

SELECTIVE SEPARATION OF METALS BY A NEW SORBENT, THE POLYETHYLENIMINE METHYLENEDIPHOSPHONIC ACID (PEIMPA)

Omar Abderrahim¹, Mohamed Amine Didi^{1*},
Bernard Moreau², Didier Villemin²

¹*Laboratory of Catalysis and Synthesis in Organic Chemistry, Chemistry
Department, Tlemcen University, BP 119, Tlemcen, Algeria*

²*ENSI Caen, University of Caen, LCMT, UMR CNRS 6507, F -14050,
Caen, France*

*Corresponding author: madidi13@yahoo.fr, Tel: (213)43213198; Fax: (213)43213198

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Abstract: A new sorbent, the polyethylenimine methylenediphosphonic acid (PEIMPA), was synthesized from commercially available polyethylenimine. After characterization by (¹H, ¹³C, ³¹P) NMR, elementary analysis, UV/VIS and FTIR, the new ion exchange polymer PEIMPA has been investigated in liquid – solid extraction of a mixture of Cd(II), Co(II), Cu(II), Fe(III), Ni(II), Pb(II) and Zn(II) cations from a mineral residue of zinc ore dissolved in nitric acid.

The selectivity of this polymer was studied as a function of *pH*. PEIMPA can sorb much higher amounts of Fe ion than Cd, Co, Cu, Ni, Pb and Zn ions. The recovery of Fe(III) is almost quantitative. Because of this remarkable affinity, the PEIMPA resin has potential for application in several fields. Further studies of the polymer are in progress.

Keywords: *phosphonic sorbent, heavy metal ions, liquid-solid extraction, selectivity, polyethylenimine methylenediphosphonic acid*

INTRODUCTION

The treatment of industrial waste solid and effluent streams is both of economic and ecological importance. For this reason, the ability to remove selectively both valuable and toxic metals from effluent streams is increasingly important in the modern world especially as regulations regarding discharge of metals are becoming more stringent. During the last decade, a considerable effort has been oriented toward the development of new ion exchange polymers capable of selectively recovering metals from aqueous effluent [1-5]. We hence became interested in the selective extraction of heavy metals from a mineral residue of zinc ore containing Cd, Co, Cu, Fe, Ni, Pb and Zn ions dissolved in nitric acid.

The commercially available ion-exchange polymers are largely based on sulphonic and carboxylic acid groups for cations and on amines or ammoniums for anion exchange [6].

Recently, some new synthesized resins have proved their great effectiveness in metals extraction, such as the diphosphonic acid resin [7], diphosphonate resin [8], Diphonix [9] and the monophosphonic / sulfonic resin [10].

Polyamines have been known for many years and are used in many domains, including extraction processes and chelation of cations [11-16]. Among all polyamines, polyethyleneimine is particularly interesting, because of its commercial availability and having a large number of chelating amine groups per mass of polymer. Modification of polyethyleneimine is easy and allows an increase of the chelating power and subsequent chelation selectivity modification. Therefore, carboxylic group or thiol have been introduced [17-20].

In our work we have introduced methylenephosphonic groups. This type of polymer to the best of our knowledge was poorly described. We have used a modified Mannich reaction first described by Modriezer and Irani [21]. The reaction was performed in distilled water under microwave irradiation according to a process developed in our laboratories [22]. This reaction conducts to a highly functionalized polymer (polyethylenimine methylenephosphonic acid or PEIMPA) possessing phosphonic and amine moieties as chelating groups. The selectivity of this new ion-exchange material was studied in the selective recovery, at different pH, of a solid waste dissolved in nitric acid (65%) containing Zn(II), Fe(III), Pb(II), Cu(II), Cd(II), Co(II), Ni(II) resulting from electrolysis of zinc starting from its ore.

EXPERIMENTAL

Reagents

Phosphorous acid " H_3PO_3 " (98%) was supplied by Across Organics. Polyethylenimine (Lupasol P) is commercially available from BASF with ratio of prim.: sec.: tert. amines (1: 1.07: 0.77) and a molecular weight (M_w) of 750,000. Hydrochloric acid 32%, nitric acid 65%, sodium hydroxide (NaOH, pellets GR for analysis) and formaldehyde 35% were purchased from Merck.

Instrumentation

Elementary analysis was carried on a Thermoquest C, H, N and S analyzer (Table 1). P composition was determined by the Pujo -Pay M. method (Table 1) [23].

