce(III) > Cu(II) > Zn(II) > Co(II) > Ni(II). The obtained results confirmed the possibility of further use of the resin for the recovery and separation of rare earth elements from solutions after Ni-MH batteries leaching.

Extended author information available on the last page of the article

Keywords Diphonix resin · Metal ions recovery · Affinity · Adsorption · Batteries

1 Introduction

Nowadays development of technology as well as production of various portable electrical devices results in creation of large amounts of wastes (Bertuol et al. 2009; Müller and Friedrich 2006; Pietrelli et al. 2005; Skowroński et al. 2015). Moreover, all European Union countries are obliged to undertake the actions ensuring a selective collection and recycling of spent galvanic cells including commonly known as batteries or accumulators. Such activities follow some legal regulations (among others, the previous—93/86/EEC, 98/101/EC, 2006/66/WE PE and Council and present 2012/19/UE about batteries and accumulators as well as their wastes). The spent batteries impose serious threat for the natural environment as they contain many dangerous substances, among others, heavy metals (HM). On the other hand, they constitute a source of valuable metals including rare earth elements (REEs). Therefore of significant importance is suitable recycling of such materials which is based not only on elimination of threat as a result of harmful elements content but also on recovery of valuable metals as a secondary raw material (Ekberg and Petranikova 2015; Müller and Friedrich 2006; Pietrelli et al. 2005, 2002).

As for commercial cells the most common are zinc–carbon batteries, disposable alkaline batteries, lithium and nickel–cadmium batteries, nickel-metal hydride or acid-lead accumulators. Of them nickel-metal hydride (Ni-MH) cells, commonly called accumulators become more and more common as they are believed to be one of more important sources of energy for various types of mobile applications, storage of stationary energy and also transport. More and more frequently they replace toxic nickel–cadmium (Ni–Cd) cells, are capable of acting in a wide range of temperatures and possess a sealed system limiting electrolyte leaks and minimizing conservation problems (Kwo-Hsiung et al. 2016; Kwo-Hsiung 2016; Meshram et al. 2015; Rodrigues and Mansur 2010; Santos et al. 2012; Tarabay and Karami 2015). The cathode of the Ni-MH cell is the porous polymer impregnated with “paste” containing active nickel compounds $\text{Ni}(\text{OH})_2$ as well as other additives stabilizing the electrode and improving its conductivity. Anode, similarly to the cathode, is composed of porous polymer impregnated with the mixture of metal ions both the rare earth and heavy metals (HMs), among others, Nd, Ce, La, Pr and Fe, Co, Ni, Cu, Zn, Al, capable of hydride formation. The active anode material are hydrogen ions which during charging and discharging of the battery are absorbed and desorbed by the above mentioned metals. The electrodes are separated from each other by a synthetic porous membrane which enables the contact of electrolyte (KOH solution) contained in

electrode space with both electrodes (Bertuol et al. 2006; Pietrelli et al. 2005; Rodrigues and Mansur 2010; Santos et al. 2012; Tarabay and Karami 2015; Young 2016). The electrode charging and discharging processes in cell can be written as: (Lucas et al. 2015; Shengqiang et al. 2015):

where M means hydrogen storage alloys while MH means metal hydride.

Therefore the nickel-metal hydride (Ni-MH) cells are one of the most frequently selected and used batteries in everyday life. They provide not only high performance but they are also a source of valuable metals, such as REEs. Rare earth elements are widely applied in many industrial branches (aviation, motorization, power engineering, lighting etc.) and high-tech applications (Chakhmouradian and Wall 2012; Meshram et al. 2016; Pietrelli et al. 2002). Lately China supply of REEs has been over 90%. In 2010 it stopped the export of these precious elements and increased their prices. Therefore an important issue is independence of REEs export from China and looking for new methods of obtaining them from other sources (Meshram et al. 2016, 2017).

Considering the fact that every year billions of spent nickel-metal hydride cells get on the consumer market, their proper management is indispensable. Their recycling can result in the double advantage as regards environmental protection and obtaining high purity valuable metals. The common methods of metals recovery from the spent Ni-MH cells include pyrometallurgical or hydrometallurgical ones. Under suitable conditions and stages of the process the hydrometallurgical method allows for selective removal or separation of metals with simultaneous minimization of by-products. Moreover, these methods are preferred for economic reasons (Jha et al. 2016; Meshram et al. 2016, 2015; Müller and Friedrich 2006; Pietrelli et al. 2002; Santos et al. 2012; Skowroński et al. 2015; Wang et al. 2012).

Pyrometallurgical methods consist in the recovery of materials by their melting in special furnaces. Their advantage is the possibility of recycling cells of various types, including those containing organic electrolytes. In turn, the relatively low efficiency of such recycling and the possibility of secondary waste generation during the process significantly limit their use. On the other hand, the hydrometallurgical processes consist in acid or alkaline leaching of properly prepared battery wastes (after machining processes).

