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Zinc(II) Extraction from Hydrochloric Acid Solutions using Amberlite XAD-7 Impregnated with Cyphos IL 101 (Tetradecyl(Trihexyl)Phosphonium Chloride)

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Abstract: Cyphos IL 101 (tetradecyl(trihexyl)phosphonium chloride) was immobilized on Amberlite XAD-7. The extractant impregnated resin (EIR) was very efficient at removing Zn(II) from HCl solutions (optimum found between 2 and 4 M HCl). Metal ions were removed as anionic chlorocomplexes ($ZnCl_4^{2-}$) by ion exchange mechanism. The sorption strongly depended on the Cyphos IL 101 concentration in the EIR. The maximum sorption capacity was close to 20 mg Zn(II) g^{-1} EIR (i.e. 0.40 mol Zn(II) mol^{-1} Cyphos IL 101). The uptake kinetics were controlled by intraparticle diffusion (D_e: 1.2 10^{-11} -6 10^{-11} $m^2\,min^{-1}$). Zn(II) can be easily desorbed using a number of eluents (including water and 0.1 M solution of HNO_3, H_2SO_4, and Na_2SO_4), which maintained performance levels over 5 cycles.

Keywords: Amberlite XAD-7, cyphos IL 101 (tetradecyl(trihexyl)phosphonium chloride), impregnated resins, ionic liquids, isotherms, kinetics, Zn(II) extraction

INTRODUCTION

The discharge of metal contaminants into the environment is subject to increasingly drastic control. Additionally, the increasing demand for base metals in industry has strongly stimulated the development of new

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processes for metal recovery from waste materials including industrial wastewater. As an example, in the case of Zn, more than 30% of annual supply proceeds from metal recycling. In the analysis of the life-cycle for Zn-based materials, it is usually considered that about 80% of the manufactured materials will be recycled (1). Among the most used secondary Zn sources which are commonly cited fly ash residues from the steel industry (2), and wastewater from the manufacturing of batteries, or from electroplating processes (3–5)...

Solvent extraction is a very efficient process for zinc recovery from concentrated solutions (6–9), as an alternative to precipitation or adsorption on resins (10–12); however, the possible release of extractants may cause environmental hazards, and the loss of solvent may impact economic benefits. Immobilizing extractants in suitable solid supports is a solution to prevent these major drawbacks. This technique allows preparing the so-called extractant impregnated resins (EIR). The most relevant criteria for the selection of the support system are:

(a) the porosity of the support (high specific surface area), and
(b) the surface properties (hydrophobicity, polarity...) (13–17).

Different techniques have been used for the immobilization of extractants, including: impregnation (13,17–19), co-polymerization (20,21), and encapsulation (22–24). A number of extractants have been investigated for the liquid-liquid extraction of Zn(II) (2,6–9,25), including Cyanex 921 (tri-octyl phosphine oxide, TOPO) that extracts zinc from HCl solutions in two forms:

(a) neutral solvated chloro-complex, or
(b) solvated ionic pairs (26).

Ionic liquids have recently received a great deal of attention due to their unique properties: Cyphos family, synthesized by Cytec, is part of the organophosphorous-based ionic liquids (27). Combining an organic cation (phosphonium salt) and either an organic or an inorganic anion, they constitute a new group of solvents, frequently considered as "green solvents": practically zero vapor pressure and temperature stability. This explains the growing interest in their application to extractive separation for organic acids (28), phenol derivatives and metal ions (mainly as solvents for conventional extractants) (29), and also to catalytic applications (30). Cyphos IL 101 (tetradecyl(trihexyl)phosphonium chloride) can extract metal ions (under the form of anionic complexes) by an ion exchange mechanism.

Several resins have been tested for manufacturing EIRs; the most common are Amberlite resins (15,31,32). Amberlite resins differ in surface properties (polarity/hydrophobicity) depending on their structure (13): hydrophobic aromatic materials (styrene–divinylbenzene copolymer, such as XAD-2, XAD-4) or moderately hydrophilic materials made of aliphatic, methylacrylate 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 a favorable parameter for the preparation of EIRs (14).