^{13}C $\{-^1\text{H}\}$, ^{31}P $\{-^1\text{H}\}$ and ^1H NMR spectra were measured on a Bruker AC 250 working at 250 MHz in D_2O / Na_2CO_3 solution. Infrared spectra were recorded on a Perkin-Elmer 684 IR spectrophotometer in KBr with absorptions in cm^{-1} . UV/VIS spectrum was obtained with a Perkin-Elmer Lambda 800 spectrophotometer. pH measurements for all solutions were taken, after dilution in distilled water (1 : 26) (mL : mL), on a potentiometer Consort C 831 (Table 3). Concentration of each metal in the aqueous phase was determined with a Perkin-Elmer atomic absorption spectrophotometer assisted by micro-computer (Model AAnalyst 300) at an appropriate wavelength.

Synthesis of Polyethyleneimine methylenephosphonic acid (PEIMPA)

A new sorbent, the polyethylenimine methylenephosphonic acid (PEIMPA), was synthesized from commercially available polyethylenimine according to the Moedrizer – Irani reaction [21]. The synthesis was performed in distilled water under microwave irradiation in a microwave mono-mode Prolabo Synthwave 402 cavity according to a methodology developed in our laboratories [22]. We have used different polyethylenimine polymers (Lupasol P, W, SK), but the work described herein refers only to Lupasol P.

In a quartz reactor, a mixture of polyethylenimine (Lupasol P, 40 mmoles, 1.72 g), phosphorous acid (40 mmoles, 3.34 g) and hydrochloric acid - water (1:1) solution (6 mL), was vigorously stirred then irradiated (150 W) in a glass cylinder reactor for one minute. A formaldehyde aqueous solution (80 mmoles) was added and irradiated for 8 minutes. The excess of formaldehyde was eliminated in vacuum and the residual solid was washed with acetone. The polymer was dialyzed in water with a nitro-cellulose membrane 0.45 μm (Bio-Rad Laboratories) to keep only the longest chains, yielding there fore 85% of PEIMPA. Analysis Found N: 13.252, P: 18.957 (Table 1) reveals the unit ratio of Phosphore / Azote = 0.64.

This new phosphonated ion-exchanger obtained is stable in a *pH* range of 0 – 14, inert against oxidizing reagents such as HNO_3 up to a concentration of 3 M.

Preparation of cations solutions

The solid mineral residual waste of zinc ore having ion metals composition (6.93 % Cd, 0.41% Co, 59.3% Cu, 0.73% Fe, 0.19% Ni, 1.5% Pb, 20.9% Zn, and about fourteen other elements whose contents are lower than 0.1%) (8 g, $d = 125 \mu\text{m}$) was dissolved in 12 mL of concentrated nitric acid (65%), and then 150 mL of H_2O were added, then the mixture was boiled for 5 minutes. After cooling down to room temperature and filtration, a green solution was obtained after dilution up to 1L and a *pH* = 1.07. After drying, the residual represents 15% of the initial weight. In seven beakers, from the feed solution (*pH* = 1.07), were transferred 10 mL in each, then *pH* were adjusted to a given value by addition of NaOH solution, filtered and subsequently concentrated on a hotplate up to a volume lower than 25 mL. Precise dilution to 25 mL was finally

accomplished with distilled water. The adjustment of pH of the solution by addition of NaOH lead to the change of the supernatant composition and was accompanied by precipitations and changes in colors. At $pH = 1.13$ there is formation of a green and fine particle precipitate. At $pH = 1.48$ a new blue precipitate appears. This phenomenon persists until a $pH = 6$ and the solution becomes more bluish. To $pH \geq 6$, NaOH addition gives no precipitation and no change in color. Quantitative data on the composition of solution phase is given in Table 2 (composition of filtrate at initial pH).

Sorption equilibrium

The new ion exchange resin PEIMPA has been investigated in liquid – solid extraction of a mixture of Cd, Co, Cu, Fe, Ni, Pb and Zn ions from the mineral residue of zinc ore dissolved in nitric acid.

In the sorption equilibrium experiments, the functionalized polymer (0.1 g) and aqueous mixtures of Cd(II), Co(II), Cu(II), Fe(III), Ni(II), Pb(II) and Zn(II) solution (10 mL), at different initial pH , were placed in 100 mL glass flask and shaken at 150 rpm for 12 h. Preliminary experiments had shown that the studied sorption was complete after 4 h. The aqueous phase was separated from the functionalized polymer by filtration and its equilibrium pH values measured. The concentrations of metal ions in the aqueous phase were determined, before and after treatment with PEIMPA, directly or after dilution if necessary with atomic absorption spectrometry (Perkin-Elmer, AA 300) (Table 2).

Resin capacity

The capacity of the PEIMPA resin for the mixture of Cd(II), Co(II), Cu(II), Fe(III), Ni(II), Pb(II) and Zn(II) cations was measured in batch experiment in which a weighed amount of resin (100 mg) was stirred for four hours with 10 mL of a nitric solution of the dissolved solid waste, at initial $pH = 5.0$, having the following composition in mg/L: [Cd(II)] = 241.92, [Co(II)] = 14.64, [Cu(II)] = 1936, [Ni(II)] = 5.04, [Pb(II)] = 29.5 and [Zn(II)] = 1080 (see figure 1).