This is followed by a series of physicochemical operations that lead to the separation and concentration of valuable components between the respective phases, up to the commercial and semi-finished products for different technological processes. The advantage of these methods is low energy expenditure and the formation of a small amount of secondary wastes. The total process usually includes the following stages: dissolving the appropriate waste fractions, purification and concentration of the resulting solution and separation of pure chemical compounds. Among advantages should be listed the following: the possibility of effective recovery of metals and high purity compounds from multi-component raw materials with low and variable concentrations of elements, low energy consumption and the process temperatures (below 373 K), the process does not require expensive reagents and complicated equipment, the possibility of solutions reuse, decrease of the emission of harmful products into the environment, recovery of high purity metals for the use in small industrial plants installation, reduction of the amount of stored materials hazardous for the environment and implementation of EU development policy (Innocenzi et al. 2017; Shengqiang et al. 2015). In this method the ion exchange with specific resins can be applied. Among them, the Diphonix resin requires special attention (Alexandratos 2007). It was proposed for Iron Control Process developed by Eichrom Industries in order to remove of Fe(III) during hydrometallurgical processing of Cu(II), Zn(II), Ni(II) and Co(II) (Gula and Dreisinger 1996; Xue et al. 2001). It was proved that for the $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ solution in 3 N H_2SO_4 after 2 h of contact, iron(III) uptake was 40% i.e., higher than for Duolite C-467 with the aminophosphonic group. Analogous results were obtained for Diphonix by McKevitt and Dreisinger (McKevitt and Dreisinger 2009). Therefore the above-mentioned resin was applied for Fe(III) removal from spent copper electrolyte in FENIX Iron Control System, Australia (Shaw et al. 2004). Moreover, Diphonix can strongly sorb actinides, especially in the IV and VI oxidation states from highly acidic (up to 10 M HNO_3) and highly salted solutions as well as transition and post-transition metals in the presence of alkali and alkaline earth metal ions i.e., Na(I) and K(I) as well as Ca(II) and Mg(II) (Chiariza et al. 1997). As for the alkaline earth metal ions sorption does not depend on the size of hydrated cations according the Gregor's theory but it is mainly due to chelation by the diposphonic groups. For 0.1 M HNO_3 the affinity series is as follows: $\text{Fe(III)} > \text{Ca(II)} = \text{Cr(III)} > \text{Zn(II)} > \text{Ag(I)} > \text{Co(II)} > \text{Sb(V)} > \text{Hg(II)}$ and for 5 M HNO_3 $\text{Fe(III)} > \text{Cr(II)} > \text{Ag(I)} > \text{Sb(V)} > \text{Co(II)} = \text{Zn(II)} = \text{Hg(II)} > \text{Ca(II)}$ (Horwitz et al. 1993). It can also be used for removal of U(VI) and such hazardous metal ions as V(V), Cr(VI), Mn(IV), Co(II), Ni(II), Zn(II), Cd(II), Hg(II) and Pb(II) from waters and wastewaters as well as Mn(II), Co(II) and Ni(II) from oil refinery process waters generated in being washed catalysts

used for desulfurization processes and Fe(III) removal in the boiler descaling operations (Phillips et al. 2008). Based on the distribution coefficients Zn(II), Cu(II) and Zn(II) ions are sorbed through the ion exchange reaction. It is also possible to sorb TcO_4^- in the form of HTcO_4 by hydrogen bonding to the phosphoryl groups. As well for the actinides D as high as 10^8 for Am from 0.1M HCl and 10^6 to 10^7 for Pu(IV), Th(IV) and U(VI) up to 1M HCl were found (Horwitz et al. 1997b). Moreover, Diphonix can be used for interferences such as U, Pu, Th, Nb, V, Mo, Zr, W, Fe, Cr, Ce, Er and Ti removal during Be determination (Maxwell III et al. 2008). Additionally, it can be used for effective separation of Zr and Hf and metal ions in the presence of the biodegradable complexing agents with EDDS and GLDA (Kołodzyńska 2010; Smolik et al. 2009).

Diphonix resin is widely used in the removal and recovery of metal ions from various solutions even at very acidic ones. It binds different metal ions forming chelate complexes with the phosphoryl groups of the diposphonic groups. The mechanism of metal ions sorption on different oxidation states (M^{n+}) onto Diphonix resin can be presented as (Chiarizia et al. 1994; Hajiev et al. 1989):

where R is the Diphonix resin matrix.

The aim of the paper was to study possibilities of recovery of metal ions contained in the Ni-MH cells through their adsorption on the commercially available Diphonix resin. The first stage of the research was the evaluation of the adsorption capacity of the Diphonix towards two metal ions La(III) and Ni(II) and the optimization of adsorption process. Desorption efficiency of the above mentioned metal ions was also examined. In the second stage preliminary studies of the adsorption process from the model solutions containing a metal ions mixture with different initial concentrations corresponding to the average content of metal ions in solution after leaching of spent Ni-MH cells was conducted. These studies can contribute to possibility of the further use of this resin for metal ions removal from real solutions after leaching of spent Ni-MH cells.

2 Materials and Methods

2.1 Resin

For the adsorption studies, the Diphonix resin was applied. This material is a commercially available multifunctional chelating resin supplied by Eichrom Industries. It was developed by the members of the Separation Chemistry Group of the Chemistry Division of Argonne National Laboratory and the University of Tennessee, Department of Chemistry.

The name Diphonix is the acronym for diphosphonic ion exchanger (Horwitz et al. 1993). It is characterized by a strong affinity for Fe(III) over the mono- and divalent metal ions. The main physicochemical properties of Diphonix are presented in Table 1. In contrast to other ion exchangers with multifunctional groups, the geminally substituted diphosphonic as well as carboxylic groups of Diphonix are not attached to the phenyl ring within the polymer matrix. This provides high hydrophilicity for kinetics of metal species (measured by the water regain). Moreover, the sulfonic functional groups are utilized to improve exchange kinetics. The performance of Diphonix can be analogous to the vinylidene-1,1-diphosphonic acid (VDPA). The protonation constants of Diphonix resin which are pK_1 and $pK_2 < 2.5$, $pK_3 = 7.24$ and $pK_4 = 10.46$ appear to be almost equal to the protonation constants of the starting material VDPA and are $pK_1 = 1.27$, $pK_2 = 2.41$, $pK_3 = 6.67$ and $pK_4 = 10.04$ (Chiariza et al. 1997; Nash et al. 1994). This provides the possibility of strong complexes formation under acidic conditions by forming coordination bonds with metal ions through phosphoryl oxygen. The crosslinking (the content of divinylbenzene) of the resin exchangers is about 10% DVB. The total capacity is 5.4 meq/g assuming two acidic protons from each phosphonate and one per sulfonate. According to Nash et al. (1994) the sulfonate functional groups are randomly distributed on the benzene rings.

In order to remove any residual contamination originating from the resin synthesis, prior to the experiments it was contacted with 1 M NaOH and HCl solutions. After that the resin was washed with distilled water. The operation was

repeated several times and then the resin was allowed to dry at room temperature.

