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Extraction of cation mixture with Di(2-ethylhexyl) phosphoric acid immobilized on amberlite resins

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ABSTRACT

Extraction of Zn(II) from acetate media as well as from a cation mixture of Zn(II), Cd(II), Co(II), Cu(II), Fe(III), Ni(II) and Pb(II) derived from a solid waste dissolved in nitric acid (65%), by resin-supported di(2-ethylhexyl) phosphoric acid (D2EHPA) was investigated. The treatment by selective extraction of this recovered solid waste is of great economic and ecological importance. The resins XAD-1180, XAD-7 and XAD-4 were impregnated by D2EHPA. The effects of pH, the concentrations, the nature and amount of impregnated resins were also examined. The extraction yield of each metal ion was determined as a function of pH. The affinity series for cations is Fe(III) >Cu(II)>Ni(II)>Zn(II)>Pb(II)>Cd(II)>Co(II). The interaction between D2EHPA and the polymeric support was examined through ^{13}C-Magic Angle Spinning Nuclear Magnetic Resonance (^{13}C-MAS-NMR), ^{31}P-MAS-NMR and Fourier Transform Infra-Red(FTIR) analyses. It was found that the adsorption of D2EHPA on the resin surface involves an alkyl-aryl interaction. The results obtained herein allow concluding that the process occurs mainly via an ion-exchange pathway, but increasing pH enhances an additional chelating process. FTIR measurements gave clear evidence of interaction between D2EHPA and the different resins, and indicate formation of metal complex in the resin phase.

KEYWORDS

MAS-NMR;
FTIR;
D2EHPA;
Resins;
Impregnation;
Extraction.

INTRODUCTION

Heterogeneous solvent extraction has recently experienced a revival through few up-to-date studies, regarding the versatility and the convenience of this technique[1,2,3,4,19].

In this regard, a growing interest has been focused towards the so-called Solvent Extractant Impregnated Resins (SEIR) that display improved extracting properties in both hydrometallurgy and water treatment

[15,16].These properties are also essential for environmental purposes[7,8]. In most cases, these novel extracting agents consist of resin–supported extractants such as styrene/divinylbenzene (SDVB) resin impregnated by di(2-ethylhexyl) phosphoric acid. Some of these SEIR are already commercially available. The advantages of such a concept arise from the significant decrease in the losses of extracting agent, the absence of organic solvent, and the improvement of the extraction kinetics, as compared with conventional liquid/liquid extraction[1,6,9,10].

Nevertheless, despite the growing interest of this concept, so far only a few fundamental studies have been dedicated to elucidate the nature of interaction between the extraction agent and its support. It has already been established that the extracting compound is adsorbed onto the polymer matrix via alkyl/alkyl interactions[1,4]. Surprisingly, the amount of metal removed from a solution by using an extracting agent immobilized on a polymer is frequently higher than that obtained through conventional liquid-liquid extraction using the same extracting agent[9,10]. In other words, the relatively high performance of SEIR cannot be explained by simple alkyl/alkyl interactions. In a continuation to our previous papers on the metal ions by liquid-liquid extraction using D2EHPA and other organophosphorus extractants[11,12]. The present study deals with recovery of metal ions from industrial waste liquors using D2EHPA impregnated on Amberlite XAD resins.

Previous work reported that such an immobilization does not modify the structure of the support, but deeper insights through ^{13}C-MAS-NMR, have shown that, when impregnated with D2EHPA, Amberlite resins undergo significant structural changes[13].

EXPERIMENTAL

Reagents and solutions

Zinc acetate and D2EHPA analytical grade, were supplied by Fluka (Switzerland). Three types of resins, also provided by Fluka were used in the present investigations, namely:

i. Amberlite XAD-4 resin: with a nonpolar polystyrene skeleton, having a 780m^2.g^{-1} specific area, a 0.51 porosity and a 5nm average pore diameter;

ii. Amberlite XAD-7 resin: with a weakly polar acrylic ester skeleton, having a 450m^2.g^{-1} specific area, a 0.55 porosity and a 8nm average pore diameter;

iii. Amberlite XAD-1180 resin: with a nonpolar polystyrene skeleton, having a 800m^2.g^{-1} specific area, a 0.60 porosity and a 30nm average pore diameter.