After filtration, a sample of the supernatant was analyzed by atomic absorption spectrometry. The amount of metals sorbed by the resin was calculated by mass balance.

RESULTS AND DISCUSSION

Analysis and characterisation of PEIMPA

The structure and purity of the final complexing agent were identified and characterized by elemental microanalysis (Table 1) and 1H and ^{13}C NMR spectroscopy. The spectra showed the expected signals due to the polyethylenimine skeleton and methylene phosphonic units as matched to the proposed structure (scheme 1).

1H NMR δ (ppm): 4.92 (N-CH₂); 2.33 (CH₂-P); 1.6 NH; ^{13}C NMR δ (ppm): 82.16 (N-CH₂), 52.1 (CH₂-P); ^{31}P NMR δ (ppm): 3.91.

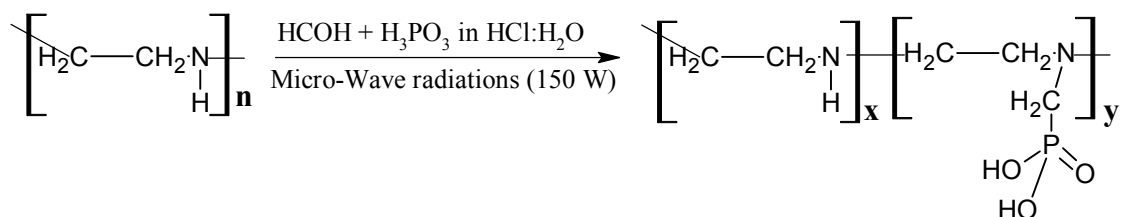
The presence of phosphonic acid was confirmed by FTIR measurement: the polymer displays characteristic bonds for P-O-C at 1050 cm⁻¹, P-OH at 2372 and 2338 cm⁻¹ and

P=O at 1172 cm^{-1} . The UV spectra shows two absorbencies at 356 and 286 nm characteristic of P=O and N–H groups respectively.

Elemental microanalysis found (table 1) suggest the structure for a fragment of the PEIMPA polymer, corresponding after calculation to $x = 5$ and $y = 9$ (Scheme 1).

Table 1. Elemental microanalysis of PEIMPA

Micro-Analysis	Found	% C	% H	% N	% O	% P
		30.8121	7.6250	13.2519	29.3535	18.9574
	Calculated ($x=5, y=9$)	30.6631	6.6989	13.5359	29.8342	19.2679



Scheme 1. Synthesis of PEIMPA from Lupasol P

Treatment of the distribution data

Quantitative data on the composition of solution phase is given in Table 2 (composition of filtrate at initial and equilibrium pH).

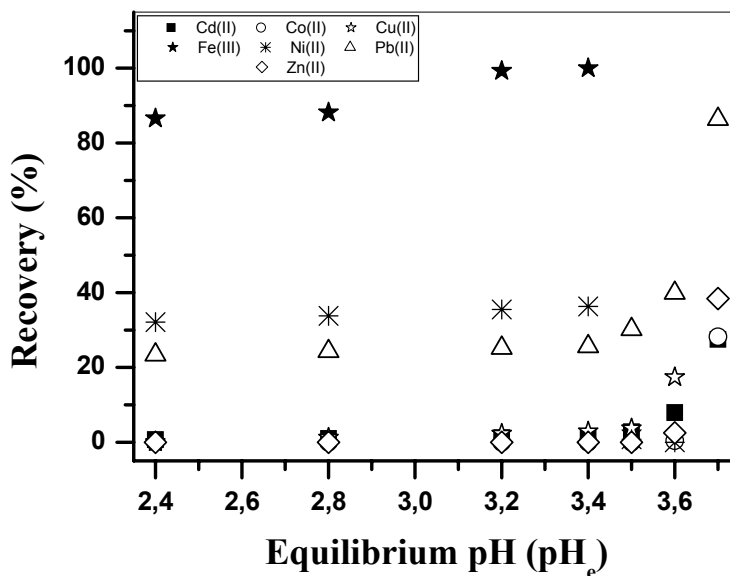


Figure 1. The recovery (%) of Cd(II), Co(II), Cu(II), Fe(III), Ni(II), Pb(II) and Zn(II) as function of equilibrium pH

The recovery (%) and the amount of sorbed (mg/g) Cd, Co, Cu, Fe, Ni, Pb and Zn ions as a function of equilibrium pH are shown in figures 1 and 2 [24].

