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Zinc(II) Extraction from Hydrochloric Acid Solutions using Amberlite XAD-7 Impregnated with Cyanex 921 (Tri-Octyl Phosphine Oxide)

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Abstract: Cyanex 921 (tri-octyl phosphine oxide) was immobilized on Amberlite XAD-7. The extractant impregnated resin (EIR) was very efficient at removing Zn(II) from HCl solutions (optimum found for 3 M HCl). The sorption strongly depended on the Cyanex 921 concentration in the EIR, and the temperature (the reaction being exothermic). The maximum sorption capacity was close to 15 mg Zn(II) g⁻¹ EIR (i.e. 0.19 mol Zn(II) mol⁻¹ Cyanex 921). The uptake kinetics were controlled by intraparticle diffusion (D_e : 0.44 10⁻¹² m² s⁻¹). Zn(II) can be easily desorbed using a number of eluents (including water and 0.1 M solution of EDTA, HNO₃, H₂SO₄, and Na₂SO₄), which maintained performance levels over 5 cycles.

Keywords: Zn(II) extraction, impregnated resins, Cyanex 921, Amberlite XAD-7, isotherms, kinetics, tri-octyl phosphine oxide

INTRODUCTION

The increasingly stringent regulations regarding the discharge of metal contaminants into the environment, and the increasing demand for metals in industry have focused the interest of the research community on the development of new approaches for the recovery of metal ions from waste materials including aqueous waste from industrial processes. In the case of zinc, about 30% of the annual industrial supply comes from metal recycling and it is commonly considered that about 80% of currently manufactured zinc-based materials will be subjected to a recycling operation at some point in their life cycle.^[1] Zinc is commonly recovered from secondary sources such as fly ash residues from the steel industry,^[2] or wastewater from the zinc-lead industry (batteries, electroplating. . .).^[3]

Zinc can be recovered from liquid solutions by a number of processes, including precipitation, sorption on resins,^[4–6] and solvent extraction.^[7–10] Solvent extraction is a very efficient process, especially in the case of concentrated solutions; however, the possible release of extractants may cause environmental hazards, and may have an economic impact. These reasons explain the increasing interest in developing techniques for immobilizing extractants on solid supports: this concept has been used for the preparation of extractant impregnated resins (EIR). A porous support, with a high specific surface area and suitable surface properties (hydrophobicity, polarity . . .) is used for sequestering extractants.^[11–15] Different techniques have been used for the immobilization of extractants, including: impregnation,^[11,15–17] co-polymerization,^[18,19] and encapsulation.^[20–22] A number of extractants have been investigated for the liquid-liquid extraction of Zn(II);^[2,7–10,23] Cyanex 921 (tri-octyl phosphine oxide, TOPO) is one of the efficient organophosphorous extractants that has been extensively studied over the last decade.^[24–27] This is typically a neutral extractant that can extract metals by a solvation mechanism. In the case of zinc extraction, it is expected that metal ions will mainly be extracted in HCl solutions in two forms:

- (a) neutral solvated chloro-complex, or
- (b) solvated ionic pairs.^[28]

Several resins have been tested for manufacturing EIRs, the most common are Amberlite resins.^[13,29,30] Amberlite resins differ in surface properties (polarity/hydrophobicity) depending on their structure:^[11] hydrophobic aromatic materials (styrene–divinylbenzene copolymer, such as XAD-2, XAD-4) or moderately hydrophilic materials made of aliphatic, methacrylate materials (such as XAD-7, XAD-8). The higher polarity of XAD-7 (dipole moment 1.8), compared to XAD-2 or XAD-4 (dipole moment 0.3), has been established as favorable parameter for the preparation of EIRs.^[12]

In the present work, Amberlite XAD-7 was selected as the support for the preparation of an EIR with Cyanex 921 using the dry impregnation method.

The EIR was used for the recovery of zinc from strongly acidic HCl solutions investigating the influence of HCl concentration on uptake efficiency and sorption isotherms. The content of Cyanex 921 was also varied in order to measure the impact of extractant loading on sorption capacities and distribution coefficients. The influence of HCl and Cyanex 921 concentrations on the uptake process was considered. The kinetics of Zn(II) uptake were studied with special attention paid to limiting mechanisms (including diffusion steps). Finally, the recycling of the EIR was studied, investigating several eluents for the desorption of Zn(II) and re-use of the resin.

MATERIALS AND METHODS

Materials

Amberlite XAD-7 was supplied by Sigma-Aldrich (Saint-Louis, U.S.A.). This is a polyacrylic acid ester type resin ($[\text{CH}_2\text{-CH}(\text{COOR})\text{-}]_n$). The physical characteristics of the resin are summarized in Table 1. Amberlite XAD-7 can be considered as a nonionic, moderately hydrophilic macroporous polymer. The resin was conditioned by the supplier with NaCl and Na_2CO_3 to retard bacterial growth. It was necessary to clean it to remove salts and monomeric material present on the resin. The resin was therefore put into contact with ketone for 24 hours at 25°C. After filtration under vacuum to remove excess ketone, the resin was rinsed with de-mineralized water. It was then washed with nitric acid (0.1 M) for 24 hours. The resin was filtered under vacuum and then rinsed with de-mineralized water to constant pH. Finally, it was put into contact with ketone for 12 hours before being filtered under vacuum and dried in a roto-vapor at 80°C.

Cyanex 921 was supplied by Cytec (Canada) in the form of a white solid, with higher solubility in aromatic diluents than aliphatic solvents; it is the tri-octyl phosphine oxide extractant (TOPO). The chemical structure is $(\text{C}_8\text{H}_{17})_3\text{P}=\text{O}$, it is a neutral organophosphorous extractant with a solvating activity. The molecular weight is 386 g mol^{-1} . Due to the length of aliphatic chains the solubility of the extractant in water is relatively low, below 1.5 mg L^{-1} , and even below in acidic solutions.

Table 1. Physical properties of Amberlite XAD-7

Particle size	20/60 mesh–250/850 μm
Superficial area	$450 \text{ m}^2 \text{ g}^{-1}$
Resin porosity	0.55
Pore size (mean value)	85–90 Å
Pore volume	$0.97\text{--}1.14 \text{ cm}^3 \text{ g}^{-1}$
Skeletal density	1.24 g cm^{-3}

Ethylenediaminetetracetic acid (EDTA) was supplied by Baker (U.S.A.). Other reagents (salts, acids . . .) were analytical grade and supplied by KEM (Mexico). Standard metal solutions were supplied by Perkin Elmer (U.S.A.).

Resin Impregnation

In the present work the extractant was immobilized on the resin by a physical technique. Different processes may be used for the physical impregnation of the resin including

- (i) the wet method
- (ii) the dry method
- (iii) the impregnation in the presence of a modifying agent, or
- (iv) the dynamic method.^[11]

Previous work has shown that the dry method increases the stability of the extractant on the resin. The dry impregnation of the resin was actually performed by contact of 5 g of conditioned Amberlite XAD-7 with 25 mL of ketone for 24 hours.^[17] Varying amounts of Cyanex 921 diluted in ketone (0.5 M) were added, under agitation, to resin slurry for 24 hours. The solvent was then slowly removed by evaporation in a roto-vapor.