In the present work, Amberlite XAD-7 was selected as the support for the preparation of an EIR with Cyphos IL 101 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 Cyphos IL 101 was also varied in order to measure the impact of extractant loading on sorption capacities and distribution coefficients. The influence of HCl and Cyphos IL 101 concentrations on the uptake process was considered. The kinetics of Zn(II) uptake were studied with a 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 the 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 ($[CH_2\text{-}CH(COOR)\text{-}]_n$). 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

Table 1. Physical properties of amberlite XAD-7

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

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.

Cyphos IL 101 (tetradecyl(trihexyl)phosphonium chloride) was supplied by Cytec (Canada), is a slightly viscous room temperature ionic liquid. It is less dense than water and colorless to pale yellow. It is immiscible with water although it is sparingly soluble in water and can dissolve up to 8% water. The chemical structure is $[\mathrm{P\ R_3R'}]^+\mathrm{Cl}^-$, where R = hexyl and R' = tetradecyl.

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

Resin Impregnation

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

1. the wet method,
2. the dry method,
3. the impregnation in the presence of a modifying agent, or
4. the dynamic method (13).

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 10 g of conditioned Amberlite XAD-7 with 25 mL of ketone for 24 hours (19). Varying amounts of Cyphos IL 101 diluted in ketone were added to resin slurry for 24 hours under agitation. The solvent was then slowly removed by evaporation in a roto-vapor.

The amount of extractant immobilized on the resin ($q_{\mathrm{Cyphos\ IL\ 101}}$) was quantified by mixing a known amount of impregnated resin (250 mg) with methanol (5 mL) for 24 hours, to remove the extractant by dissolving. The washing treatment was repeated once. Preliminary studies have shown that twice washing was sufficient for completely removing the extractant from the resins. The solvent was finally separated from the resin, which was dried at 100°C for 24 hours. The mass difference ($M_{\mathrm{Cyphos\ IL\ 101}}$) between impregnated ($M_{\mathrm{XAD\text{-}7/Cyphos\ IL\ 101}}$) and the washed resin ($M_{\mathrm{XAD\text{-}7}}$) was used to calculate the amount of extractant immobilized on the EIR:

$$q_{\mathrm{Cyphos\ IL\ 101}} = \frac{M_{\mathrm{XAD\text{-}7/Cyphos\ IL\ 101}} - M_{\mathrm{XAD\text{-}7}}}{M_{\mathrm{XAD\text{-}7/Cyphos\ IL\ 101}}} \qquad (1)$$

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 and 8 M. The extractant content in the EIR was varied between 25 and 580 mg g^{-1}. 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 at controlled temperature (20°C). 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 isotherms were performed using several impregnated resins (q: 100, 310 and 400 mg Cyphos IL 101 g^{-1} EIR) and Zn(II) solution (20–160 mg Zn L^{-1}) in HCl 3 M at controlled temperature (10°C, 20°C, and 40°C).

Sorption kinetics were performed by mixing Amberlite XAD-7 impregnated with Cyphos IL 101 (q: 88, 190, and 400 mg Cyphos IL 101 g^{-1} EIR) with a Zn(II) solution (20, 40, and 60 mg Zn L^{-1}) in HCl 3 M (m/V: 4 g L^{-1}). Agitation was maintained at 150 rpm all along the sorption process at controlled temperature (10°C, 20°C, and 40°C). Samples (less than 2.5 mL) were regularly collected and analyzed for residual Zn concentration. 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 0.1 g of EIR (q: 400 mg Cyphos IL 101 g^{-1} 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 M H_2SO_4; 0.1 M HNO_3; 0.1 M Na_2SO_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, 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. The desorption was operated in two successive and identical steps in order to improve the yield of metal release.

RESULTS AND DISCUSSION

EIR Characterization

Figure 1 shows the amount of Cyphos IL 101 loaded on the resin versus the initial amount of the extractant in the impregnation bath, with superimposition of the experimental points and the theoretical line (showing the Cyphos IL 101 content under the hypothesis of complete immobilization of the extractant under selected conditions). The good superimposition of the theoretical line with experimental results confirms the high efficiency of the impregnation process. Varying the amount of extractant in the impregnation bath produced EIRs whose loading varied between 25 and 580 mg Cyphos IL 101 g^{-1} EIR. At the highest concentrations of Cyphos IL 101, resin loading tended to level off at a value close to 1.12 mmol Cyphos IL 101 g^{-1} EIR. This is indicative of the maximum sorption capacity to be expected for metal recovery, depending on the stoichiometry of the extracted species. Increasing the amount of extractant would result in a partial release of the extractant from the saturated resin. In order to avoid possible extractant release during metal sorption,