Table 2. *Quantitative data on the liquid – solid extraction of the mixture of cations by polyethylenimine methylenephosphonic acid*

Initial <i>pH</i>	Composition of filtrate before extraction (mg/L)	Equilibrium <i>pH</i>	Composition of filtrate after extraction (mg/L)
2.4	[Cd] = 241.9 [Co] = 14.6 [Cu] = 2070.4 [Fe] = 25.6 [Ni] = 6.54 [Pb] = 52.2 [Zn] = 1080.0	2.4	[Cd] = 240.2 [Co] = 14.6 [Cu] = 2070.0 [Fe] = 3.4 [Ni] = 4.4 [Pb] = 40.0 [Zn] = 1080.0
3.0	[Cd] = 241.9 [Co] = 14.6 [Cu] = 2076.6 [Fe] = 20.8 [Ni] = 6.4 [Pb] = 49.1 [Zn] = 1080.0	2.8	[Cd] = 239.5 [Co] = 14.6 [Cu] = 2042.8 [Fe] = 2.5 [Ni] = 4.7 [Pb] = 37.2 [Zn] = 1080.0
3.4	[Cd] = 241.9 [Co] = 14.6 [Cu] = 2063.2 [Fe] = 18.2 [Ni] = 6.3 [Pb] = 45.3 [Zn] = 1080.0	3.2	[Cd] = 239.0 [Co] = 14.6 [Cu] = 2016.0 [Fe] = 0.1 [Ni] = 4.1 [Pb] = 33.9 [Zn] = 1080.0
3.7	[Cd] = 241.9 [Co] = 14.6 [Cu] = 2058.0 [Fe] = 2.6 [Ni] = 6.3 [Pb] = 39.8 [Zn] = 1080.0	3.4	[Cd] = 238.6 [Co] = 14.6 [Cu] = 1999.2 [Fe] = 0.0 [Ni] = 4.0 [Pb] = 29.6 [Zn] = 1080.0
5.0	[Cd] = 241.9 [Co] = 14.6 [Cu] = 1936.0 [Ni] = 5.0 [Pb] = 29.5 [Zn] = 1080.0	3.5	[Cd] = 235.2 [Co] = 14.6 [Cu] = 1864.8 [Ni] = 5.0 [Pb] = 20.6 [Zn] = 1080.0
5.8	[Cd] = 191.2 [Co] = 10.0 [Cu] = 6.7 [Ni] = 3.4 [Pb] = 14.2 [Zn] = 353.0	3.6	[Cd] = 176.4 [Co] = 10.0 [Cu] = 5.52 [Ni] = 3.4 [Pb] = 8.5 [Zn] = 344.0
5.9	[Cd] = 78.6 [Co] = 2.0 [Pb] = 5.5 [Zn] = 26.8	3.7	[Cd] = 56.9 [Co] = 1.45 [Pb] = 0.7 [Zn] = 16.5

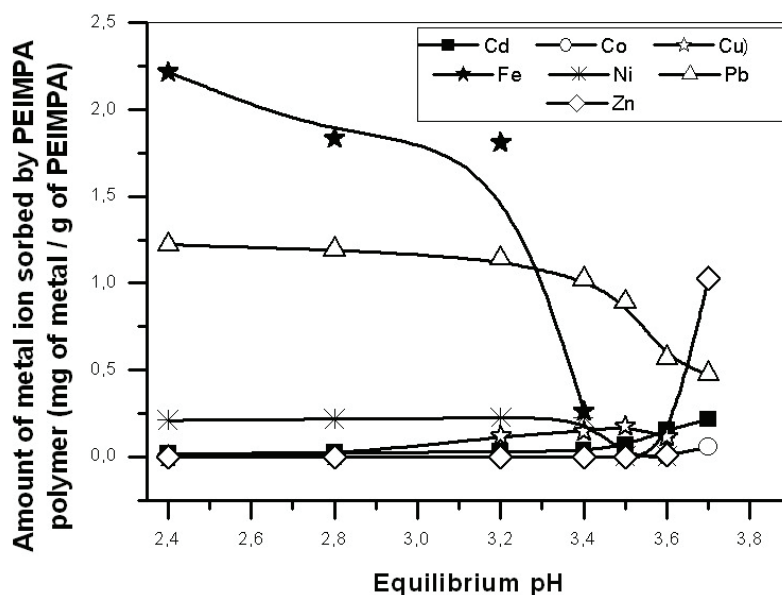
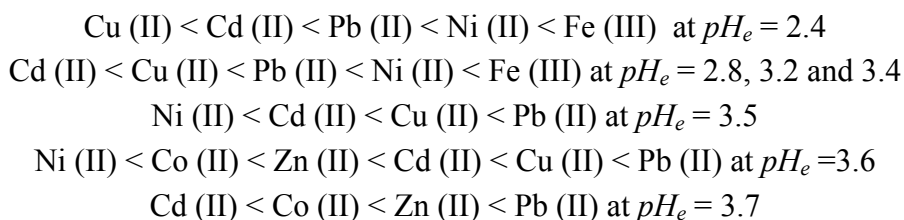