The amount of extractant immobilized on the resin ($q_{\text{Cyanex 921}}$) was quantified by the following procedure. A known amount of impregnated resin (250 mg) was mixed with methanol (5 mL) for 24 hours to remove the extractant by dissolving. The washing treatment was repeated once. The solvent was finally separated from the resin, which was dried at 100°C for 24 hours. The mass difference ($M_{\text{Cyanex 921}}$) between impregnated ($M_{\text{XAD-7/Cyanex 921}}$) and washed resin ($M_{\text{XAD-7}}$) was used to calculate the amount of extractant immobilized on the EIR:

$$q_{\text{Cyanex921}} = \frac{M_{\text{XAD-7/Cyanex921}} - M_{\text{XAD-7}}}{M_{\text{XAD-7/Cyanex921}}} \quad (1)$$

ZINC SORPTION

Sorption experiments were performed on metal solutions containing, unless specified, a fixed concentration of 20 mg metal L⁻¹ (0.31 mM). The solutions were prepared by dilution at fixed concentration (C_0 : mg L⁻¹) with HCl at varying concentrations between 0.5 M and 8 M. The extractant content in the EIR was 444 mg g⁻¹, unless specified. The solution was mixed with the resin at a fixed solid to liquid ratio (i.e. m/V: 4 g L⁻¹; m: mass of resin; V: volume of solution) for preliminary experiments. The mixture was maintained under agitation for 24 hours using a reciprocal shaker (Cole Parmer 51502, U.S.A.) at a velocity of 150 rpm. The solution

was then filtered and the residual metal concentration (C_{eq} , mg L^{-1}) was analyzed in the filtrate by atomic absorption spectrometry (AAS, Perkin Elmer 3110). The amount of metal sorbed on the EIR (q , mg g^{-1}) was calculated by the mass balance equation: $q = V(C_0 - C_{eq})/m$. The distribution coefficient was obtained by the equation: $D = q/C_{eq}$ (L kg^{-1}). The detailed experimental conditions are given in the captions of the figures.

Sorption kinetics were performed by mixing Amberlite XAD-7 impregnated with Cyanex 921 (q : $444 \text{ mg Cyanex 921 g}^{-1} \text{ EIR}$) with a Zn(II) solution (40 mg Zn L^{-1} , i.e. 0.61 mM) in HCl (3 M). Agitation was maintained at 150 rpm all along the sorption process. Samples (less than 2.5 mL) were regularly collected and analyzed for residual Zn concentration. The total volume loss did not exceed 10% , minimizing the impact of this parameter on the kinetic profile.

Zinc Desorption and EIR Recycling

The EIR was loaded with zinc by contact of 100 mg of EIR (q : $444 \text{ mg Cyanex 921 g}^{-1} \text{ EIR}$) with 25 mL of a Zn(II) solution (20 mg Zn L^{-1} in HCl, 3 M) for 24 hours. The resin was then filtered and the amount of zinc adsorbed on the resin was calculated by the mass balance equation. The desorption was performed by putting the loaded EIR into contact with 25 mL of the eluent ($0.1 \text{ M H}_2\text{SO}_4$; 0.1 M HNO_3 ; 0.1 M E.D.T.A. ; $0.1 \text{ M Na}_2\text{SO}_4$; and de-mineralized water) for 24 hours. The mixture was then filtered and the zinc concentration measured to evaluate the amount of zinc desorbed, and this amount was compared to the amount adsorbed to determine the desorption efficiency. For the study of EIR re-use, sorption and desorption were performed under similar experimental conditions, using the different eluents.

RESULTS AND DISCUSSION

EIR Characterization

Figure 1 shows the amount of Cyanex 921 loaded on the resin versus the initial amount of the extractant in the impregnation bath. The continuous line shows the theoretical values obtained assuming complete immobilization of the extractant on the resin. The experimental determination of Cyanex 921 (operated by weight measurements before and after removing of the extractant with methanol) gave values very close to the theoretical curve. This indicates that the impregnation process was very efficient. Varying the amount of extractant in the impregnation bath produced EIRs whose loading varied between $28 \text{ mg Cyanex 921 g}^{-1} \text{ EIR}$ and $654 \text{ mg Cyanex 921 g}^{-1} \text{ EIR}$. At the highest concentrations of Cyanex 921, resin loading tended to level off at a value close to $1.5 - 1.7 \text{ mmol Cyanex 921 g}^{-1} \text{ EIR}$. This is indicative

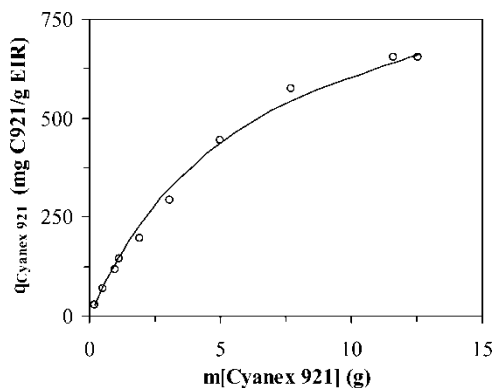


Figure 1. Influence of the amount of Cyanex 921 in the impregnation bath on its immobilization on Amberlite XAD-7 (m: 6.5 g). Line represents the theoretical values.

of the maximum sorption capacity to be expected for metal recovery, depending on the stoichiometry of the complex extractant-metal, and the possible interactions of the EIR with the aqueous solution (acid extraction. . .). Increasing the amount of extractant would result in a partial release of the extractant from the saturated resin (not shown). Water and HCl extraction were also increased by HCl concentration and Cyanex 921 loading, resulting in a substantial increase in the volume of the extractant phase and a partial expulsion of the organic phase that remained immobilized on the external surface of the particle. Though the deposition of this external phase on the surface of the particle seems to be quite stable, the possibility of a partial loss of extractant due to friction between the particles under strong agitation cannot be totally rejected. In order to avoid possible extractant release during metal sorption, the impregnation yield was maintained at a lower level, except in the experiments on the influence of extractant loading on metal uptake performance. Standard conditions were set with a Cyanex 921 impregnation level of 444 mg g^{-1} (i.e. $1.15 \text{ mmol Cyanex 921 g}^{-1}$ EIR), though data may be presented with higher extractant loadings.