Two solutions were prepared:

i. The first set of aqueous 0.1M solutions(A) of zinc (II) acetate was prepared at different pH values by addition of different amounts of CH_3COOH;

ii. The second set of aqueous solutions(B) was obtained by dissolving a solid residue produced after zinc recovery by electrolysis from a zinc ore, of mineralogical composition: 54% Zn, 32% S, 6% Fe, 3% SiO_2, 1-2% Pb, 0.5% Cu, 0.5% Cd, 0.4% Co, 0.25% Ni, and about fourteen other elements whose contents are lower than 0.1%, at different pH values as follow: 8g of the solid residue was dissolved in 12mL of concentrated nitric acid (65%), then 150mL of distilled water added and the mixture was boiled. After filtration, the solution was diluted to 1 litre. It was green and had a pH 1.07. After drying, the insoluble residue represented 15% of the initial weight. From this solution, 10mL sample were introduced in a 50mL flask, and the pH was further adjusted with aqueous NaOH solution, filtered and then evaporated to a volume of 25mL.

Instrumentation

The metal concentration in the aqueous phase was determined through atomic absorption spectrophotometry (Perkin-Elmer, Model Analyst 300). A Bruker Advance 400 spectrometer was used for ^{13}C and ^{31}P MAS NMR analysis. FTIR spectra were registered using a Perkin-Elmer 8300 spectrophotometer. Potentiometric measurements were recorded on a Consort C 831 instrument.

Impregnation procedure

Samples of 10.0g of each dry resin (XAD-4, -7 and -1180) were contacted, at 20°C, with 2g of D2EHPA dissolved in 50mL chloroform, under continuous stirring for 4 hours, the chloroform was then thoroughly evaporated, and the resulting impregnated resins were washed with distilled water and dried under vacuum, at room temperature[14].

Sorption equilibrium

All sorption studies were carried out at room temperature (25±2°C) in batch conditions. In 100 mL glass-stoppered flask, 10mL of aqueous solutions containing zinc acetate or the mixture of Zn(II), Cd(II), Co(II), Cu(II), Fe(III), Ni(II) and Pb(II) were mixed and mechanically shaken at 150 rpm with 0.1g of impregnated resin until equilibrium was achieved(4 hours). After phase separation the equilibrium pH was measured and the metal content in the aqueous phase determined.

Resin capacity

The capacity of the impregnated resin for zinc metal species was measured in batch experiments in which a weighed amount of impregnated resin (0.1g) was stirred for fours hours with 10mL of 0.2M(13.08g/L) solution of the metal. After filtration, a sample of the supernatant was analysed. The amount of metal sorbed by the resin was calculated by mass balance.

The maximum metals sorption for a mixture of six cations was also determined using 0.1g of impregnated resin, equilibrated with 10mL of metal solution having the composition[Cd]=204.8 mg/L, [Co]=16.24mg/L, [Cu]=339.5mg/L, [Ni]=6.03mg/L, [Pb]=1.52mg/L and[Zn]=954.4mg/L for 4 hours.

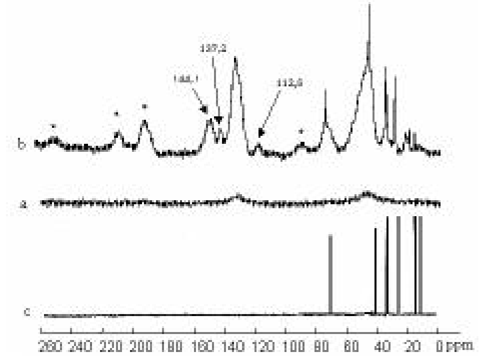


Figure 1: ^{13}C-CP-MAS NMR of XAD-1180 resin (6KHz) and ^{13}C NMR liquid D2EHPA

a- Strating resin; b- after impregnation with D2EHPA; c- ^{13}C NMR liquid D2EHPA; * Rotation peaks

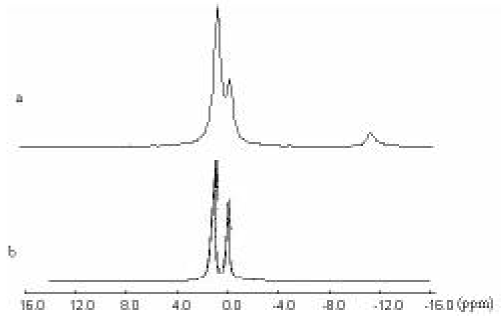


Figure 2 : (a) ^{31}P-CP-MAS NMR of resin XAD-1180 impregnated with D2EHPA(14KHz); (b) ^{31}P NMR of liquid D2EHPA

RESULTS AND DISCUSSION

^{13}C NMR solid spectroscopic study on the impregnated resin

The XAD-1180 Amberlite resin impregnated with D2EHPA (D2EHPA/XAD-1180) was characterized by both ^{13}C and ^{31}P solid (MAS-NMR) and liquid state NMR (figure 1 and 2). For the ^{13}C MAS-NMR analysis, cross polarization from ^{1}H to ^{13}C(CP) was employed (CP ^{13}C MAS-NMR).