Figure 2. The amount of metals sorbed by PEIMPA versus equilibrium pH

The pH plot (figure 1) shows the polymer's ability to distinguish the different analytes, quantitatively extract Fe(III) from equilibrium $pH_e = 2.4$ to 3.4 and partially extract Pb(II) (86%) and Ni(II) (36%). The divalent cation Pb(II) is also discriminate by the polymer (figure 1). The highest selectivity was toward Fe(III) followed by Pb(II), while Co(II) and Zn(II) were not extracted at $pH_e = 2.4$ to 3.5 [9]. Ni(II) was better recovered at low pH_e . This result shows that extraction is independent from cations oxidation degree. Figure 1 and table 2 shows that the elements were extracted in an increasing order according to equilibrium pH (pH_e) as follows:



Resin capacity

Figure 2 and table 2 show that the amount of the most sorbed metal ions were Fe(III) and Pb(II), but their sorption decreases with increasing equilibrium pH . The highest metals sorption capacity, from the multi-metals nitrate solution, has been evaluated for all analytes and was found to be 8.70 mg/g at equilibrium $pH = 3.5$.

The PEIMPA ion-exchanger has a higher retention capacity (8.70 mg/g) compared to XAD-2 functionalized by 2,3-dihydroxypyridine (Cd: 6,8 mg/g) [25], divinylbenzene-styrene functionalized by 2-(p-vinylbenzylamino)-alkanoic acid (Cu: 0,26 mg/g, Zn: 0,22 mg/g) [26] and a macroporus resin obtained by radical polymerization of copper(II) methacrylate complexes with water, pyridine, 4-vinyl pyridine, and ethylene glycoldimethacrylate (Cu: 3,28 mg/g) [27].

Comparison of FTIR spectra of the clear brown solid resin and the green solid complex “PEIMPA-Metals” recovered after extraction showed a shift of P=O bond from 1172 to 1108 cm⁻¹. The observed shift in P=O frequency mode indicates the formation of metal complexes in the solid phase (P=O–Metal) [28, 29]. The bands in the 560 – 500 cm⁻¹ region are attributed to δ(POO) deformation [30].

To explain and describe quantitatively the distribution of the ions between the ion exchanger and the solution, the laws of adsorption can be used. The applicable mathematical treatments generally lead to modified Langmuir or Freundlich isotherms [31]. The measure of the pH of the aqueous solution before and after extraction, pH_i and pH_e respectively (Table 3), shows that extraction by cationic exchange is also important with a decrease of the initial pH . The two modes of extraction, adsorption and cation exchange, are both present.

Table 3. *pH variations of aqueous solution before and after extraction*

N° of filtrate	1	2	3	4	5	6	7
pH_i	2.4	3.0	3.4	3.7	5.0	5.8	5.9
pH_e	2.4	2.8	3.2	3.4	3.5	3.6	3.7

In the case of the organic resins, in addition to the ion exchange and interstitial and pore diffusion, it one can also have adsorption in the form of monolayers.

The Langmuir model is the most frequently employed to describe experimental data of adsorption isotherms. The following relation represents the model:

$$C_{res} = \frac{K \cdot C_{sol} \cdot C_E}{1 + K \cdot C_{sol}} \quad (1)$$

where C_E is the maximum adsorption capacity of the polymer (mg·kg⁻¹), C_{sol} is the equilibrium concentration of metal in solution (mg·L⁻¹), C_{res} is the amount adsorbed at equilibrium (mg·kg⁻¹) and K is constant. The parameters in the Langmuir isotherm are usually estimated by linear regression. The Langmuir isotherm can be linearized according to reciprocal Langmuir equation ($1/K_d = C_{sol}/C_{res}$ vs $X_{sol} = C_{sol}/C_0$), where K_d is the partition coefficient and C_0 is the initial concentration of metal in solution (mg·L⁻¹) [32].

For small ionic fractions (X_{sol}) of Fe (III) ion in solution (Figure 3), we observe a linearity corresponding to the variation expected in the standard case of a Langmuir isotherm. This suggests that the extraction, under these conditions, is governed by adsorption in the form of monolayers, in addition to the ion exchange.

For Cd(II), Co(II), Cu(II), Ni(II), Pb(II) and Zn(II) the initial conditions of extraction shows $X_{sol} \approx 1$. Under these conditions, the Langmuir isotherm is not applicable.