2.2 Reagents and solutions

The model solutions of single metal ions Ni(II) and La(III) as well as the mixture of metal ions i.e., Nd(III), Ce(III), La(III), Fe(III), Co(II), Ni(II), Cu(II), Zn(II) at different initial concentrations were used in adsorption studies. The qualitative and quantitative compositions of the solutions were selected based on that of the real solution after leaching of Ni-MH cells with nitric acid. All experiments were performed using nitric acid concentration at the concentration 0.2 M.

The stock solution of La(III) with a concentration of 1000 mg/L was prepared using lanthanum(III) oxide (La_2O_3 , Specpure, JMC, England). This oxide was initially heated in the FB Thermo Scientific Series oven (USA) at 1173 K for 4 h. After this time, the sample was put into the exsiccator to cool. Next, an appropriate amount of the oxide was weighed and taken up with a solution of nitric acid. At first, the oxide was treated with 1 M HNO_3 solution and then several drops of the concentrated acid solution was added for complete La_2O_3 dissolution. The solutions were quantitatively transferred to conical flasks and supplemented with the 0.2 M HNO_3 solution. The stock solution of Ni(II) with a concentration of 1000 mg/L was prepared by dissolving a suitable amount of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ salt (Avantor Performance Materials Poland S.A.) in the 0.2 M HNO_3 solution. The solutions of lower concentrations were prepared by appropriate

Table 1 Physicochemical characteristics of the Diphonix resin (Chiariza et al. 1997; Kołodziejńska 2010)

Matrix	Polystyrene-divinylbenzene (PS-DVB)
Structure	gel
Functional groups	diphosphonic, sulfonic, carboxylic
Ionic form	H^+
Total capacity (meq/g)	5.6
Particle size range (mm)	0.074–0.150
Density (g/mL)	1.05–1.11
Moisture content (%)	60–70
Max temperature range (K)	313
Operating pH range	0–12

dilution of the La(III) and Ni(II) stock solutions using nitric acid solution at the concentration 0.2 M.

The stock solution of mixture metal ions was prepared in such a way that the metal ions concentrations corresponded to the average real concentrations in the leaching solution i.e., 91 mg/L of Nd(III), 129 mg/L Ce(III), 712 mg/L La(III), 1175 mg/L Fe(III), 326 mg/L Co(II), 2688 mg/L Ni(II), 94 mg/L Cu(II) and 90 mg/L Zn(II). The solutions of Nd(III) was prepared from Nd_2O_3 in the same way as shown above. The following metal salts (at appropriate amount) were used to prepare the remaining solutions: $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (POCh S.A., Poland), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Avantor Performance Materials Poland S.A.). The mixture of metal ions was completed with the 0.2 M HNO_3 solution.

2.3 Apparatus

The laboratory shakers Elpin + type 357 (water bath shaker) and Elpin + type 358A (Poland) were used for experiments. A PHM 82 laboratory pH-meter (Radiometer, Copenhagen) was used for measuring the pH values.

The metal ions concentrations were determined by an inductively coupled plasma optical emission spectrometer (ICP-OES, 720 ES, Varian). The wavelengths used for the analysis of Nd(III), Ce(III), La(III), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) were 401.224, 446.021, 333.749, 259.940, 238.892, 216.555, 327.395 and 206.200 nm, respectively. The ICP-OES instrument was calibrated using the ICP standards for all analysed metal ions. For the preparation of all standards and blank samples, the ultrapure nitric acid was used to avoid any matrix interference.

The surface morphology of the Diphonix resin was studied using scanning electron microscopy (SEM) and atomic force microscopy (AFM). The SEM images were made using the Quanta 3D FEG instrument (FEI Company) and the AFM analysis was performed by using the NanoScope V microscope from Veeco (USA). The MULTIZOOM AZ 100M optical microscope (Nikon, Japan) was also used for the resin Diphonix surface analysis and obtaining an image with the extended depth of field (the EDF image). The parameters of porous Diphonix resin structure were determined measuring the adsorption/desorption isotherms of nitrogen at 77 K. To this end the ASAP 2420 instrument from Micromeritics Instrument Corporation (USA) was used. Before measurements the samples were degassed at 343 K. The surface area and pore size distribution (volume and pore diameter) were determined by means of the Brunauer–Emmett–Teller (BET) and the Barrett–Joyner–Halenda (BJH) methods, respectively.

A point of zero charge (pH_{pzc}) of the Diphonix was determined using the potentiometric titration method for the three

ionic strengths (0.1, 0.01 and 0.001 M NaCl). The suspensions of the resin (0.3 g) and NaCl solution (30 mL) were mixed using a magnetic stirrer and titrated with the standard solutions (0.1 M HCl and 0.1 M NaOH). To this end the Dosino and Titrand kit (Metrohm) was used. The pH_{pzc} of Diphonix was also determined using the drift method. For this purpose, 0.3 g of the resin and 30 mL of the pH-adjusted 0.01 M NaCl solution was added into a flask and stirred for 24 h. The initial pH of solution was in the range of 2–12. After stirring, the solution was separated from the resin beads by filtration and then pH solutions (pH_1) were measured. At the end, the dependence of $\text{pH}_1 - \text{pH}_0$ from pH_0 was plotted on the graph. The point of intersection with the x axis gives the pH_{pzc} value.

The water content in the resin Diphonix was also determined. The high-end titrator for volumetric and coulometric Karl Fischer titration equipped with the 807 Dosino dosing unit and the stove (Titrand, Metrohm) was used. The resin was previously dried in a laboratory dryer at 378 K to get rid of moisture and the representative sample of 0.1 g was selected for further water determination.

The Fourier transform infrared (FTIR) spectroscopy including an attenuated total reflectance (ATR) sampling module (Model Cary 630, Agilent Technologies, USA) was used to record the FTIR spectra of the Diphonix. After the spectrum measurement the baseline and ATR corrections were applied.

2.4 Adsorption studies

In order to assess the adsorption capacity of Diphonix resin in relation to metal ions and to optimize process conditions, the effects of the following conditions: HNO_3 concentration, phase contact time, initial metal ions concentration and temperature were investigated. The adsorption process using a static method, at the constant ratio of the solution volume to the resin mass (100:1) and the constant shaking conditions (180 rpm, amplitude 8) was conducted.