In figure 1-a, the ^{13}C CP/MAS-NMR spectrum of the starting resin indicates the presence of broad signals at 40 and 125ppm corresponding respectively to the alkyl and the aryl chains[15]. The ^{13}C CP/MAS-NMR spectrum of D$_2$EHPA/XAD-1180 is illustrated by figure 2-b. Broad peaks were observed and attributed to resin carbon atoms having reduced mobility. In contrast, sharp signals were attributed to species displaying relatively higher mobility, presumably those molecules adsorbed on the resin surface.

It is worth mentioning that there exists a narrow similarity between D2EHPA peaks in figure 1-b (10.4, 13.5, 22.8, 28.6, 29.5, 39.8 and 68.7ppm) and those observed on an analogous liquid ^{13}C NMR spectrum of the same compound in figure 1-c(10.9, 14.1, 23.0, 23.3, 29.0, 30.0, 40.1 and 69.6ppm). Hence, one must expect that adsorption on the resin support does not imply significant modification of D2EHPA molecules.

Surprisingly, three new broad peaks were observed at 112.8, 137.2 and 144.1ppm in the impregnated sample. The occurrence of these new peaks could be explained by a modification of the chemical environment around the aromatic ring of the resin due to the presence of adsorbed D2EHPA molecules. This observation suggests that the immobilization of D2EHPA on the resin surface arises from an alkyl-aryl interaction. The peaks indicated by *are those of rotation, corresponding to a bad homogeneity of the analyzed sample and which correspond to any signal.

It was also found that the measured acidity of the aqueous phase increases during extraction, as shown in TABLE 1 (see initial and equilibrium pH). Thus, it clearly appears that the hydrophilic extracting group (P(O)(OH)) of D2EHPA is implied in the cation exchange. The remaining hydrophobic part may be involved only in the impregnation of the resin (see SCHEME 1).

The ^{31}P MAS NMR spectrum of D2EHPA/XAD-1180, recorded at a spinning rate of 14KHz, is illustrated by figure 2-a. Three peaks were observed at 0.9, -0.1 and -11.2ppm. Their integration, using DMFIT gave the following values: 70.4 %, 22.7 % and 7.3%[16]. The relatively high number of peaks observed by the solid state ^{31}P NMR analysis (figure 2-a), as compared to the liquid NMR in $CDCl_3$ (figure 2-b) must not be surprising, if one takes into account that, in the solid state, the hydrogen bonds can produce various phosphorus species having various chemical environments[17,18].

FTIR Spectroscopic studies on the metal extraction

The comparison between the IR spectra of D_2EHPA and those of the three resins before and after impregnation showed slight shifts of the mean characteristic frequencies, namely P=O, C-O-P and C=O (TABLES 1, 2 and 3).

For instance, in the D2EHPA/XAD-7 data, one observed slight changes in the C=O stretching frequency from 1732cm^{-1} to 1724cm^{-1} and the P-O-C bending frequency from 1045cm^{-1} to 1051 cm^{-1}. Similar changes were also recorded for D2EHPA/XAD-4 and D2EHPA/XAD-1180 in addition to the displacement of the characteristic frequency $\nu_{P=O}$ of the P=O bond from 1238cm $^{-1}$ to 1219cm $^{-1}$. These frequency shifts provide clear evidence of an effective interaction between D2EHPA and each resin.

The FTIR spectra of the D2EHPA resin samples obtained after the metal extraction step have been recorded and IR absorption frequencies assignments to the polymeric matrixes and to D2EHPA molecule are given in TABLES 1, 2 and 3. It is seen that the characteristic frequency $\nu_{P=O}$ of the P=O bond of both compounds and the species formed after the interaction of both molecules have been shifted from 1238-

TABLE 1: Some fundamental frequencies (in cm^{-1}) of D2EHPA, XAD-4 and XAD-4 impregnated by D2EHPA before and after Zn(II) extraction

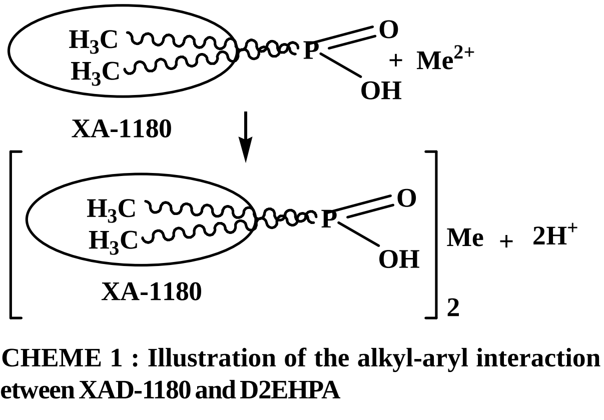
D2EHPA	XAD-4	XAD 4/D2EHPA	XAD-4/D2EHPA /Zn(II)	Assignments
2966	3028, 2932	3018, 2930	2932	ν_s C-H
	1604	1639		ν_s C=C
1421	1553, 1356	1550, 1456, 1377		ν_{as} C-H
1238		1219	1066	ν_s P=O
1045		1041	1031	ν_s P-O-C