These values are consistent with those obtained by other groups on the immobilization of extractants on Amberlite resins. Rovira et al. immobilized DEHTPA (diethylhexyl)thiophosphoric acid) on Amberlite XAD-2 resin with extractant loadings varying between 0.24 and $1.14 \text{ mmol DEHTPA g}^{-1}$ XAD-2.^[31] Higher extractant loadings were reached by immobilizing Ionquest 801 (2-ethylhexylphosphonic acid mono-2-ethylhexyl ester) on Amberlite XAD-7, up to $2.85 \text{ mmol Ionquest 801 g}^{-1}$ XAD-7.^[32] Lower values (i.e. $0.33 \text{ mmol LIX 79 g}^{-1}$ Amberlite XAD-2) were cited for the immobilization of LIX 79 (guanidine-type extractant),^[33] and the immobilization of DEHPA (di-(2-ethylhexyl)phosphoric acid) on Amberlite XAD-2 (i.e. $0.6 \text{ mmol DEHPA g}^{-1}$ XAD-2).^[34]

Impact of Resin Impregnation on Zn(II) Recovery

Blank experiments were performed for Zn(II) sorption using Amberlite XAD-7 resins (without impregnation) at different HCl concentrations (between 0.5 and 8 M). The values were compared to those obtained with Cyanex 921/XAD-7 impregnated resins (extractant loading: 444 mg Cyanex 921 g⁻¹ EIR). While raw resin hardly adsorb zinc (the uptake efficiency was below 6%), metal recovery efficiency was systematically higher than 40%, and higher than 85% for HCl solutions ranging in concentration between 1 and 6 M (Fig. 2). Under the selected experimental conditions the maximum efficiency was obtained in 3–4 M HCl solutions: zinc recovery reached 98%. It is thus evident that most of the binding capacity of the EIR was due to Cyanex 921, though the proper binding potential of Amberlite XAD-7 cannot be completely neglected. Similar experiments have been performed in the case of gold recovery from acidic solutions using Amberlite XAD-7 in its free form and impregnated with Cyanex 471 (triisobutyl phosphine sulfide).^[35] In this system, surprisingly the uptake efficiency for gold was not significantly increased by the impregnation of the resin. The strong binding ability of the free resin was attributed to resin degradation, which resulted in the formation of hydrolysis products in the form RCOOH that could extract Au(III) in the form of an ion pair. Recently, Laatikainen and Paatero have proposed several mechanisms for the binding of gold chloro-complexes on Amberlite XAD-7.^[36]

- protonation of carbonyl groups by HCl and subsequent exchange with tetrachloroauric acid;
- hydrophobic interactions with adsorbable complexes of low charge.

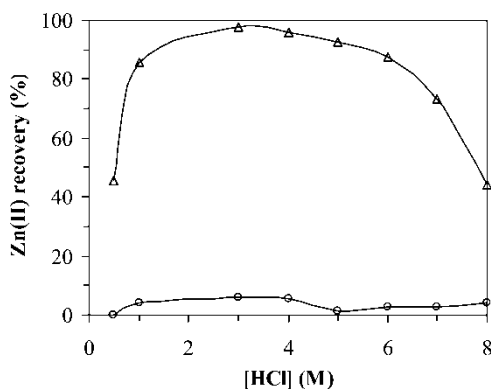


Figure 2. Comparison of Zn(II) recovery using Amberlite XAD-7 resin (circle) and Amberlite XAD-7/Cyanex 921 impregnated resin (triangle)—Influence of HCl concentration (C_0 : 20 mg Zn L⁻¹; m/V: 4 g L⁻¹; T: 25°C; $q_{\text{Cyanex 921}}$: 444 mg g⁻¹).

However, they conclude that the protonation mechanism (also observed in mild acidic conditions) is not sufficient to explain the high sorption levels obtained in their study. They consider that hydrophobic interactions may be more likely to justify these high distribution coefficients. This phenomenon was not observed in the present case: impregnation was required to achieve substantial Zn(II) binding.

Influence of HCl Concentration on Zn(II) Recovery

Figure 3 shows the influence of HCl concentration on the recovery of Zn(II) by EIR for different Cyanex 921 loadings under selected experimental conditions (T: 25°C; C₀: 20 mg Zn L⁻¹; m/V: 4 g L⁻¹). The efficiency of the process was measured considering both the recovery efficiency (Fig. 3a) and the distribution coefficient (Fig. 3b). There was a continuous increase in the efficiency of the process with increasing resin loading. This enhancement of recovery efficiency was much greater at low extractant loading than at high content, where the differences for loadings greater than 444 mg g⁻¹ were not very marked. Loading the resin with a concentration close to this value seems to be a good compromise for the preparation of a stable and efficient EIR.

The impact of the HCl concentration was basically the same, regardless of the Cyanex 921 content. A strong increase in Zn(II) recovery was observed when the HCl concentration was increased from 0.5 M to 1 M. The efficiency continued to increase slightly up to 3 M HCl concentration. Above 3 M HCl the efficiency of the process significantly decreased. In a first attempt to interpret the extraction mechanism, the recovery profile can be correlated to the diagram of species distribution for Zn(II) in HCl solutions (Fig. 4). In order to construct this diagram, the constants by Fedorov et al. were used at high HCl concentrations (3–8 M),^[37] while for low HCl concentrations (0.5–2) the constants proposed by Smith and Martell were used.^[38] Some constants values were obtained by interpolation considering the reported values. The values of these constants are summarized in Table 2. At low HCl concentration (i.e. 1 M) Zn is distributed almost homogeneously between anionic species (ZnCl₄²⁻ and ZnCl₃⁻), neutral species (ZnCl₂) and cationic species (ZnCl⁺ and Zn²⁺). When the concentration of HCl is increased to above 2 M, the quantity of cationic species becomes negligible (less than 10%) while anionic species predominate (more than 60%). At high HCl concentration (above 3M) anionic forms represent more than 80% of total Zn(II) species, with a clear predominance of ZnCl₄²⁻, the complex with the highest negative charge.

Figure 5 describes the different reactions that may be involved in the extraction process:

- (a) HCl extraction by solvation (HClL_x);
- (b) extraction of solvated neutral metal species (ZnCl₂L_x);