In the first stage, the effect of HNO_3 (0.2, 0.5, 1, 1.5 and 2 M) on the adsorption of La(III) and Ni(II) ions was studied. The adsorption process was performed at room temperature, at the initial metal ions concentration equal to 50 mg/L and phase contact time equal to 120 min. Next, the effect of phase contact time was examined from 1 to 120 min. The initial La(III) and Ni(II) ions concentration was equal to 50 mg/L. The effect of the initial concentrations from 25 to 600 mg/L was also determined. The influence of temperature in the range from 293 to 313 K on the La(III) and Ni(II) ions adsorption efficiency was evaluated. The studies were carried out at the initial metal ions concentration of 50 mg/L and for time equal to 120 min.

In the second stage, the adsorption kinetics of the mixture metal ions on the Diphonix was examined. The stock solution was diluted 20-fold and the efficiency of the adsorption

process was determined by shaking a suitable amount of the resin and solution under the following conditions: phase contact time from 1 to 120 min, room temperature and 0.2 M HNO_3 solution.

The resin affinity towards the above metal ions contained in the mixture was also estimated. For this purpose the distribution coefficient (D) was determined. Adsorption process was conducted under the following conditions: initial metal ions concentration equal to 50 mg/L, 0.2 M HNO_3 solution, time shaking equal to 120 min.

After the predetermined time, the all solutions were filtered using a 0.45 μm pore size filter. The solutions pH was measured and the metal ion content was analysed. The resin aliquots were allowed to dry at room temperature for further desorption studies. The all studies were performed in three replicates, therefore, the results obtained were averaged. The measurement precision in each series was within 5%.

2.5 Desorption studies

Desorption studies were carried out using the 0.5, 1 and 2 M HNO_3 solutions as eluting agents. The desorption process of Ni(II) and La(III) ions (initial concentration 50 mg/L) as well as the mixture of metal ions from the Diphonix resin was performed. The 0.1 g dried and loaded resin and 10 cm^3 of eluent solution were shaken in the Erlenmeyer flasks, stirring at 180 rpm for 120 min at room temperature. The final concentrations of metal ions after the desorption process were determined.

2.6 Data analysis

2.6.1 Basic parameters characterizing adsorption process

Based on the adsorption studies such parameters as the amount of adsorbed metal ions at time t (q_t), adsorption capacity (q_e), adsorption effectiveness (% S) as well as the distribution coefficient (D) were determined. The values of these parameters were calculated using the following equations:

$$q_t = (C_0 - C_t)V/m \quad (4)$$

$$q_e = (C_0 - C_e)V/m \quad (5)$$

$$\%S = ((C_0 - C_t)/C_t) \times 100\% \quad (6)$$

$$D = ((C_0 - C_e)/C_e) \times (V/m) \quad (7)$$

where C_0 is the initial concentration of metal ions (mg/L), C_e , C_t are the concentrations of metal ions at equilibrium and at time t (mg/L), respectively, V is the solution volume (L) and m is the resin mass (g).

The desorption efficiency of metal ions (% D) was also evaluated using the following equation:

$$\%D = 100\% \times (C_{des}/C_o) \quad (8)$$

where C_{des} is the concentration of metal ions in the aqueous phase after desorption (mg/L) and C_o is the initial concentration of metal ions (mg/L).

2.6.2 Kinetic studies

During adsorption from the liquid phase, the mass transport takes place in two main stages which are: external diffusion from the liquid to the surface of adsorbent beads and internal diffusion inside the adsorbent beads. The identification of the mechanism limiting the rate of the process is made the reaction kinetics behaviour. In order to evaluate the mechanism of the metal ions adsorption process on the Diphonix and to interpret the experimental data, several known kinetic models were used: the pseudo-first order (PFO), pseudo-second order (PSO), intraparticle diffusion (IPD) and Boyd models presented by following equations, respectively (Kiruba et al. 2014; Yuanfeng et al. 2016).

$$\log(q_e - q_t) = \log(q_e) - k_1 t / 2.303 \quad (9)$$

$$t/q_t = (1/k_2 q_e^2) + (t/q_e) \quad (10)$$

$$q_t = k_i t^{1/2} + C_i \quad (11)$$

$$F = 1 - (6/\pi^2) \exp(-Bt) \quad (12)$$

$$Bt = -0.4977 - \ln(1 - F) \quad (13)$$

where q_e and q_t are the adsorbed metal ions amounts at equilibrium and at time t (mg/g), respectively, t is the phase contact time (min), k_1 is the PFO equilibrium rate constant ($1/\text{min}$), k_2 is the PSO equilibrium rate constant ($\text{g}/(\text{mg min})$), k_i is the IPD rate constant ($\text{mg}/(\text{g min}^{1/2})$), C_i is the IPD constant related to the boundary layer thickness, F is the metal ion adsorbed fraction at time t , Bt is the F mathematical function.

2.6.3 Equilibrium studies

The equilibrium isotherms analysis is useful for description of adsorbate ions behaviour during the adsorption process. The information about the affinity of the adsorbate ions for the resin and the interactions way at equilibrium can be obtained analyzing the equilibrium isotherm data. In order to describe the adsorption equilibrium data of metal ions adsorption onto the Diphonix, three adsorption isotherm models were used: Langmuir, Freundlich and Temkin models (Arthy and Saravanakumar 2013; Babaeiveli et al. 2014; Khalil et al. 2016):

$$1/q_e = (1/q_m K_L C_e) + (1/q_m) \quad (14)$$

$$\log q_e = \log K_F + ((1/n) \log C_e) \quad (15)$$

$$q_e = \ln(K_T C_e) RT / A_T \quad (16)$$

where q_e is the adsorption capacity (mg/g), q_m is the maximum monolayer adsorption capacity (mg/g), K_L is the Langmuir constant related to the adsorption energy (L/mg), C_e is the metal ions concentration at equilibrium (mg/L), K_F is the multilayer adsorption capacity ((mg/g)(L/mg)^{1/n}), $1/n$ is the Freundlich constant related to the surface heterogeneity and the adsorption favourability, R is the gas constant (8.314 kJ/mol K), T is the temperature (K), A_T is the Temkin constant related to the adsorption heat (J/mol), K_T is the Temkin constant related to the maximum binding energy (L/g).