TABLE 2 : Some fundamental frequencies (in cm^{-1}) of D2EHPA, XAD-7 and XAD-7 impregnated by D2EHPA before and after Zn(II) extraction

D2EHPA	XAD-7	XAD 7/D2EHPA	XAD-7/D2EHPA /Zn(II)	Assignments
2966	2976	2962-2936	2962-2936	ν_s C-H
	1732	1750	1710	ν_s C=O
1421	1553, 1470, 1391	1466, 1391	1553, 1466, 1391	ν_{as} C-H
1238		1238	1149	ν_s O-P=O
1045		1051		ν_s P-O-C
	1153	1153		ν_s O-C-O

TABLE 3: Some fundamental frequencies (in cm^{-1}) of D2EHPA, XAD-1180 and XAD-1180 impregnated by D2EHPA before and after Zn(II) extraction

D2EHPA	XAD-1180	XAD 1180/D2EHPA	XAD-1180/D2EHPA /Zn(II)	Assignments
2966	3500-3000, 2924	3441, 2932	3441, 2932	ν_s C-H
	1635, 1514,1450	1635, 1510, 1458		ν_s C=C
1421	1530, 1456	1530, 1456, 1320		ν_{as} C-H
1238		1219	1091	ν_s P=O
1045		1041	1030	ν_s P-O-C



SCHEME 1 : Illustration of the alkyl-aryl interaction between XAD-1180 and D2EHPA

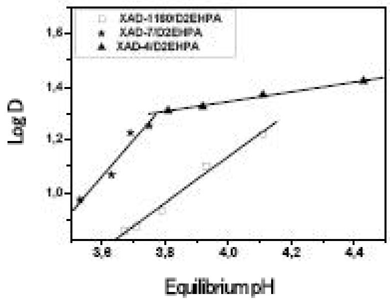


Figure 3: Variation of the distribution coefficient of Zn(II) as a function of equilibrium pH for the different XAD/ D2EHPA resins
$[Zn^{2+}]_0$= 0.2M, equilibrium time = 4 hours, T= 25°C

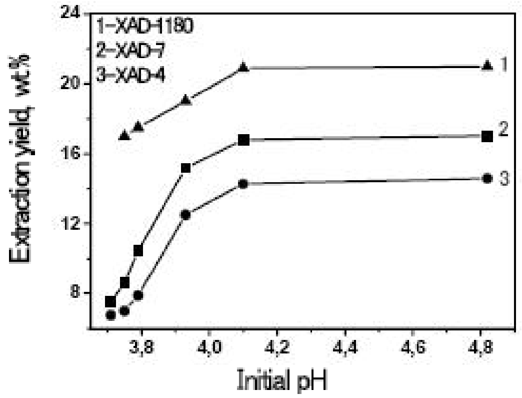


Figure 4; Extraction yield of Zn (II) versus initial pH.
$[Zn^{2+}]_0$= 0.2M, equilibrium time=4hours, T= 25°C

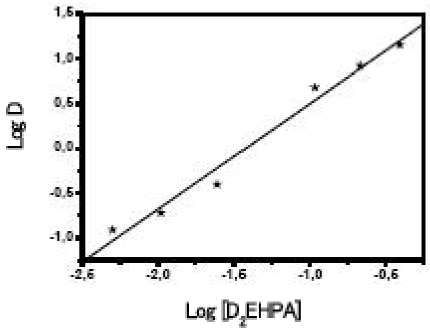


Figure 5: Effect of the extractant concentration on the distribution ratio of Zn(II)
$[Zn^{2+}]_0$= 0.2M, equilibrium time = 4hours, T= 25°C

1219cm^{-1} to 1149-1066cm^{-1}. The changes in the P=O band reflects the charge density of the phosphoryl oxygen atom and can be regarded as a measure of its coordinative activity. For this reason, the observed shifts in P=O frequency after the extraction step indicate the formation of metal complex in the resin phase by a solvatation process of Zn(II) by D2EHPA through its phosphoryl groups[2]. Two additional bands were also registered in the 550-450cm^{-1} region where the POO$^-$ and POC deformation occur[19,20].

Extraction of zinc(II) on D2EHPA impregnated XAD-4, -7 and -1180 resins

Effect of pH

Sorption isotherm experiments were carried out to investigate Zn(II) extraction with XAD/D2EHPA resins from 0.2M Zn(CH$_3$COO)$_2$ solution at different values of initial pH. Metal distribution data(D), defined by equation(1) and was plotted as log D versus Equilibrium pH in figure 3.

$$\mathbf{D = \overline{Zn(II)}\,/Zn(II)_{aqueous}} \qquad (1)$$

where the bar idicates the specie inthe resin phase.