Simulation by the factorial design

With the aim of parametrizing the sorption of the various cations by our polymer, the effects of the molar ratio X_{sol} of the considered cation and of the pH aqueous solution resulting from extraction and filtration of the solid phase, were estimated by expressing the $1/K_d$ (K_d is the calculated partition coefficient) as follows:

$$1/K_d = A_0 + A_1X_1 + A_2X_2 + A_{12}X_1X_2 \quad (2)$$

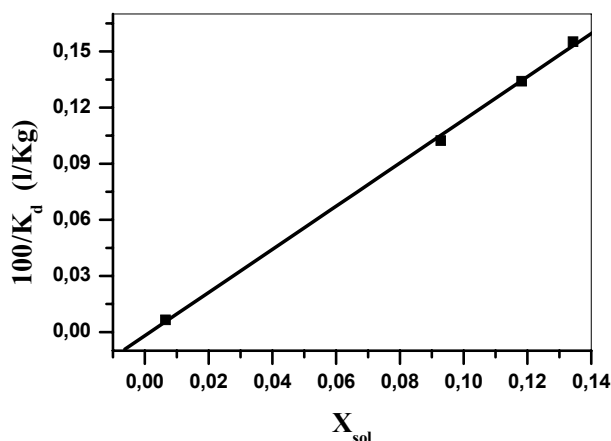


Figure 3. Adsorption isotherm for Fe (III). Variation of $1/K_d$ as function of X_{sol}

This expression is determined by the linear regression method [33].

$$X_1 = \frac{pH_e - \frac{pH_{e(max)} + pH_{e(min)}}{2}}{\frac{pH_{e(max)} - pH_{e(min)}}{2}} \quad (3)$$

$$X_2 = \frac{X_{sol} - \frac{X_{sol(max)} + X_{sol(min)}}{2}}{\frac{X_{sol(max)} - X_{sol(min)}}{2}} \quad (4)$$

Expression of $1/K_d$ according to coded variables (X_1 , X_2) and real variables (pH_e , X_{sol}) are given in table 4. The expression of $1/K_d$ for Fe(III) has not been given because $1/K_d \sim 0$.

From these equations we remark that the influence of pH and X_{sol} and their combined effects on K_d varies from an element to another. The variations of pH_e and X_{sol} have an additive effect for these cations. The combined effect of pH_e and X_{sol} are positive for Cd (II), Zn (II) and Ni (II), but negative for Cu (II), Co (II) and Pb (II).

CONCLUSIONS

A new type of ion exchange polymer based on the commercially available polyethylenimine polymer (Lupasol P) was developed in this study.

This new phosphonated ion-exchanger obtained is stable in a 0 – 14 pH range, inert against oxidizing reagents such as HNO_3 up to a concentration of 3 M. The sorption selectivity of this polymer was studied in aqueous nitric solution containing Cd(II), Co(II), Cu(II), Fe(III), Ni(II), Pb(II) and Zn(II) with pH control in the minimal configuration of one stage of extraction. This selectivity was pH dependant.

At $pH_i \leq 3.7$, a study of the selectivity shows that the PEIMPA presents a high affinity toward Fe (III) (recovery yield = 100%) and partially extract Pb(II) (86%) and Ni(II)

(36%). The divalent cation Pb(II) is also discriminate by the polymer. Under these conditions, we observed that the extraction of Fe(III) was governed by an adsorption in a monolayer form, in addition to ion exchange. Co(II) and Zn(II) were not extracted at $pH_i \leq 5.0$ and Ni(II) was better recovered at low pH_i . Other applications of this resin are under development.

Table 4. Expression of $1/K_d$ according to coded and real variables

Cations	Expressions of $1/K_d$
Cd(II)	$* \quad 1/K_d = -0.1855 + 0.5915X_1 + 1.2486X_2 - 0.9584 X_1X_2$ $** \quad 1/K_d = -160.4491 + 42.437pH_e + 164.470X_{sol} - 43.342X_{sol}.pH_e$
Co(II)	$* \quad 1/K_d = 0.4434 - 0.3049X_1 - 1.1048X_2 + 0.1371X_1X_2$ $** \quad 1/K_d = 24.7383 - 7.16pH_e - 24.0124X_{sol} + 7.0167X_{sol}.pH_e$
Cu(II)	$* \quad 1/K_d = 0.1797 - 0.0695X_1 + 0.1212X_2 + 0.304 X_1X_2$ $** \quad 1/K_d = 5.1822 - 1.5435pH_e - 3.632X_{sol} + 1.1865X_{sol}.pH_e$
Ni(II)	$* \quad 1/K_d = 6.2224 - 4.9057X_1 + 7.3928X_2 - 7.1072X_1X_2$ $** \quad 1/K_d = -168.1540 + 47.3715pH_e + 244.4811X_{sol} - 68.4187X_{sol}.pH_e$
Pb(II)	$* \quad 1/K_d = 0.0847 - 0.0803X_1 - 0.0673X_2 + 0.0650X_1X_2$ $** \quad 1/K_d = 1.7725 - 0.4945pH_e - 2.1895X_{sol} + 0.6114X_{sol}.pH_e$
Zn(II)	$* \quad 1/K_d = -11.2344 + 11.3627X_1 + 12.9718X_2 - 12.8595X_1X_2$ $** \quad 1/K_d = -626.3538 + 169.1887pH_e + 648.9227X_{sol} - 175.2214X_{sol}.pH_e$