2.6.4 Thermodynamic studies

In order to evaluate the nature of the adsorption process, the thermodynamic parameters like the enthalpy change (ΔH°), the entropy change (ΔS°) and the Gibbs free energy change (ΔG°) were determined. Among them, the ΔG° is the fundamental parameter for evaluation of adsorption process spontaneity. The value of the ΔG° was obtained using the following equation:

$$\Delta G^\circ = -RT \ln K_c \quad (17)$$

$$K_c = q_e / C_e \quad (18)$$

where K_c is the thermodynamic equilibrium constant.

The other thermodynamic parameters were estimated using the van't Hoff equation:

$$\ln K_c = \Delta S^\circ / R - \Delta H^\circ / RT \quad (19)$$

Plotting $\ln K_c$ against $1/T$ the values of ΔS° and ΔH° as the intercept and the slope of the plot can be obtained (Yuanfeng et al. 2016).

3 Results and discussion

3.1 Resin characteristics

3.1.1 SEM, EDF and AFM studies

The morphology of Diphonix resin surface are studied by means of the SEM, EDF and AFM methods. Based on the SEM results (Fig. 1a) it can be concluded that the resin surface is homogeneous and the resin beads are spherical. Unfortunately, it is not possible to obtain the information about the porosity of the resin surfaces directly by generating SEM images of the resin. Because the interpretation of the resin image by the extended depth of field is difficult, to this end the software for the 3-D visualization of in-focus topography was applied. The idea is to merge a stack of micrographs taken at different focal positions (aligned along the optical axis) into a single, entirely focused composite image. Based on this method the results obtained by means of optical microscope are presented in Fig. 1b. The resin is yellow/brown. Due to the change of the colour of Diphonix (it acts as an indicator), the mechanism of the sorption can be established. The AFM analysis allowed to present the resin surface in the two-dimensional (2D) and three-dimensional (3D) spaces which are shown in Fig. 2a, b, respectively. The AFM images showed that the resin surface morphology is rough and porous. The determined roughness of the resin was 0.26 nm.

Fig. 1 a SEM and b EDF images of the Diphonix resin

Fig. 2 2D (a) and 3D (b) AFM images of the Diphonix

Fig. 3 The point of zero charge of the Diphonix determined by the potentiometric titration method

3.1.2 ASAP studies

Based on the analysis of nitrogen adsorption/desorption isotherm the pore and surface characteristics of the Diphonix were determined and the results were described below. A very low specific surface area of this material equals to $0.2 \text{ m}^2/\text{g}$ was obtained. This small value does not exclude this material as a potential adsorbent. In this case, the presence of many functional groups in its structure is more important, which allows it to be very efficiently binding with

metal ions. The total pore volume and the BJH pore diameter of the non-loaded resin were 0.0003 mL/g and 4.52 nm , respectively. According to the IUPAC classification the average pore diameter is in the mesoporosity range ($2\text{--}50 \text{ nm}$).

3.1.3 pH_{pzc} studies and water contents determination

The point of zero charge (pH_{pzc}) and the water content in the resin structure were also determined. The pH_{pzc} of the Diphonix resin determined by the potentiometric titration method is presented in Fig. 3. The pH_{pzc} value obtained using this method is 2.18 being close to that obtained by the drift method (1.85). Analysis of the water content by the Karl Fischer method showed that the resin sample contains 18.8% hydration water in its structure which was confirmed by the FTIR analysis.

3.1.4 FTIR studies

The Fourier transform infrared spectra of the resin Diphonix before and after Ni(II) and La(III) ions adsorption are shown in Fig. 4. They are very similar and contain different overlapping bands characteristic of the resin structure. A broad band in the $3600\text{--}3200 \text{ cm}^{-1}$ region is characteristic of the O–H groups of the acid and residual hydration water (Abderrahim et al. 2006; Lazar et al. 2014). The peaks at about 2926 cm^{-1} are due to the aliphatic C–H stretching vibrations derived from the methyl groups in the main chain of resin. These bands are characteristic

Fig. 4 FTIR spectra of the Diphonix before and after La(III) and Ni(II) ions adsorption

of the polystyrene structure (Lazar et al. 2014; Singare 2011). The bands at about 2263 and 2103 cm^{-1} can be attributed to the O-H vibrations derived from the resin functional group. These are the bands of the stretching

vibrations ($\nu(\text{P-OH})$, $\nu(\text{S-OH})$) (Abderrahim et al. 2006; Singare 2011). The band in the 1650–1550 cm^{-1} region is attributed to the presence of simple C=C bonds in the styrene–divinylbenzene structure (Lazar et al. 2014). The peaks at 1423 cm^{-1} are assigned to the asymmetric deformation vibrations of CH_2 groups in the resin structure. The absorption peaks at 1119 and 993 cm^{-1} correspond to the stretching symmetric and asymmetric vibrations of the sulfonic and phosphonic groups in the resin structure. The peak at 825 cm^{-1} is attributed to the C-H out of plane deformation vibrations in the benzene ring. This band is associated with the crosslinking of divinylbenzene and the presence of sulfonic groups at the ring (Abderrahim et al. 2006; Lazar et al. 2014; Nekrasova et al. 2010). Additionally, the adsorption bands in the 1200–900 cm^{-1} region are attributed to the S=O stretching vibrations in sulfonate and P=O stretching vibrations in the phosphonate functional groups e.g. 1119, 993, 821 cm^{-1} . Especially in the range 1000–800 cm^{-1} the asymmetric and symmetric vibrations of the P(OH) groups are located. For the Diphonix resin and Diphonix-Ni(II) the bands are quite similar being located at 993 and 994 cm^{-1} . However, for Diphonix-La(III) it is located at 998 cm^{-1} (Alexandratos and Zhu 2018; Chiarizia et al. 1995).