The sorption of Zn(II) with D2EHPA impregnated XAD-4, 7 and 1180 resins can be expressed by the following stoichiometric relation[14].

$$\mathrm{Zn^{2+} + (2+q-t)\overline{HR} + t\,CH_3COO^- \Leftrightarrow \overline{Zn(CH_3COO)_t R_{(2-t)}(HR)_q} + (2-t)H^+} \qquad (2)$$

where HR represents the D2EHPA.

Figure 3 show that for XAD-7 the straight line gives an integer (2 –t ≅ 1), equation 2 becomes:

$$\mathrm{Zn^{2+} + (q-1)\overline{HR} + CH_3COO^- \Leftrightarrow \overline{Zn(CH_3COO)_t R_{(2-t)}(HR)_q} + H^+} \qquad (3)$$

For Amberlite XAD-4 and 1180 the slope of the straight lines gives a non-integer, 1.5 and 0.2, respectively. Use of the slope analysis to determine the stoichiometry in these case lead to erroneous results because the concentration of D2EHPA in the resin is limited to a narrow range[14].

The influence of initial pH on the extraction of zinc(II) from solution A is reported in figure 4. Extraction yield was defined by the following equation:

$$\mathbf{R(\%) = \frac{\overline{[M^{n+}]}}{[M^{n+}]_0}.100\%} \qquad (4)$$

where $[M^{n+}]$ is the amount of metal in the resin phase and $[M^{n+}]_0$ the initial concentration.

As a general feature, increasing pH induces an increase in the extraction. This mainly due to a specific behaviour of D2EHPA, already reported elsewhere[26]. D2EHPA acts both as an ion-exchanger and chelating agent and that the ratio between these two competitive processes varies according to the pH. In our experiments, one observes that increasing pH ought to favour an additional extracting capacity.

Effect of D2EHPA concentration on XAD resins

Extraction of Zn(II) were carried out on XAD-7/D2EHPA resin from 0.2M $Zn(CH_3COO)_2$ solution with various various D2EHPA concentration going from 5 to 389mmol.kg^{-1}. Extraction was found to increase with increasing concentration of D2EHPA. Graphs of log D vs. log [D2EHPA] was plotted in figure 5.

From This figure the slope of the straight line equal ~1. Accordingly, equation 3 becomes:

$$Zn^{2+} + \overline{HR} + (CH_3COO^-) \Leftrightarrow \overline{Zn^{2+}(CH_3COO)R^-} + H^+ \quad (4)$$

Then the extraction of this metal ion can be explained by assuming the formation of complex with the following composition $Zn(CH_3COO)R$[22]. The FTIR spectroscopic studies of the D2EHPA/XAD-7 after the extraction step indicate the existence of this metal-extractant complex in the resin phase.

Effect of resin type

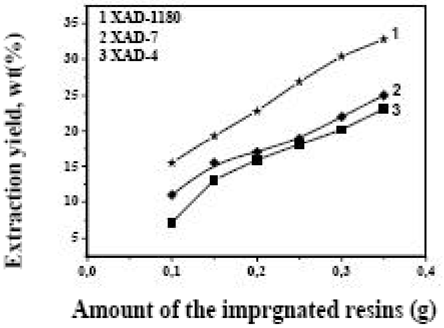


Figure 6 : Extraction yield of Zn (II) versus the amount of the impregnated resins

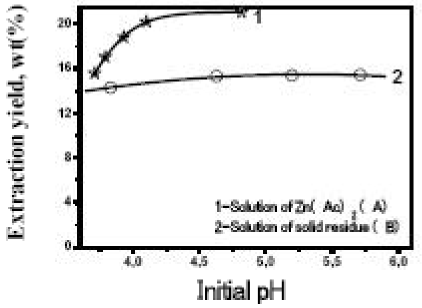


Figure 7: Extraction yield of Zn (II) from solutions A and B versus initial pH

$[Zn^{2+}]_0$= 0.2M, equilibrium time =4 hours, T=25°C

Experimental results showed that Zn(II) is not extracted by not impregnated XAD-4, -7 and 1180 amberlite resins with extractants[2,14]. It is noteworthy that, the highest extraction yields were obtained using the XAD-1180 resin, irrespective of pH, as illustrated by figure 6. This presumably was due to the higher specific surface area and the larger diameter pore of this resin, these features ought to result in increased loading of D2EHPA on the resin surface and, subsequently, in improved extraction capacity.