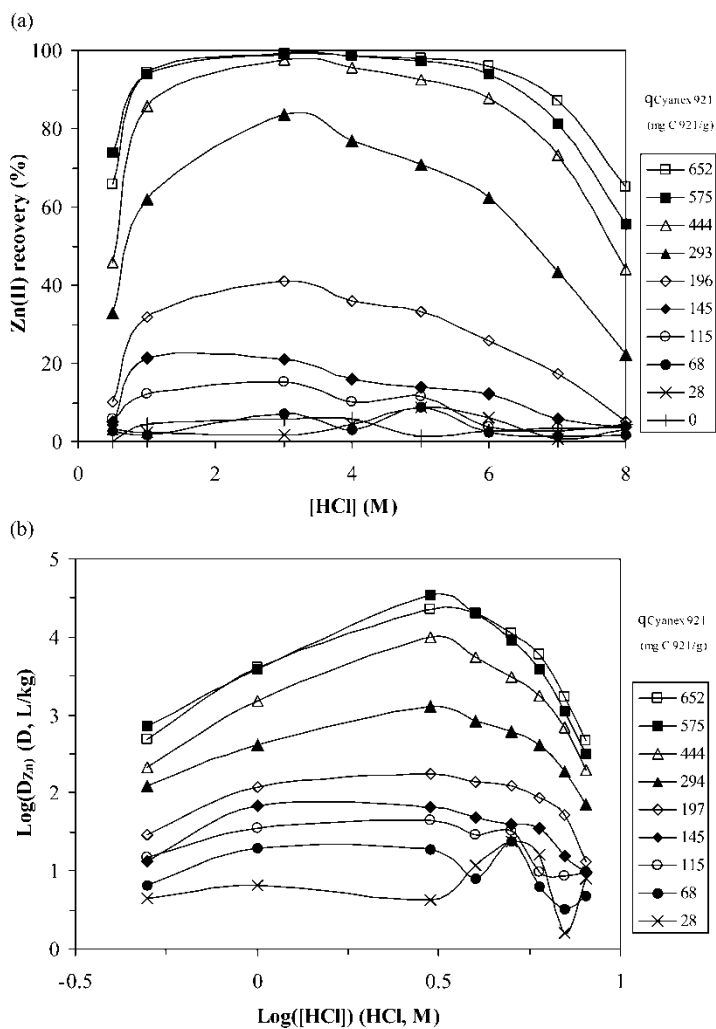


Figure 3. Influence of HCl concentration on Zn(II) recovery using Amberlite XAD-7/Cyanex 921 for different extractant loadings—(a) Extraction efficiency; (b) Distribution coefficient (C_0 : 20 mg Zn L⁻¹; m/V: 4 g L⁻¹; T: 25°C).

(c) extraction of anionic species ($ZnCl_3^-$ and $ZnCl_4^{2-}$), which are removed in the form of solvated ion pairs with protons ($HZnCl_3L_x$ and $H_2ZnCl_4L_x$).

Although Cyanex 921 is known to extract metal ions through a solvation mechanism: it has a marked preference for neutral species (in this case $ZnCl_2$), and the mechanism involving the extraction of ions pairs may significantly contribute to Zn(II) removal, depending on experimental conditions.

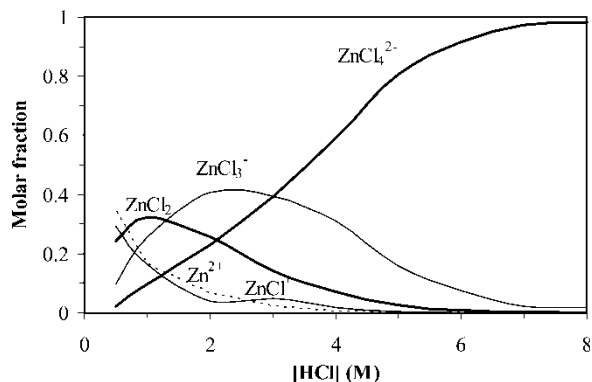
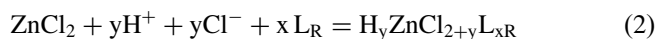


Figure 4. Zn(II) species distribution diagram in HCl solutions.

The typical mechanism is described by the equation:



where R represents the species in the resin phase and y varies between 0 and 2. The number of extractant units (x) involved in the formation of the extracted form may also vary with HCl concentration (Fig. 5). For example, in the case of Fe(III) and Cd(II), x varies between 1 and 4 (paper in preparation). Cortina et al. reported the extraction of Zn(II) in the form of ZnCl_2L using an Amberlite XAD-2 resin impregnated with TOPO.^[39]

The enhancement of extraction efficiency is clearly related to the formation of favorable species for solvation as the concentration of HCl increases up to 3 M. At higher HCl concentration, the decrease in extraction

Table 2. Overall formation constants for chloride complexes of Zn(II)

I (M)	$\log \beta_1$	$\log \beta_2$	$\log \beta_3$	$\log \beta_4$
0	0.46 ^a	0.60 ^a	0.50 ^a	0.20 ^a
0.5	0.23 ^c	0.45 ^c	0.35 ^c	-0.01 ^c
1	0.00 ^a	0.30 ^c	0.20 ^c	-0.23 ^c
2	-0.50 ^a	0.00 ^a	-0.10 ^a	-0.65 ^c
3	-0.19 ^b	-0.19 ^b	-0.22 ^b	-0.70 ^b
4	0.10 ^b	0.06 ^b	0.10 ^c	-0.22 ^b
5	0.23 ^c	0.38 ^c	0.44 ^c	0.44 ^c
6	0.36 ^b	0.69 ^b	0.78 ^b	1.10 ^b
7	0.43 ^b	1.06 ^b	1.10 ^b	1.90 ^b
8	0.52 ^b	1.19 ^b	1.46 ^b	2.28 ^b

^aFrom Smith and Martell.^[38]

^bFrom Fedorov et al.^[37]

^cConstants values obtained by interpolation considering the reported data.

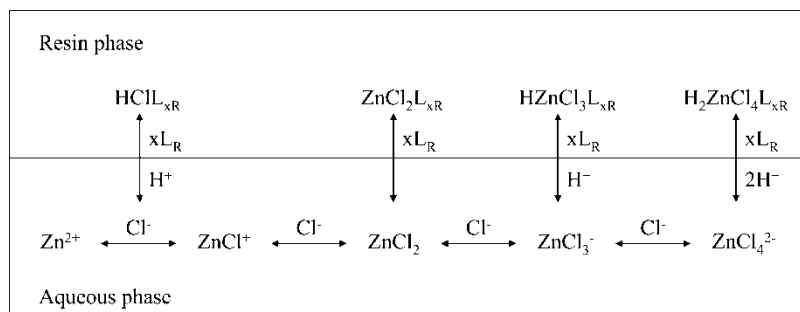


Figure 5. Exchanges and reactions involved in Zn(II) extraction using Amberlite XAD-7/Cyanex 921.

efficiency may be correlated to a competition of HCl with metal species for extraction. This competitive effect strongly appears under unfavorable conditions (i.e. low extractant loading) as observed on Fig. 3a. However, solvent extraction studies have confirmed that solvating organophosphorous extractants can co-extract HCl. Regel et al. showed that Zn(II) is extracted by Cyanex 921 in kerosene in several forms (i.e. ZnCl_2L_3 , HZnCl_3L_3 , $\text{H}_2\text{ZnCl}_4\text{L}_2$) by varying the stoichiometric ratio between metal, ligand and HCl.^[8] In the case of Zn(II) extraction with TBP (in xylene solvent) ZnCl_2L_2 , HZnCl_3L_3 , $\text{H}_2\text{ZnCl}_4\text{L}_2$ species have been identified.^[7] Similar co-extraction of HCl was cited in the recovery of Au(III) (HAuCl_4L and HAuCl_4L_2) with Cyanex 921 in xylene,^[27] and with Cyanex 925 in xylene (HAuCl_4L_2).^[40] Barroso et al. report direct HCl extraction by Cyanex 925 in xylene:^[40] they concluded that HCl is extracted in the form HClL in the 1–6 M HCl range, while above 6 M HCl concentration the acid is extracted in the form $(\text{HCl})_2\text{L}$. Unfortunately, there is no literature available on the equilibrium constants regarding the extraction of HCl by EIRs. Experiments performed to determine HCl extraction on Cyanex 921/Amberlite XAD-7 were hampered by the difficulty of evaluating the relative fractions of HCl present in the porous network and bound to the extractant.