3.2 Effect of HNO_3 concentration

On the beginning in adsorption tests the effect of HNO_3 concentration on La(III) and Ni(II) ions adsorption capacity on Diphonix resin was studied. The results are illustrated in Fig. 5. A decrease in adsorption capacity of the resin (q_e) relative to the metal ions with the increasing HNO_3 concentration was observed. Metal ions adsorption is much lower using 2 M HNO_3 than 0.2 M HNO_3 indicating a strong competition for the active sites of the studied ions than for

Fig. 5 Effect of HNO_3 concentration on the La(III) and Ni(II) ions adsorption on the Diphonix

Fig. 6 Effect of phase contact time on the adsorbed amount of La(III) and Ni(II) ions on the Diphonix

hydronium ions. Better adsorption results with La(III) ions were obtained which indicates that the resin has a greater selectivity towards rare earth ions than towards Ni(II) ions. Metal ions with a higher charge are more strongly bound by the resin functional groups.

3.3 Effect of phase contact time and kinetic studies

Figure 6 presents the dependence of phase contact time on the amount of adsorbed metal ions (q_t). It can be seen that in the case of La(III) ions equilibrium is established almost immediately which suggests a very strong affinity of ions for the resin. In the case of Ni(II) ions, the equilibrium is achieved a little later after about 10 min.

Based on the effect of phase contact time the reaction kinetics was determined. For this purpose, different kinetic models were used. The PFO and PSO models were applied to determination of kinetic parameters. However, they are not useful for describing a more detailed mechanism of the metal ions adsorption process. For this purpose the IPD and Boyd models were applied. A linear regression of the models was used to determine kinetic parameters. The obtained values for the PFO, PSO, IPD and Boyd models are listed in Table 2.

The experimental data was compared with that determined from the kinetic models. For this purpose the coefficient of determination, R^2 was used. The R^2 value equal to unity indicates the La(III) and Ni(II) ions adsorption process proceeds according to the second order kinetics. The value of the constant rate, k_2 , determined for the PSO model, decreases with the increase of the concentration of the metal ions solution, which means that the increase in

Table 3 Comparison of adsorbed amounts of La(III) and Ni(II) ions on Diphonix resin depending on the metal ion concentration

Concentration (mg/L)	Adsorbed amount (mg/g)	
	La(III)	Ni(II)
25	2.67 ± 0.13	1.54 ± 0.08
50	5.30 ± 0.27	2.91 ± 0.15
100	11.25 ± 0.56	5.03 ± 0.25
150	16.20 ± 0.81	7.47 ± 0.37
200	20.50 ± 1.02	9.91 ± 0.49
300	30.03 ± 1.50	15.13 ± 0.76
400	39.51 ± 1.98	19.01 ± 0.95
600	59.41 ± 2.97	26.69 ± 1.33

Table 2 Calculated parameters for the used kinetic models

Kinetic model	Parameter	La(III)			Ni(II)		
		50	100	200	50	100	200
Pseudo-first order	q_{exp} (mg/g)	5.30	11.25	20.50	2.91	5.03	9.91
	q_1 (mg/g)	0.01	0.02	0.03	0.21	0.30	0.14
	k_1 (1/min)	0.02	0.06	0.08	0.09	0.09	0.01
	R^2	0.452	0.855	0.993	0.849	0.979	0.404
Pseudo-second order	q_2 (mg/g)	5.30	11.25	20.50	2.91	5.04	9.91
	k_2 (g/mg min)	20.11	17.30	10.75	1.43	1.08	0.88
	R^2	1.000	1.000	1.000	1.000	1.000	1.000
Intraparticle diffusion	k_{i1} (mg/g min ^{1/2})	0.01	0.01	0.01	0.16	0.03	0.14
	C_1	5.29	11.22	20.45	2.38	4.75	9.51
	R^2	0.906	0.952	0.840	0.802	0.848	0.841
	k_{i2} (mg/g min ^{1/2})	—	—	—	0.01	0.02	0.04
	C_2	—	—	—	2.87	4.83	9.76
	R^2	—	—	—	0.792	0.809	0.875
Boyd	Bt	0.0070	0.0072	0.0079	0.0057	0.0059	0.0033
	R^2	0.849	0.979	0.805	0.842	0.855	0.994

Fig. 7 Effect of initial solution concentration on the adsorbed amount of metals at equilibrium onto the Diphonix resin

concentration causes a decrease in the sorption process rate. For the solid–liquid adsorption process, it is important to determine the rate controlling step. There can be the following steps or their combination: a film diffusion i.e. diffusion of the adsorbate ions through the boundary layer or a pore diffusion i.e. diffusion of the adsorbate ions through the pores (Ali et al. 2016). Based on the IPD results it can be concluded that Ni(II) ions adsorption onto the resin takes place in two stages and La(III) ions adsorption occurs in one stage by surface adsorption. Based on the nonlinear Boyd plot it can be inferred that chemical reaction or film diffusion can be responsible for controlling the reaction rate (Arthy and Saravanakumar 2013; Khalil et al. 2016; Viegas et al. 2014).

3.4 Effect of initial concentration and equilibrium studies

Adsorption effectiveness is also depends on the initial metal concentration. On the basis of the data presented in Table 3

Table 4 Calculated adsorption parameters for the isotherm models

Isotherm model	Parameter	La(III)	Ni(II)
Langmuir	q_m (mg/g)	98.73	45.75
	K_L (L/mg)	0.88	0.01
	R^2	0.989	0.945
Freundlich	K_F [(mg/g)(L/mg) $^{1/n}$]	41.57	2.23
	$1/n$	0.76	0.71
	R^2	0.989	0.996
Temkin	A_T (J/mol)	16.27	7.17
	K_T (L/g)	11.99	14.79
	R^2	0.932	0.905

and Fig. 7 it can be noticed that increasing the initial concentration influences the increase of adsorption capacity (q_e) of the resin in relation to the tested metal ions. Due to the stronger affinity of La(III) ions for the resin as compared to the Ni(II) ions, nearly 100% adsorption efficiency of La(III) ions was obtained over the whole concentration range. The Ni(II) adsorption efficiency is in the range of about 50 to about 70% for the lowest and highest concentrations, respectively.