As compared to XAD-4, the XAD-7 resin impregnated with the same amount of D2EHPA (0.6 mol D2EHPA/kg resin) displays a relatively higher extraction capacity, arising most likely from the presence of ester groups on the resin frameworks. The ester group can act as an additional chelating site. From the FTIR spectra of the D2EHPA/XAD-7 resin, before and after the metal extraction step, (TABLE 2) it is seen that the caracteristic frequency of the C=O bond have been shifted from 1750 to 1710cm^{-1}. This result indicates that C=O groupment intervenes in the Zn(II) complexation.

As a general tendency for the three resins, the extraction yield increased proportionally with increasing amount of impregnated resins(figure 6). Such a result was expected and can be explained in terms of increased amount of supported D2EHPA. The slight discrepancy observed between the three resins impregnated may arise from the intrinsic properties of the resin that can also play a certain role in the extraction process.

Effect of solution nature

Both sets of solutions A and B containing Zn(II) were contacted with the D2EHPA/XAD-1180 samples under the same operating conditions. The results obtained for the sorption of the Zn(II) from solution A (only Zn(II)) and from solutions B(containing Zn, Cd, Co, Cu, Fe, Ni and Pb) are presented in figure 7.

Figure 7 shows that the Zn extraction yield from solution A is higher than from solutions B.

For instance, for a given pH of ca. 5, the Zn extraction yield is ca 21.4 % from solution A. For a similar pH, the extraction yield is 15.4% for solutions B, suggesting a detrimental effect of the presence of other cations. This can be explained in terms of competitivity in the cations interactions with extracting sites[23]. In other words, one must expect that the Zn

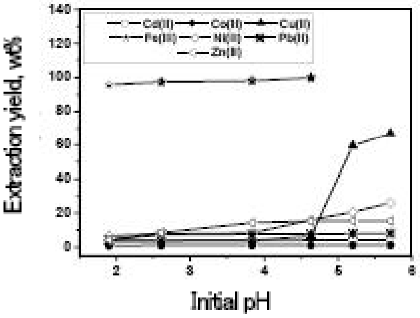


Figure 8: Cations extraction yield from solutions B versus initial pH ; 1. Fe^{3+}; 2. Cu^{2+}; 3. Ni^{2+}; 4. Zn^{2+}; 5. Pb^{2+}; 6. Cd^{2+}; 7. Co^{2+}. Equilibrium time=4 hours, T=25°C

TABLE 4: Quantitative data on the liquid-solid extraction of the mixture of cations by XAD-1180/D2EHPA

Initial pH	Composition of filtrate before extraction (mg/L)	Equilibrium pH	Composition of filtrate after extraction (mg/L)
1.90	[Cd]=238.1,[Co]=17.0, [Cu]=2180.0, [Fe]=34.2, [Ni]=9.0, [Pb]=8.4, [Zn]=1306.4.	1.81	[Cd]=229.0, [Co]=16.8, [Cu]=2123.6, [Fe]=1.4, [Ni]=8.4, [Pb]=8.0, [Zn]=1250.8
2.61	[Cd]=233.2, [Co]=16.5, [Cu]=2145.6, [Fe]=16.2, [Ni]=8.2, [Pb]=8.4, [Zn]=1306.4.	2.19	[Cd]=223.2, [Co]=16.5, [Cu]=2068.0, [Fe]=0.4, [Ni]=7.7, [Pb]=7.8, [Zn]=1196.8
3.83	[Cd]=225.9, [Co]=16.3, [Cu]=2034.0, [Fe]=5.7, [Ni]=6.9, [Pb]=6.8, [Zn]=1179.2.	2.41	[Cd]=216.9, [Co]=16.1, [Cu]=1953.6, [Fe]=0.1, [Ni]=6.3, [Pb]=6.3, [Zn]=1010.8
4.63	[Co]=16.1, [Cu]=1953.6, [Fe]=2.2, [Ni]=6.5, [Pb]=6.0, [Zn]=1162.0.	2.44	[Co]=15.9, [Cu]=1827.2, [Fe]=0.0, [Ni]=5.5, [Pb]=5.5, [Zn]=983.6
5.20	[Cd]=204.8, [Co]=16.2, [Cu]=339.5, [Ni]=6.0, [Pb]=1.5, [Zn]=954.4.	2.47	[Cd]=196.5, [Co]=16.0, [Cu]=137.4, [Ni]=4.70, [Pb]=1.4, [Zn]=807.6
5.71	[Cd]=191.9, [Co]=15.6, [Cu]=260.2, [Ni]=4.6, [Pb]=0.9, [Zn]=796.0.	2.51	[Cd]=184.0, [Co]=15.4, [Cu]=85.8, [Ni]=3.4, [Pb]=0.8, [Zn]=673.6

extraction will be progressively hindered as the amount of a competitive cation is increased.