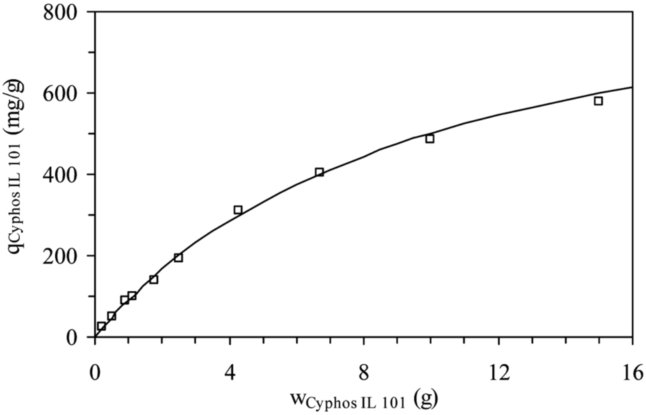


Figure 1. Influence of the amount of Cyphos IL 101 in the impregnation bath on its immobilization on Amberlite XAD-7 (m: 10 g). Line represents the theoretical values.

the impregnation yield was maintained at a lower level, except in the experiments on the influence of extractant loading on metal uptake performance.

These values are consistent with those obtained by other groups on the immobilization of extractants on Amberlite resins. Rovira et al. immobilized DEHTPA (di-(2-ethylhexyl)thiophosphoric acid) on Amberlite XAD-2 resin with extractant loadings varying between 0.24 and 1.14 mmol DEHTPA g^{-1} XAD-2 (33). Higher extractant loadings were reached by immobilizing Ionquest 801 (2-ethylhexylphosphonic acid mono-2-ethylhexyl ester) on Amberlite XAD-7, up tos 2.85 mmol Ionquest 801 g^{-1} XAD-7 (34). Lower values (i.e. 0.33 mmol LIX 79 g^{-1} Amberlite XAD-2) were cited for the immobilization of LIX 79 (alkylguanidine-type extractant) (35), and the immobilization of DEHPA (di-(2-ethylhexyl)phosphoric acid) on Amberlite XAD-2 (i.e. 0.6 mmol DEHPA g^{-1} XAD-2) (36). In the case of Cyanex 272 and Cyanex 302 impregnation in Amberlite XAD-2, Gonzalez et al. obtained values as high as 1.1 and 1.7 mmol extractant g^{-1} XAD-2, respectively (37). More recently, Navarro et al. reached Cyanex 921 loadings in Amberlite XAD-7 EIR as high as 1.5–1.7 mmol Cyanex 921 g^{-1} XAD-7 (38).

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). Raw resin hardly adsorbs zinc (the uptake efficiency was below 6%). Under comparable experimental conditions, the sorption efficiency exceeded 60% when resins where impregnated with Cyphos IL 101 at concentrations greater than 300 mg g^{-1}, on a wide range of HCl concentrations (i.e. 1–7 M). Most of the binding capacity of the EIR was due to Cyphos IL 101, though the proper binding potential of Amberlite XAD-7 can not be completely neglected.

Influence of HCl Concentration on Zn(II) Recovery

Figure 2 shows the influence of HCl concentration on the recovery of Zn(II) by EIR for different Cyphos IL 101 loadings under selected experimental conditions (T: 20°C; C_0: 20 mg Zn L^{-1}; m/V: 4 g L^{-1}). There was a continuous increase in the efficiency of the process with increasing resin loading. This enhancement of recovery efficiency was much greater at moderated extractant loading than at high content, where the differences for loadings greater than 400 mg g^{-1} were not very marked. Loading the