The distribution coefficient increased with increasing HCl concentration up to 3 M (presence of appreciable amounts of cationic species not subject to solvation); above this limit concentration a strong decrease in the distribution coefficient was observed, certainly due to strong competition from HCl extraction. At any rate, the change in the slopes of the curves clearly establishes that different species are extracted depending on HCl concentration and Cyanex 921 loading. The slope of the increasing section was more marked in the case of high Cyanex 921 loading; for low extractant loadings, the positive effect of increased HCl concentration was only detectable between 0.5 M and 1 M, and between 1 and 3 M the distribution coefficient tended to level off. It is also interesting to observe that for high

extractant loadings (i.e. 575 and 652 mg Cyanex 921 g⁻¹ XAD-7) the curves overlapped for HCl concentrations between 1 and 5 M. Under these experimental conditions, the extraction efficiencies are closed to 100% and the differences between the distribution coefficients are not significant.

Influence of Cyanex 921 Loading on Zn(II) Recovery

Figure 6 shows the impact of Cyanex 921 loading on Zn(II) recovery (at different initial Zn concentrations) using Cyanex 921/Amberlite XAD-7 in 3 M HCl solutions. As expected, increasing the amount of extractant on the EIR significantly improved Zn(II) sorption capacity. At low loading (below 200 mg Cyanex 921 g⁻¹ EIR), the uptake capacity slightly increased independently of initial metal concentration. With higher loadings the differences

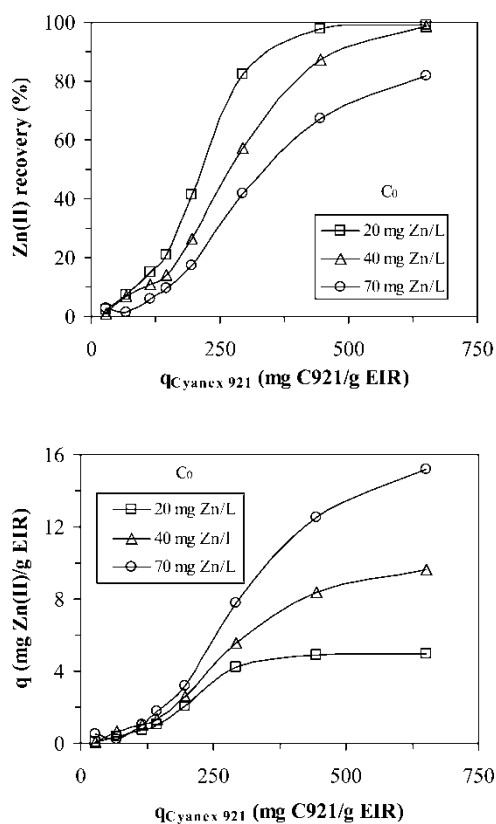


Figure 6. Influence of Cyanex 921 loading in the EIR on Zn(II) recovery and sorption capacity for different initial concentrations of Zn(II) in solution (C_0 : 20/40/70 mg Zn L⁻¹; m/V: 4 g L⁻¹; T: 25°C).

were more marked for the different Zn(II) concentrations: at low Zn(II) concentration (i.e. 20 mg Zn L^{-1}) the sorption capacity tended to level off above $300 \text{ mg Cyanex 921 g}^{-1}$ EIR, due to the large excess of extractant compared to the amount of metal (which is not fully saturated); at high Zn(II) concentration (i.e. 70 mg Zn L^{-1}) the impact of extractant loading was more significant. The extractant became progressively more saturated. From these results it is important to observe that extractant loading needs to be greater than $200 \text{ mg Cyanex 921 g}^{-1}$ EIR for significant binding of Zn(II).

The distribution coefficient of Zn(II) was also strongly influenced by the loading of the resin, regardless of HCl concentration, as indicated in Fig. 7. In the case of simple systems involving the extraction of a single complex for one HCl concentration, the plot of the logarithm of the distribution coefficient versus the logarithm of extractant concentration shows a linear trend, whose slope gives the number of extractant molecules involved in the extraction reaction. Figure 7 clearly shows that the present system is much more complex since it is not possible to determine uniform linear trends. Due to the difficulty in modeling the extraction system, the equilibrium concentration of the extractant was not available. However, the large excess of Cyanex 921 immobilized on the resin, compared to zinc concentration, allowed this equilibrium concentration to be approximated by the total concentration of the extractant. For each curve (HCl concentration), several linear segments can be observed due to differences in the predominant species in both phases. The slopes varied between 0 and 4. The highest distribution coefficients (up to 10^4 L kg^{-1}) were obtained at high Cyanex 921 loadings with HCl concentrations

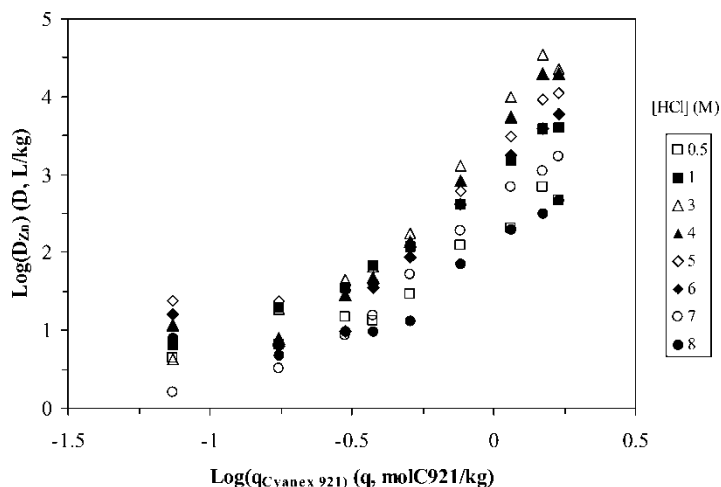


Figure 7. Influence of Cyanex 921 loading on the Zn(II) distribution coefficient for different HCl concentrations (C_0 : 20 mg Zn L^{-1} ; m/V : 4 g L^{-1} ; T : 25°C).

close to 3 M. On the contrary, the distribution coefficients were significantly lower at low Cyanex 921 loadings with high HCl concentrations due to

- (a) a low number of extractant sites, and
- (b) the competition of HCl molecules for extraction.

Sorption Isotherms

Influence of Cyanex 921 Loading on Zn(II) Sorption Isotherms

Figure 8 compares Zn(II) sorption isotherms for EIRs with different Cyanex 921 loadings. As expected, increasing the loading of Cyanex 921 on the resin increased its sorption capacity. The shape of the curve was basically the same, characterized by a sharp initial slope followed by a plateau. The sorption isotherms were modeled using the Langmuir equation:

$$q = \frac{q_m b C}{1 + b C} \quad (3)$$

where q_m is the maximum sorption capacity or sorption capacity at saturation of the monolayer (mg g^{-1}), and b is the Langmuir constant (affinity coefficient of the sorbent for the solute).

Table 3 gives the parameters of the model obtained for various extractant loadings at 25°C.