Resin capacity

The maximum metal sorption for zinc was studied using 0.1g of impregnated resin, equilibrated with excess amount of initial metal ion solution A (10ml, 13.08g/L) for 4h. After filtration, the value obtained was found to be 274.64mg/1 g of impregnated resin (4.2mmol/g) at equilibrium pH=4.82. This impregnated resin had a high retention capacity for zinc compared to XAD-2 functionalized by 2,3-dihydroxypyridine(Cd: 6.8mg/g)[24], divinyl benzene-styrene functionalized by 2-(p-vinylbenzylamino)-alkanoic acid (Cu: 0.26, Zn: 0.22mg/g)[24], a macroporus resin obtained by radical polymerization of copper(II) methacrylate complexes with water, pyridine, 4-vinyl pyridine, with ethylene glycoldimethacrylate(Cu: 3.28mg/g)[25], Dipex(Th (IV):86.1, U(VI):145.7, Nd(III): 45.4, Fe(III): 32.1, Ca(II): 45.0 and Ba(II): 45.0mg/g)[9] and modified silica beads impregnated with LIX 84 (Cu: 15.25mg/g)[27].

The maximum metal sorption for a mixture of six cations was also studied using 0.1g of impregnated resin, equilibrated with 10mL of initial metal ions solution B([Cd]=204.8mg/L, [Co] =16.24mg/L, [Cu]=339.5 mg/L, [Ni] = 6.03mg/L, [Pb]=1.52mg/L and [Zn]= 954.4mg/L) for 4h. After filtration the value obtained was found to be 35.8 mg/g at equilibrium pH = 2.47.

Extractability and Selectivity

Investigation of the effects of various cations on the extraction of Zn(II) showed the ability of the D2EHPA/XAD-1180 material to distinguish the different analytes and extract them, from initial pH=1.90 to 5.71(TABLE 4 and figure 8). The removal efficiency of iron showed the highest value among the six metals studied, which was extracted with a yield higher than 96% at any pH[9]. The removal of cobalt from the aqueous solutions was negligible at the given pH range.

Under these conditions, the extraction ability of XAD-1180/D2EHPA resin, as a function of initial pH, in the order (Figure 8):

Co (II)<Cd (II)<Pb (II) ≈ Zn (II) ≈ Cu(II)<Ni (II)<Fe (III) at pH_i =1.90; Co (II)<Cd (II) ≈ Cu (II)<Pb (II)<Ni (II)<Zn (II)<Fe (III) at pH_i = 2.61 and 3.83; Co (II)<Cd (II)<Cu (II)<Pb (II)<Zn (II)<Ni (II)<Fe (III) at pHi = 4.63; Co (II)<Cd (II)<Pb (II)<Zn (II)<Ni (II)<Cu (II) at pH_i = 5.20 and 5.71.

This sequence which relates to a real solution with more than seven cations is different (except for Fe) from that seen for D2EHPA alone. This is why a decrease of Zn(II) extraction yield in the presence of other cations. From a multi-elements synthetic solution, the extraction ability of XAD-2/D2EHPA resin decrease as a function of pH in the order Cu<Cd<Zn, However, the extraction ability of D2EHPA in organic solvents decrease as a function of pH in the order Cd<Cu<Zn[2]. The same behaviour observed in separation factors in extraction of Cu, Cd and Zn from a reels solution on XAD-1180/ D2EHPA resin and by D2EHPA in organic solvent shows a no change of the extraction ability of D2EHPA molecules adsorbed on Amberlite XAD-1180.

Different behaviour observed between XAD-1180 and XAD-2 resins seems to indicate that the extraction reactions depends enormously on the composition of the solution, more there are elements more the ability of extractant changes. This result indicate that the extraction can be explained in terms of a competitive process between the polymeric matrix, the D2EHPA molecules, H_3O^+ of aqueous solution, the metal ions even those in the trace state and water molecules[2].

CONCLUSION

The results obtained herein allow to concluding that:

a. The ^{13}C solid state NMR study indicates that the immobilization of D2EHPA on XAD-1180 resin arise from an alkyl-aryl interaction. The acidity increase observed after extraction suggests that the process occurs preponderantly via an ion-exchange pathway, due to the hydrophilic extracting part (P(O)(OH)) of D2EHPA.

b. FTIR measurements gave clear evidence of interaction between D2EHPA and the different resins, and indicate formation of metal complex in the resin phase.

c. The Zn extraction yield decreases in the presence of other competitive cations that are also extracted. This is well argued by the affinity of the resin impregnated towards the various cations. The removal efficiency of iron ions shows the highest value among the six metal studied, which is extracted with a yield higher than 96% at any pH. The removal of cobalt ions from the aqueous solutions is negligible at the given pH range.

d. The extraction yield increases proportionally with the amount of impregnated resins. The specific surface area and the number of accessible extracting sites are critical factors that influence greatly the efficiency of the Zn extraction process. As compared to XAD-4, the XAD-7 impregnated with the same amount of D2EHPA sample displays a relatively higher extraction capacity, arising most likely from the presence of ester groups on the resin frameworks. There ester group can act as additional chelating agents.