* - Coded variables, ** - Real variables

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REFERENCES

1. Dietz, M.L., Horwitz, E.P., Sajdak, L.R., Chiarizia R.: An improved extraction chromatographic resin for the separation of uranium from acidic nitrate media, *Talanta*, **2001**, 54, 1173–1184.
2. Snukiškis, J., Kaušpėdienė, D.: Kinetics of the combined sorption of copper(II) and nonionic surfactant by carboxylic acrylcationic exchanger, *Separation and Purification Technology*, **2001**, 24, 59–65.
3. Kavakli, P.A., Seko, N., Tamada, M., Güven, O.: A highly efficient chelating polymer for the adsorption of uranyl and vanadyl ions at low concentrations, *Adsorption*, **2004**, 10, 309–315.
4. Lemos, V.A., Baliza, P.X., Santos, J.S. et col.: A new functionalized resin and its application in preconcentration system with multivariate optimization for nickel determination in food samples, *Talanta*, **2005**, 66, 174–180.

5. Zhang, A., Wei, Y., Kumagai, M., Koma, Y.: A new partitioning process for high-level liquid waste by extraction chromatography using silica-substrate chelating agent impregnated adsorbents, *Journal of Alloys and Compounds*, **2005**, **390**, 275–281.
6. Cox, M.: Extraction techniques in the treatment of metalliferous effluents, *12th Romanian international conference on chemistry and chemical engineering RICCE-12*, 13-15 September **2001**, Bucharest – Romania.
7. Horwitz, E.P., Chiarizia, R., Dietz, M.L.: DIPEX: a new extraction chromatographic material for the separation and preconcentration of actinides from aqueous solution, *Reactive & Functional Polymers*, **1997**, **33**(1), 25–36.
8. Alexandratos, S.D., Trochimczuk, A.W., Crick, D.W., Horwitz, E.P., Gatrone, R.C., Chiarizia, R.: Synthesis and ion-complexing properties of a novel polymer-supported reagent with diphosphonate ligands, *Macromolecules*, **1996**, **29**(3), 1021–1026.
9. Chiarizia, R., Horwitz, E.P., Alexandratos, S.D., Gula, M.J.: Diphonix Resin: A review of its properties and applications, *Separation Science & Technology*, **1997**, **32**, 1–35.
10. Alexandratos, S.D., Shelley, C.A., Horwitz, E.P., Chiarizia, R.: A mechanism for enhancing ionic accessibility into selective ion exchange resins, *Solvent Extraction and Ion Exchange*, **1998**, **16**(4), 951–966.
11. Zeevaart, J.R., Louw, W.K.A., Kolar, Z.I., Jansen van Rensburg, F.E., Dormehl, I.C.: Biodistribution and pharmacokinetics of variously molecular sized ^{117m}Sn(II)- polyethyleneiminomethyl phosphonate complexes in the normal primate model as potential selective therapeutic bone agents, *Arzneimittel-forschung-drug research*, **2004**, **54**(6), 340–347.
12. Pina, C.M., Putnis, C.V., Becker, U., Biswas, S., Carroll, E.C., Bosbach, D., Putnis, A.: An atomic force microscopy and molecular simulations study of the inhibition of barite growth by phosphonates, *Surface Science*, **2004**, **553**(1–3), 61–74.
13. Jarvis, N.V., Zeevaart, J.R., Wagener, J.M., Louw, W.K.A., Dormehl, I.C., Milner, R.J., Killian, E.: Metal-ion speciation in blood plasma incorporating the water-soluble polymer, polyethyleneimine functionalised with methylenephosphonate groups, in therapeutic radiopharmaceuticals, *Radiochimica Acta*, **2002**, **12**, 237–246.
14. Dong, S., Zhang, H., Zhang, J.: Preparation of chelating resins with good adsorption properties for noble metals, *U.S. Patent 9821265*, CAN 129:16769 (**1998**).
15. Zhang, C., Wu, H., Wen, W.G.: Syntheses and adsorption properties of chelating resins with amino and mercapto groups, *Wuhan Gongye Daxue Xuebao*, **1993**, **15**(4), 22–26.
16. Ergozhin, E.E., Mukhitdinova, B.A., Utkelov, B.A.: Method of obtaining chelating ion exchangers, *U.S.S.R. Patent 754839*, CAN 119:50174 (**1992**).
17. Rivas, B.L., Maturana, H.A., Angne, U., Catalan, R.E., Perich, I.M.: Preparation and properties of resins with adsorption properties for heavy metal ions, *European Polymer Journal*, **1988**, **24**(10), 967–970.