Increasing the loading of the resin resulted in an increase in both the maximum sorption capacity and the affinity coefficient. The maximum sorption capacity obtained for Cyanex 921 loadings of 293 mg g^{-1} EIR (i.e. 0.759 mmol Cyanex 921 g^{-1} EIR) and 444 mg g^{-1} EIR (i.e. 1.150 mmol

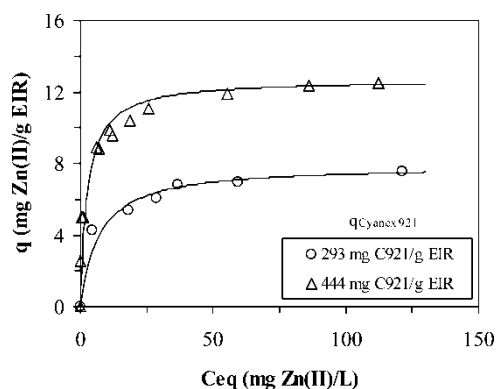


Figure 8. Influence of Cyanex 921 loading of the EIR on Zn(II) sorption isotherms (Line: modeling of experimental data using the Langmuir equation; [HCl]: 3M; T: 25°C; m/V: 4 g L^{-1}).

Table 3. Parameters of the Langmuir equation obtained for selected experimental conditions ([HCL]: 3M; m/V: 4 g L⁻¹)

Cyanex 921 loading (mg g ⁻¹)	Temperature (°C)	q _m (mg Zn g ⁻¹ EIR)	b (L mg ⁻¹)	R ²
293	25	7.91	0.145	0.998
444	25	12.7	0.383	0.999
444	40	10.0	0.882	0.996
444	50	9.13	0.312	0.995

Cyanex 921 g⁻¹ EIR) were 7.9 mg Zn g⁻¹ EIR (i.e. 0.121 mmol Zn g⁻¹ EIR) and 12.7 mg Zn g⁻¹ EIR (i.e. 0.194 mmol Zn g⁻¹ EIR). The stoichiometric molar ratios between Zn and Cyanex 921 at saturation on EIRs were 0.16 and 0.17 for low and high Cyanex 921 loadings respectively: the saturation of the extractant immobilized on the resin was independent of resin loading.

Influence of Temperature on Zn(II) Sorption Isotherms

The sorption isotherms were determined at different temperatures (in the range 25–50°C) under selected experimental conditions ([HCL]: 3 M; m/V: 4 g L⁻¹; q_{Cyanex 921}: 444 mg Cyanex 921 g⁻¹ EIR). The maximum sorption capacity, obtained by the plateau value for high residual metal concentration, decreased with the temperature, indicating that the reaction is exothermic: 12.7 mg Zn g⁻¹ EIR, 10.0 mg Zn g⁻¹ EIR and 9.1 mg Zn g⁻¹ EIR at 25°C, 40°C and 50°C, respectively (Fig. 9). Table 3 shows the parameters of the Langmuir equation obtained at the selected temperatures.

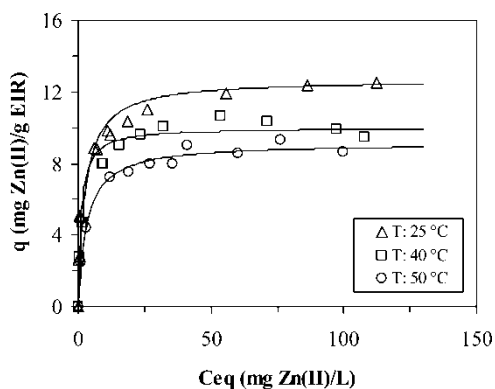


Figure 9. Influence of temperature on Zn(II) sorption isotherm using Amberlite XAD-7/Cyanex 921 (Line: modeling of experimental data using the Langmuir equation; [HCL]: 3M; m/V: 4 g L⁻¹; q_{Cyanex 921}: 444 mg g⁻¹).

Uptake Kinetics

The sorption kinetics are another important parameter in the design of EIRs. Several steps may control sorption kinetics:

- (a) mass transfer of the solute through the external film and in the porous network (surface and homogeneous diffusion);
- (b) reaction kinetics.

In most cases, binding in sorbents is controlled by diffusion mechanisms rather than the reaction rate; though some systems have been shown to be governed by a reaction mechanism in relation with the parallel ionic reactions (which change the speciation of the ions involved in the principal reaction). Since the pioneering work on dynamics of ion exchange processes by Streat^[41] and Helfferich,^[42] Juang and Ju discussed a series of simplified modeling systems derived from the homogeneous diffusion model (HDM) and shrinking core model (SCM).^[43] The HDM involves counterdiffusion of exchangeable species in quasi homogeneous media, with a contribution from film diffusion (HDM-FD) and/or particle diffusion (HDM-PD). Solute molecules and exchangeable species (immobilized on the resin) follow a similar diffusion mechanism (but in the opposite direction). In the case of the SCM, a sharp virtual boundary exists between the reacted shell of the particle and the unreacted core, and this boundary moves towards the center of the particle.^[44,45] This model was developed with different systems depending on the controlling step: film diffusion (SCM-FD), particle diffusion (SCM-PD) and chemical reaction rate (SCM-CR).^[43] A number of mathematical equations have been developed to simulate these mechanisms, they are listed below:

Homogeneous Diffusion Model

$$\text{Film diffusion: } F_1(X) = -\ln(1 - X) = f(t) \quad (4)$$

$$\text{Particle diffusion: } F_2(X) = -\ln(1 - X^2) = f(t) \quad (5)$$

Shrinking Core Model

$$\text{Film diffusion: } G_X = X = g\left(\int_0^t C(t)dt\right) \quad (6)$$

$$\begin{aligned} \text{Particle diffusion: } G_2(X) &= 3 - 3(1 - X)^{2/3} - 2X \\ &= g\left(\int_0^t C(t)dt\right) \end{aligned} \quad (7)$$

$$\text{Chemical reaction rate: } G_3X = 1 - (1 - X)^{1/3} = g\left(\int_0^t C(t)dt\right) \quad (8)$$

where X is the fractional approach to the equilibrium, i.e. $q(t)/q_{eq}$, the amount adsorbed at time t divided by the amount of metal adsorbed at equilibrium. Plotting F_i and G_i functions versus time and the integral term (respectively) determined the most appropriate mechanism for describing the controlling step. The curve giving a straight line (good correlation measured by the correlation coefficient) is the predominant limiting step.