REFERENCES

[1] J.L.Cortina, N.Miralles, A.M.Sastre, M.Aguilar; Hydrometallurgy, **37**, 301 **(1995)**.

[2] J.L.Cortina, N.Miralles, A.M.Sastre, M.Aguilar; Reactive Funct.Polym., **32**, 221 **(1997)**.

[3] M.Rovira, L.Hurtado, J.L.Cortina, J.Arnaldos, A.M.Sastre; Solvent Extraction and Ion Exchange, **16(2)**, 545 **(1998)**.

[4] C.V.S.B.Rao, A.Suresh, T.G.Srinivasan, P.R.V.Rao; Solvent Extraction and Ion Exchange, **21**, 221 **(2003)**.

[5] M.Rovira, J.Herranz, J.L.Cortina, N.Miralles, J. Arnaldos, A.M.Sastre; Editors M.Cox, M.Hidalgo, M.Valiente; Society of Chemical Industry, London, 1285 **(2001)**.

[6] T.H.Hai, T.Mikiya; Industrial Engineering Chemical Research, **42(17)**, 4050 **(2003)**.

[7] M.C.Yebra, A.Garcia, N.Carro, A.Moreno-Cid, L.Puig; Talanta, **56**, 777 **(2002)**.

[8] P.K.Tewari, A.K.Singh; Talanta, **56**, 735 **(2002)**.

[9] E.P.Horwitz, R.Chiarizia, M.L.Dietz; Reactive & Functional Polymers, **33**, 25 **(1997)**.

[10] R.Chiarizia, D.R.McAlister, A.W.Herlinger; Separation Science and Technology, **40**, 69 **(2005)**.

[11] M.A.Didi, A.Elias, D.Villemin; Solvent Extraction and Ion Exchange, **20**, 407 **(2002)**.

[12] A.Elias, M.A.Didi, D.Villemin, A.Hamidi; Hydrometallurgy, **63,** 49 **(2002)**.

[13] M.A.Didi, Abderrahim, O.Actas; 'Colloquium Spectroscopicum International XXXIII', Edited J. Manuel, C.Fernandez, J.Miguel, V.Perez; Granada, Spain, 282 **(2003)**.

[14] R.S.Juang; Part A: Physical Science and Engineering, **23(3)**, 353 **(1999)**.

[15] K.L.Hubbard, J.A.Finch, G.D.Darling; Reactive & Functional Polymers, **36**, 17 **(1998)**.

[16] D.Massiot, F.Fayon, M.Capron, I.King, S.Le Calve, B.Alonso, J.O.Durand, B.Bujoli, Z.Gan, G.Hoatson; Magn.Research Chemical, **40**, 70 **(2002)**.

[17] R.Arad-Yellin, M.Zangen, H.Gottlieb, A. Warshawsky; J.Chem.Soc.Dalton.Trans., 2081

(1990).

[18] P.A.Jaffres, D.Villemin, V.Montouillout, C. Fernandez, J.Chardon, S.J.Sopkova-de Oliveira; Mol.Cryst.Liq.Cryst., **389**, 87 **(2002)**.

[19] L.C.Thomas; 'The identification of functional groups in organophosphorus compounds.In Analysis of Organic Materials', An International Series of Monographs, R.Belcher, D.M.W.Anderson (Eds); Academic Pres, London, **(1974)**.

[20] L.C.Thomas; Heyden, London, **(1974)**.

[21] K.Kongolo, M.D.Mwema, A.N.Banza, E.Gock; Minerals Engineering, **16**, 1371 **(2003)**.

[22] N.E.Belkhouche, M.A.Didi, D.Villemin; Solvent Extraction and Ion Exchange, **23**, 677 **(2005)**.

[23] O.Abderrahim, M.A.Didi, B.Moreau, D.Villemin; Solvent Extraction and Ion Exchange, **24**, 943 **(2006)**.

[24] G.Venkatesh, A.J.Kumar, A.K.Singh; Microchimica Acta, **149(3-4)**, 213 **(2005)**.

[25] W.Kuchen, J.Schram; Angew.Chem.Int.Ed.Engl., **27(12)**, 1695 **(1988)**.

[26] J.Yi, J.S.Kim; J.Chem.Technol.Biotechnol., **74**, 544 **(1999)**.

[27] Y.Koide, K.Tsujimoto, H.Shoshendji, M.Maeda, M.Takagi; Bull.Chem.Soc.Jpn., **71**, 789 **(1998)**.