Based on the equilibrium results presented in Table 4, it can be concluded that the adsorption process follows the Freundlich isotherm. This is confirmed in the high value of the coefficient of determination, R^2 . This points out that adsorption of Ni(II) and La(III) ions is not limited to the formation of monolayers. The relatively high R^2 values in the Temkin isotherm model indicate that the main mechanism of the adsorption process are the electrostatic interactions between the metal ions and the resin. The Langmuir constant, K_L indicates the metal ions affinity for the Diphonix resin. Based on the values obtained for the Ni(II) and La(III) ions it can be specified that La(III) ions have a higher affinity for the resin than Ni(II) ions. The Freundlich parameter, K_F points out to the binding force between the metal ions and the resin. For La(III) ions the K_F value is much higher than for Ni(II) ions. As follows La(III) ions are more strongly bound with the resin surface than Ni(II) ions. The $1/n$ parameter is responsible for surface heterogeneity or adsorption favourability. When $1/n$ is smaller than 1, the adsorption process is favourable and when it gets close to zero, the resin surface is more heterogeneous. The $1/n$ values for Ni(II) and La(III) ions about 0.70 indicate that the adsorption process is favourable and that the resin surface is more homogeneous than heterogeneous (Khalil et al. 2016).

3.5 Effect of temperature and thermodynamic studies

When assessing the effect of temperature, it was noticed that its increase does not significantly affect the adsorption capacity of the resin in relation to the studied metal ions. In the case of La(III) ions, the adsorption capacity of the resin over the entire temperature range is 5.30 mg/g. However, at 313 K the adsorption capacity of the resin in relation to

Table 5 Thermodynamic parameters of adsorption process

Parameter	La(III)	Ni(II)
ΔH° (kJ/mol)	− 6.98	− 11.71
ΔS° (J/mol K)	12.14	− 43.92
ΔG° (kJ/mol)	293 K	− 26.81
	303 K	− 27.46
	313 K	− 28.17

Ni(II) ions is 3.17 mg/g and is only slightly higher than the value obtained at 303 K and 293 K (3.14 and 2.91 mg/g, respectively).

Based on the influence of temperature on the metal ions adsorption the thermodynamics and adsorption process nature were also evaluated. The determined values of thermodynamic parameters are listed in Table 5. The negative enthalpy change value (ΔH°) indicates the exothermic nature of the adsorption process of La(III) and Ni(II) ions. In addition, the value of ΔH° below 40 kJ/mol indicates the physical nature of adsorption, i.e., intermolecular forces are between the metal ions and the resin surface. The positive ΔS° value suggests an increase in the adsorption of La(III) ions on the adsorbent surface, while a the negative value of the ΔS° indicates a decrease in the randomness during the adsorption of Ni(II) ions. Furthermore, in both cases the process is spontaneous and thermodynamically favourable as indicated by the negative values of free Gibbs enthalpy, ΔG° over the entire temperature range. The values of ΔG° , which are about -20 kJ/mol or higher can indicate the existence of both physical (electrostatic interactions) and chemical interactions (coordination bonds) during the adsorption of La(III) ions on the resin. Moreover, the values of ΔG° in the range -20 – 0 kJ/mol or below indicate the electrostatic nature of the Ni(II) ions adsorption process which shows that physisorption contributes significantly to the adsorption process (Bentiss et al. 2005; Issaadi et al. 2011; Konicki et al. 2017; Reguay et al. 2016).

3.6 Distribution coefficient comparison for REE and HM ions

The Diphonix affinity for metal ions was presented using the distribution coefficient, D , which is a mass-weighted partition coefficient between the liquid adsorbate phase and solid

Fig. 8 Distribution coefficients for rare earth elements and heavy metal ions

phase (Yantasee et al. 2009). Figure 8 presents the comparison of the distribution coefficients of rare earth elements i.e. La(III), Ce(III), Pr(III), Nd(III) and heavy metal ions Fe(III), Ni(II), Co(II), Cu(II) and Zn(II) as a main constituents of Ni-MH batteries determined in HNO_3 media. Taking into account the obtained distribution coefficients, it is evident that Diphonix resin exhibits strong affinity for REEs and Fe(III). In the case of remaining metal ions, lower values of the distribution coefficient were obtained. The highest D value was obtained for La(III) and the lowest for Ni(II). This may indicate that La(III) ions are most strongly sorbed by Diphonix, while Ni(II) ions are the weakest sorbed. Based on the D value, a series of metal ions affinity was determined for the Diphonix resin: La(III) > Pr(III) > Fe(III) > Nd(III) > Ce(III) > Cu(II) > Zn(II) > Co(II) > Ni(II).

3.7 Desorption studies

Desorption studies was also performed to evaluate the regeneration abilities of Diphonix resin. Nitric acid(V) in concentrations of 0.5, 1 and 2 M was used as a desorbing agent. The higher the concentration of desorbing agent, the higher the efficiency of the desorption process. Despite that the resin adsorbed more effectively La(III) ions than Ni(II) ones (their adsorption efficiency was about 100% and 60%, respectively) their desorption efficiency was changed. The maximum desorption efficiency of La(III) ions was about 50% while for Ni(II) ions was almost 90% using 2 M HNO_3 .

Diphonix with the biphosphonic and sulfonic functional groups can be considered as a polymer acting with the dual-mechanism with hydrophilic cation exchange and specific functional groups. Therefore it can be easily regenerated using both 6 M HCl and mixture of 2 M H_2SO_4 , 5 g/L Cu(I) (applied as a catalyst) and 0.44 M H_2SO_3 solutions at 358 K. For 6 M HCl the process can be as follows with 90% of Fe(III) elution efficiency (Alexandratos et al. 2000; Horwitz et al. 1997a, b):

For the latter conditions 64% of Fe(III) can be eluted.