Figure 10 shows that the model corresponding to the predominance of particle diffusion resistance (HDM-PD) was the only model that linearly fitted experimental data. In the SCM, the curve corresponding to the chemical reaction rate control gave a good correlation coefficient. However, for the initial minutes of contact there was a strong curvature, which shows that this model is not suitable for describing the system. The particle diffusion curve (SCM-PD) gave a poor correlation coefficient compared to the results obtained with the homogeneous diffusion model controlled by particle diffusion. Additionally, the ordinate intercepts for models describing

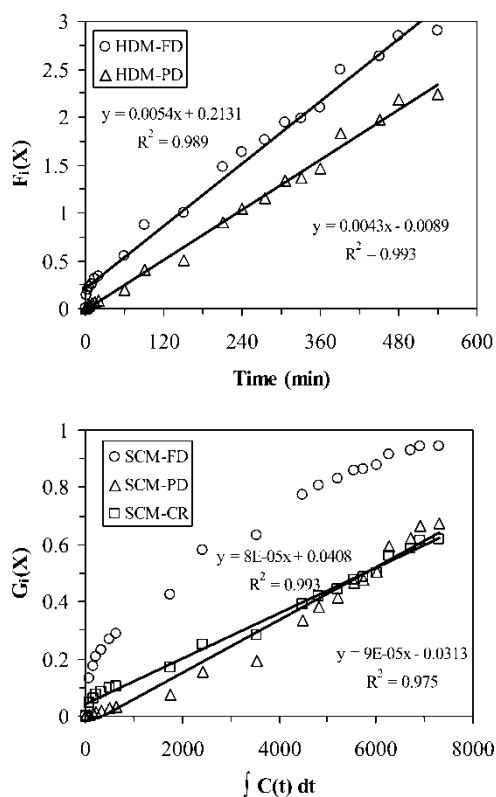


Figure 10. Testing of the controlling kinetic step. Homogeneous diffusion model (HDM) and shrinking core model (SCM). Film diffusion (FD), particle diffusion (PD), and chemical reaction rate (CR) (T: 25°C; m/V: 4 g L⁻¹; [HCl]: 3 M; C₀: 40 mg L⁻¹; q_{Cyanex 921}: 444 mg g⁻¹).

a control of the kinetics by film diffusion are far from the origin indicating that these models are not appropriate for describing the controlling phenomenon in the course of extraction process (though its contribution in the initial phase of contact is not negligible). This is a first indication that particle diffusion is the controlling mechanism for the zinc sorption kinetics.

The external film diffusion can be experimentally approximated by a simple equation, developed by McKay and Allen, assuming the film diffusion to be the controlling step:^[46,47]

$$\frac{C(t)}{C_0} = \frac{1}{1 + mK} + \frac{mK}{1 + mK} \exp\left(-\frac{1 + mK}{mK} k_f \frac{A}{V} t\right) \quad (9)$$

where, k_f is the external diffusion coefficient ($m s^{-1}$), A is the total external surface area available for contact with the solution (m^2), V the volume of solution (m^3), m is the sorbent dosage ($4 g L^{-1}$) and K is $q_m * b$ (Langmuir constants, here: $4.864 L g^{-1}$).

Plotting $\ln(C(t)/C_0 - 1/(1 + mK)) = \phi(C(t))$ versus t gives the external diffusion parameter k_f (by determination of the slope of the linear part).

$$\begin{aligned} \phi[C(t)] &= \ln\left[\frac{C(t)}{C_0} - \frac{1}{1 + mK}\right] \\ &= -\left(\frac{1 + mK}{mK} k_f \frac{A}{V}\right)t + \ln\left[\frac{mK}{1 + mK}\right] \end{aligned} \quad (10)$$

The ratio A/V was determined using the equation:

$$\frac{A}{V} = \frac{6m}{(1 - \epsilon_p)d_p\rho_p} = \frac{6m}{d_p\rho_{p,app}} \quad (11)$$

where ϵ_p is the porosity of EIR particles ($\epsilon_p = 0.55$), d_p the mean diameter of EIR ($d_p = 0.55$ mm), ρ_p and $\rho_{p,app}$ are the true and apparent densities of EIR respectively. The apparent density ($\rho_{p,app} = 1.00 g mL^{-1}$) was obtained taking into account the skeletal density of the resin ($\rho_p = 1.24 g L^{-1}$), the porosity of the resin and the amount of extractant immobilized in the resin ($q_{Cyanex 921} = 444 mg g^{-1}$ EIR), assuming that the free volume was partially occupied by the extractant and that resin volume remained constant. The apparent dry density of the resin (raw resin not impregnated was $0.558 g mL^{-1}$), after hydration the density approached $1.05 g mL^{-1}$. Several tests were carried out by dropping EIR into HCl solutions (of varying concentration and varying density) and testing the flotation of sorbent particles. This experimental approach was consistent with the values obtained by calculation. According to these assumptions, the outer surface of the adsorbent per unit volume of the particle-free suspension (A/V) was close to $43 m^{-1}$. Figure 11 shows the modeling of film diffusion. The coefficient k_f (film diffusion coefficient) was $3.7 \cdot 10^{-6} m s^{-1}$.

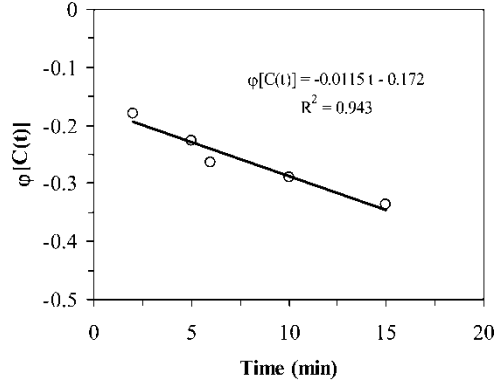


Figure 11. Modeling of film diffusion (T: 25°C; m/V: 4 g L⁻¹; [HCl]: 3 M; C₀: 40 mg L⁻¹; q_{Cyanex 921}: 444 mg g⁻¹).

The intraparticle diffusion coefficient (D_e , effective diffusivity, m² s⁻¹) was determined using Crank's equation, assuming the solid to be initially free of metal, and the kinetics to be controlled by intraparticle diffusion resistance:^[48]

$$\frac{q(t)}{q_{eq}} = 1 - \sum_{n=1}^{\infty} \frac{6\alpha(\alpha + 1) \exp(-D_e q_n^2 t / r^2)}{9 + 9\alpha + q_n^2 \alpha^2} \quad (12)$$

$q(t)$ and q_{eq} are the concentrations of the metal in the resin at time and equilibrium respectively.

And q_n non-zero roots of the equation:

$$\tan q_n = \frac{3q_n}{3 + \alpha q_n^2} \quad (13)$$

$$\text{with } \frac{q}{VC_0} = \frac{1}{1 + \alpha} \quad (14)$$

These simplified model equations fitted well with the experimental data (Fig. 12). Ten hours of contact were necessary to reach an equilibrium. This long contact time is significantly greater than the time required to reach equilibrium for liquid-liquid extraction with other metal systems (tetrachloroaurate):^[27] with liquid-liquid extraction, metal recovery was effective within the first 5 minutes of contact. This may be explained by the contribution of intraparticle mass transfer resistance, as pointed out by Juang and Lin with other EIR/metal systems.^[44,45]

The diffusion coefficient for external mass transfer resistance was 3.7 10⁻⁶ m s⁻¹, while the effective diffusivity was 0.44 10⁻¹² m² s⁻¹. This value of the intraparticle diffusion coefficient is consistent with the diffusivities obtained by Juang and Lin,^[44,45] in the case of Amberlite XAD-2 and

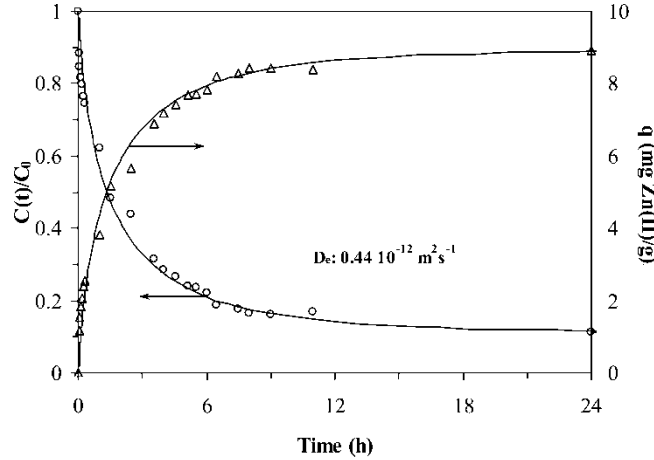


Figure 12. Modeling of extraction kinetics using the simplified intraparticle diffusion equation (Crank's equation) (T: 25°C; m/V: 4 g L⁻¹; HCl concentration: 3 M; C₀: 40 mg L⁻¹; q_{Cyanex 921}: 444 mg g⁻¹).