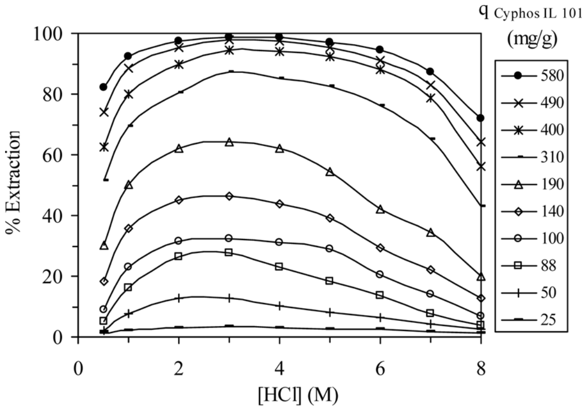


Figure 2. Influence of HCl concentration on Zn(II) recovery using Amberlite XAD-7/ Cyphos IL 101 for different extractant loadings. (C_0: 20 mg Zn L^{-1}; m/V: 4 g L^{-1}; T: 20°C).

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 HCl concentration was basically the same, regardless of Cyphos IL 101 content. A strong increase in Zn(II) recovery was observed when HCl concentration was increased from 0.5 M to 1 M. The efficiency continued to increase slightly up to 4 M HCl concentration. Above 4 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 chloride solutions (Fig. 3). In order to draw this diagram, the overall formation constants of Zn(II) chlorocomplexes reported by Belousov and Alovyainikov were used (β_1: 3.1, β_2: 1.1, β_3: 0.6, β_4 : 0.1) (39). At low HCl concentration (i.e. 0.5–2 M) the predominant Zn(II) species is the cationic complex $ZnCl^+$. When the concentration of HCl is increased to above 2 M, the quantity of cationic species becomes negligible while the anionic species $ZnCl_3^-$ predominates. The $ZnCl_4^{2-}$ species only predominates above 6 M HCl.

The extraction process can be described by the general reaction:

$$ZnCl_x^{2-x} + y\ L^+Cl^{-1} + w\ Cl^- \rightleftarrows (L^+)_yZnCl_z^{y-} \qquad (2)$$

where $ZnCl_x^{2\text{-}x}$ is the predominant species in solution, L^+Cl^- is the Cyphos IL 101 impregnated in the resin (L^+: tetraalkylphosphonium) and $(L^+)_yZnCl_z^{y-}$ is the Zn species adsorbed in the EIR. Two kinds of complexes can be extracted (i.e. $L^+ZnCl_3^-$ or $(L^+)_2ZnCl_4^{2-}$); this

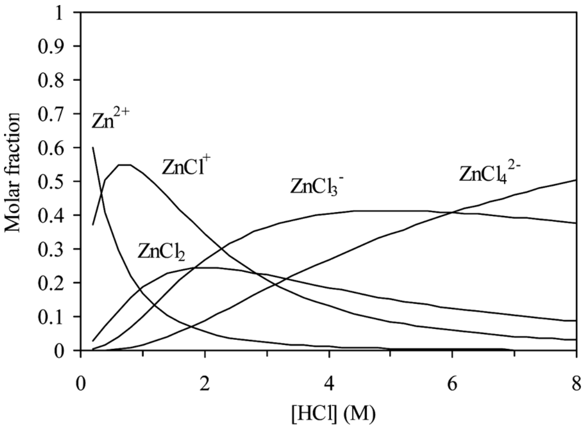


Figure 3. Zn(II) species distribution diagram in HCl solutions.

means that the number of chloride ions exchanged (w) may vary with the extracted species and the predominating Zn species. The stoichiometric ratio was determined using the method of slope analysis. Figure 4 shows the plot of log D versus log $q_{\text{Cyphos IL101}}$ for different HCl concentrations (in the range 0.5–8 M). The slopes were systematically close to 2 (Table 2), regardless of HCl concentration. For low extractant concentrations, a little deviation of the plot compared to the linear trend was observed, probably attributable to a small extraction of Zn(II) by the resin support. The value of the slope (i.e. close to 2) suggests that the extracted species

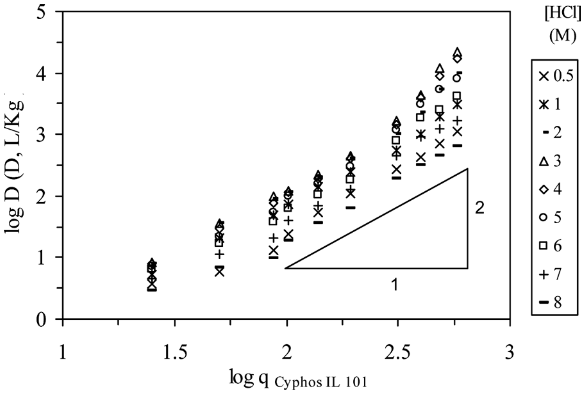


Figure 4. Influence of Cyphos IL 101 loading on the Zn(II) distribution coefficient for different HCl concentrations (C_0: 20 mg Zn L^{-1}; m/V: 4 g L^{-1}; T: 20°C).