Fe^{3+} exploited in Eq. 21 leads to the shift of Eq. 22 to the right and therefore the overall process can be described as follows:

Fig. 9 Adsorption and desorption effectiveness of mixture metal ions on Diphonix resin

Almost 100% elution of Fe(III) can be achieved with the eluant with the excess of 1 g/L Ti(III) and 300 g/L sulfuric acid at room temperature. Enhancement of the elution of iron with Ti(III) in the presence of H_2SO_4 can be attributed

to reduction of Fe(III) and competitive adsorption of Ti(IV) (Lee and Nicol 2007).

3.8 Metal ions mixture adsorption/desorption

Effectiveness of the adsorption and desorption processes of metal ions mixture is illustrated in Fig. 9. As can be noticed metal ions adsorption in the + III oxidation state is much more efficient (about 100%) than adsorption of metal ions in the + II oxidation state (60% effectiveness). In turn the desorption efficiency of metal ions in + III and + II oxidation states is about 40% and 90%, respectively. Desorption of Fe(III) ions is negligible (about 2%). It can be argued that Fe(III) ions are much more strongly adsorbed by the resin, not only on its surface but also in the resin pores. This information is confirmed by the manufacturer's data because the resin Diphonix is used for removal of Fe(III) ions. On the basis of the adsorption tests (the same initial metal ions concentrations), the series of selectivity of the Diphonix resin in relation to the studied metal ions was determined and presented as follows: $\text{La(III)} > \text{Fe(III)} > \text{Nd(III)} > \text{Ce(II I)} > \text{Cu(II)} > \text{Zn(II)} > \text{Co(II)} > \text{Ni(II)}$. This series is similar to the results obtained in the adsorption of metal ion mixtures with different initial concentrations.

Table 6 Adsorption capacity of REEs and HMs for various materials

Material	Optimal pH	Initial concentration (mg/L)	Element recovered	Adsorption capacity (mg/g)	Refs.
Magnetic nanoparticles CuFe_2O_4	7–8	3–20	La, Ce	42.02 (La) 40.16 (Ce)	Tu and Johnston (2018)
Calcium alginate	5	50–200	La, Cu	37.59 (La) 15.09 (Cu)	Kolodynska and Fila (2018)
Cyanex 272 impregnated Amberlite XAD-7 resin	2.5	751 (La) 113 (Nd)	La, Nd	11.1 (La) 1.69 (Nd)	İnan et al. (2018)
Synthetic aluminosilicate zeolite	–	–	Ni, Cu, Fe	140 (Ni) 160 (Cu) 560 (Fe)	Shilina et al. (2017)
Oxidized ordered mesoporous carbons	5	–	Ni, Co	126–145 (Ni) 135–148 (Co)	Marciniak et al. (2018)
Chelating resin 1,8-(3,6-dithiaoctyl)-4-polyvinylbenzenesulphonate (dpvbs)	5.5 6	150	Cu Fe, Co, Ni	46.07 (Cu) 44.68 (Fe) 30.94 (Co) 28.47 (Ni)	Khalil et al. (2018)
Diphonix resin	2	25–600	La, Ni	59.41 (La) 26.69 (Ni)	This study
		4.55 (Nd)	Nd, Ce, La, Fe, Co, Ni, Cu, Zn	0.65 (Nd)	
		6.45 (Ce)		1.00 (Ce)	
		35.6 (La)		6.65 (La)	
		58.75 (Fe)		3.48 (Fe)	
		16.30 (Co)		1.74 (Co)	
		134.40 (Ni)		14.86 (Ni)	
		4.7 (Cu)		0.15 (Cu)	
		4.5 (Zn)		0.41 (Zn)	

3.9 Comparison of adsorption capacity of REEs and HMs with various materials

The adsorption capacity of the Diphonix resin for the recovery of La(III), Ce(III), Nd(III), Fe(III), Ni(II), Co(II), Cu(II) and Zn(II) was compared with that of various materials reported in the literature and the obtained results are included in Table 6. They indicate that the Diphonix resin is characterized by good adsorption properties. Compared to various materials, Diphonix adsorbs efficiently both rare earth and heavy metals when pH is equal to 2, implying that this resin has a great potential in recovery of REEs and HMs even in strongly acidic solutions. Additionally, Diphonix has the highest adsorption capacity for La(III) ions (59.41 mg/g) in comparison to the other listed materials, such as magnetic nanoparticles CuFe_2O_4 (42.02 mg/g), calcium alginate (37.59 mg/g) and Cyanex 272 impregnated Amberlite XAD-7 resin (11.1 mg/g). Thus, this material is a promising adsorbent for recovery of rare earth and heavy metals from different solutions.

4 Conclusions

In this paper Diphonix resin was chosen for adsorption studies responsible for the multifunctional and twofold nature of metal ions binding with its surface due to the presence of three functional groups in its structure. The acid diphosphate groups present in the resin are specific for many metal ions and play an important role in the adsorption process. Due to the extraordinary coordination properties of the phosphonic group, it is possible to form high-stability metal complexes even under strongly acidic conditions. The Diphonix resin provides unique exchange kinetics because the hydrophilic groups of sulfonic acid allow quick access of metal ions to selective diphosphonic groups in the polymer matrix. The Diphonix was characterized by very good adsorption capacity in the nitric acid especially in 0.2 M HNO_3 media. In the case of single Ni(II) and La(III) ions the equilibrium of the adsorption process was achieved rapidly which indicates a high affinity of the adsorbed ions for the resin. Adsorption equilibrium state was obtained after about 10 min. Satisfactory results were achieved in the whole range of concentrations. Preliminary studies of metal ions mixture adsorption turned out to be equally effective. Particularly good results with rare earth ions were obtained. It was found that the Diphonix can be an effective material for recovery and separation of the rare earth elements and strategic metal ions contained in the solutions after Ni-MH cells leaching where the leaching agent is nitric acid. However, based on the study results, it was found that Fe(III) ions also adsorbed with high efficiency which

could make further research using real solutions difficult. The first step in this case could be to eliminate the interfering factors by their precipitation, sediment analysis and then a series of activities associated with the recovery and separation of other components. Studies using the real solutions after Ni-MH leaching and the Diphonix resin are planned in further.

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