XAD-4 EIR (impregnated with D2EHPA): they found values ranging between 1.1×10^{-12} and $2.6 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$ for Cu; while in the case of Zn recovery the diffusivities were in the range 1.6×10^{-12} – $3.2 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$ for Amberlite XAD-2 EIR and lower for Amberlite XAD-4 EIR (i.e. 1.3×10^{-12} – $2.7 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$). Hinojosa Reyes et al. used a Cyanex 301/Amberlite XAD-7 system for cadmium recovery from phosphoric acid:^[17] they obtained intraparticle diffusivities in the range 0.2×10^{-12} – $3.8 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$ (higher than the diffusivities obtained with Amberlite XAD-2 under similar experimental conditions). Serasols et al. found that the effective diffusion coefficient (for Au and Zn recovery from HCl solutions using DEHPA/Amberlite XAD-2) varied linearly with the initial concentration:^[49,50] the values obtained for a concentration comparable to those we used was of the same order of magnitude (0.2×10^{-12} – $1.4 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$).

The Biot number, B_i (dimensionless), which serves to determine the predominant controlling diffusion mechanism, was determined using the following equation:^[51,52]

$$B_i = \frac{k_f d_p}{D_e} \quad (15)$$

Here, the Biot number was found to be close to 584. A Biot number greater than 1 indicates that the predominant controlling mechanism is resistance to intraparticle mass transfer and confirms the preliminary conclusion deduced from Fig. 10.

Zn(II) Desorption and EIR Recycling

To make the EIR competitive and efficient for metal recovery it is important to verify whether the metal can be desorbed from loaded resin and whether the EIR can be re-used with reduced loss of activity. For this purpose the resin was subjected to a series of 5 cycles of sorption and desorption using different eluents: water, 0.1 M EDTA, 0.1 M HNO₃, 0.1 M H₂SO₄, and 0.1 M Na₂SO₄. Table 4 summarizes the results obtained over the five cycles, showing the sorption capacity (q_{sorption}), and the equivalent desorbed amount ($q_{\text{desorption}}$), as well as the individual and cumulated desorption efficiencies. All the eluents gave perfect desorption of Zn(II): the desorption percentage varied for the different steps, but the cumulative desorption was systematically close to 100%. Basically all the eluents maintained good sorption performances over the 5 cycles, indicating that re-use of the EIR is possible. The only significant decrease in sorption performance was observed in the case of EDTA, for which

Table 4. Sorption and desorption of Zn(II) from loaded EIR using water, 0.1 M EDTA, 0.1 M HNO₃, 0.1 M H₂SO₄, and 0.1 M Na₂SO₄, over 5 sorption/desorption cycles

Eluent	1st Cycle	2nd Cycle	3rd Cycle	4th Cycle	5th Cycle
EDTA					
q_{sorption}	8.18	7.74	7.51	7.29	7.17
$q_{\text{desorption}}$	7.70	8.47	7.51	7.34	7.09
%Desorption	94	109	100	101	99
Cumul. Des. %	94	102	105	100	100
H₂O					
q_{sorption}	8.34	8.32	7.93	7.95	8.16
$q_{\text{desorption}}$	8.35	7.44	7.93	7.98	7.79
%Desorption	100	89	100	100	95
Cumul. Des. %	100	95	95	100	98
Na₂SO₄					
q_{sorption}	8.46	8.38	8.30	8.20	8.17
$q_{\text{desorption}}$	8.44	8.31	8.07	8.15	7.98
%Desorption	100	99	97	99	98
Cumul. Des. %	100	99	98	98	99
H₂SO₄					
q_{sorption}	8.20	8.14	7.66	7.64	8.03
$q_{\text{desorption}}$	8.33	7.32	8.79	8.87	7.87
%Desorption	102	90	115	116	98
Cumul. Des. %	102	96	102	115	107
HNO₃					
q_{sorption}	8.32	8.14	7.96	7.94	7.91
$q_{\text{desorption}}$	8.02	8.27	8.27	7.94	7.97
%Desorption	96	102	104	100	101
Cumul. Des. %	96	99	103	102	100

the sorption capacity continuously decreased (to reach a 12% loss of sorption capacity after the fifth cycle). Since the desorption of Zn(II) with EDTA was very efficient, the decrease in sorption capacity is not due to the accumulation of Zn(II) in the EIR but more probably to a progressive release of the extractant during the sorption/desorption steps. During desorption with EDTA, turbid solutions were obtained, probably due to partial precipitation of EDTA. This precipitation may result from the release of HCl from the loaded sorbent into the EDTA solution (acidification of the solution). Precipitated EDTA may, in turn, adsorb low amounts of extractant, inducing a progressive decrease in the sorption efficiency. The use of this kind of organic acid for metal re-extraction in impregnated resins is thus not a practical solution and should be avoided.

CONCLUSION

The impregnation of Amberlite XAD-7 with Cyanex 921 enables the preparation of an efficient EIR for Zn(II) recovery from HCl solutions. A Cyanex 921 content close to 450 mg g⁻¹ EIR seems to be a good compromise between sorption performance and extractant stability in the EIR. Sorption reaches a maximum in 3 M HCl solutions with sorption capacities close to 12 mg Zn g⁻¹ EIR. Resistance to intraparticle diffusion is the controlling step for uptake kinetics: the intraparticle diffusion coefficient is close to 0.44 10⁻¹² m² s⁻¹. The sorption capacity decreased with temperature, indicating that the sorption is exothermic. Zinc is adsorbed via a solvation mechanism involving the formation of different complexes with different stoichiometric ratios between Zn, the extractant and HCl (which is co-extracted), depending on the experimental conditions. These various complexes make the modeling of the system over the whole range of HCl concentrations quite complex since the equilibrium constants for HCl extraction by the EIR are not available (research in progress). The desorption of Zn(II) from loaded EIR proved quite easy: 0.1 molar solutions of Na₂SO₄, H₂SO₄ or HNO₃ and even water can efficiently recover Zn(II), maintaining comparable sorption and desorption efficiencies for at least 5 sorption/desorption cycles.

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