18. Barnes, J.H., Bates, C., Hartley, F.R.: The removal of heavy metals from aqueous solution using a recoverable poly[N-(dithiocarboxylate)iminioethene] column, *Hydrometallurgy*, **1983**, 10(2), 205–217.
19. Geckeler, K., Lange, G., Eberhardt, H., Bayer, E.: Preparation and application of water-soluble polymer-metal complexes, *Pure and Applied Chemistry*, **1980**, 52(7), 1883–905.
20. Sauer, N.N., Ehler, D.S., Duran, B.L.: Lead extraction from contaminated soil using water-soluble polymers, *Journal of Environmental Engineering*, **2004**, 130(5), 585–588.
21. Moedritzer, K., Irani, R.: The direct synthesis of α -aminomethyl phosphonic acids. Mannich-type reactions with orthophosphorous acid, *Journal of Organic Chemistry*, **1966**, 31, 1603 –1607.
22. Elias, A., Didi, M.A., Villemin, D., Semaoune, T., Ouattas, S.: Synthesis of mono- and dialkylphosphates by the reactions of hydroxycompounds with the phosphorus pentaoxide under microwave irradiation, *Phosphorus, Sulfur & Silicon*, **2004**, 179, 1–9.
23. Pujo-Pay, M., Raimbault, P.: Improvement of the wet-oxidation procedure for simultaneous determination of particulate organic nitrogen and phosphorus collected on filters, *Mar. Ecol. Prog. Ser.*, **1994**, 105, 203–207.
24. Hai, T.H., Mikiya T.: Removal of Bi, Cd, Co, Cu, Fe, Ni, Pb and Zn from an aqueous nitrate medium with bis(2-ethylhexyl) phosphoric acid impregnated kapok fiber, *Ind. Eng. Chem. Res.*, **2003**, 42, 4050–4054.
25. Venkatesh, G., Kumar A.J., Singh, A.K.: 2,3-Dihydroxypyridine loaded Amberlite XAD-2 (AXAD-2-DHP): Preparation, sorption–desorption equilibria with metal ions, and applications in quantitative metal ion enrichment from water, milk and vitamin samples, *Microchimica Acta*, **2005**, 149(3–4), 213–221.
26. Koide, Y., Tsujimoto, K., Shoshendji, H., Maeda, M., Takagi, M.: Adsorption of metal ions to surface-template resins prepared with amphiphilic styrene monomers bearing amino carboxylic acid, *Bull. Chem. Soc. Jpn.*, **1998**, 71, 789–796.
27. Kuchen, W., Schram, J.: Metal-ion-selective exchange resins by matrix imprint with methacrylates, *Angew. Chem. Int. Ed. Engl.*, **1988**, 27(12), 1695–1697.
28. Cortina, J.L., Miralles, N., Sastre, A.M., Aguilar, M.: Solid-liquid extraction studies of divalent metals with impregnated resins containing mixtures of organophosphorus extractants, *Reactive & Functional Polymers*, **1997**, 32, 221–229.
29. Ferraro, J.R., Herlinger, A.W., Chiarizia, R.: Correlation of the asymmetric and symmetric POO- frequencies with the ionic potential of the metal ion in compounds of organophosphorus acid extractants: a short review, *Solvent Extraction and Ion Exchange*, **1998**, 16(3), 775–794.
30. Thomas, L.C.: *Interpretation of the infrared spectra of organophosphorus compounds*, Heyden, London, **1974**.
31. Schöneberger, A., Bart, H.J.: Reactive sorption of heavy metals by extractant-impregnated-polymers. Sorption equilibria and kinetics, *13th International congress of chemical and process engineering CHISA '98*, 23-28 august **1998**, Prague, Czech Republic.

32. Calace N., Di Muro A., Nardi E., Petronio, B.M., Pietroletti, M.: Adsorption isotherms for describing heavy – metal retention in paper mill sludges, *Ind. Eng. Chem. Res.*, **2002**, **41**, 5491–5497.
33. Eriksson L., Johansson E., Kettaneh-Word N., Wikström C., Wold, S.: *Design of experiments-principles and applications*, **2000**, Umetrics AB-Sweden.