Table 2. Linear regression for the plots log D vs. log q $_{\text{Cyphos IL 101}}$ and log D vs. log a $_{\text{HCl}}$ C_0: 20 mg Zn L^{-1}; m/V: 4 g L^{-1}; T: 20°C).

Log D vs. log $q_{\text{Cyphos IL 101}}$

[HCl] (M)	Slope	Intercept	R^2
0.5	1.94	– 2.42	0.976
1	1.97	– 2.08	0.995
2	2.17	– 2.24	0.983
3	2.46	– 2.73	0.971
4	2.43	– 2.73	0.976
5	2.30	– 2.59	0.982
6	2.14	– 2.42	0.977
7	2.00	– 2.35	0.981
8	1.81	– 2.27	0.976
Average	2.14	– 2.43	0.980

Log D vs. log $a_{\text{HCl.}}$ ([HCl] : 0.5–2 M)

q $_{\text{Cyphos IL 101}}$(mg g^{-1})	Slope	Intercept	R^2
25	0.43	0.75	0.998
50	1.05	1.27	0.927
88	1.09	1.65	0.933
100	0.88	1.82	0.909
140	0.75	2.11	0.912
190	0.76	2.39	0.955
310	0.77	2.77	0.984
400	0.97	3.04	0.995
490	1.16	3.35	0.997
580	1.25	3.57	1.000
Average	0.96	2.44	0.957

Log D vs. log a $_{\text{HCl}}$ ([HCl] : 3–8 M)

$q_{\text{Cyphos IL 101}}$ (mg g^{-1})	Slope	Intercept	R^2
25	– 0.32	1.19	0.846
50	– 0.54	1.96	0.969
88	– 0.75	2.56	0.942
100	– 0.61	2.61	0.877
140	– 0.59	2.82	0.919
190	– 0.65	3.18	0.935
310	– 0.70	3.80	0.899
400	– 0.85	4.36	0.884
490	– 1.10	4.93	0.962
580	– 1.20	5.26	0.967
Average	– 0.78	3.50	0.928

contained about two moles of Cyphos IL 101 per mole of metal extracted. This also means that $(L^+)_2ZnCl_4{}^{2-}$ is the most probable adsorbed species.

Figure 5 shows the plot of log D versus log a_{HCl} for EIR containing increasing concentrations of Cyphos IL 101 (i.e. 25–580 mg Cyphos IL 101 g^{-1} EIR), where a_{HCl} is the mean activity of H^+ and Cl^- ions. The slope of the linear section of the curve allows determining the number of chloride ions that are involved in metal sorption taking into account the impact of ionic strength. The mean activity coefficients used in this section were obtained from Robinson and Stokes (40). All the series show a similar trend, corresponding to a positive slope for low concentrations of HCl and a negative slope for high HCl concentrations. Table 2 summarizes the values obtained by linear regression for both 0.5–2 M (log a_{HCl}: -0.417–0.331) and 3–8 M (log a_{HCl}: 0.647–1.953) HCl concentrations. In the low HCl concentration range the slope was close to $+1$ (mean value: 0.96); this means more than two times higher than the level reached for the lowest Cyphos IL 101 loading (i.e. 25 mg L^{-1}). The value of the slope suggests that only one chloride ion was involved in the extraction reaction at low HCl concentration. Figure 3 shows that $ZnCl^+$ is the predominant species under selected experimental conditions. This makes possible suggesting that the extraction (involving two molecules of Cyphos IL 101 and 1 molecule of chloride ions per molecule of zinc) followed the reaction:

$$ZnCl^+ + 2L^+Cl^- + Cl^- \rightleftarrows (L^+)_2ZnCl_4^{2-} \qquad (3)$$

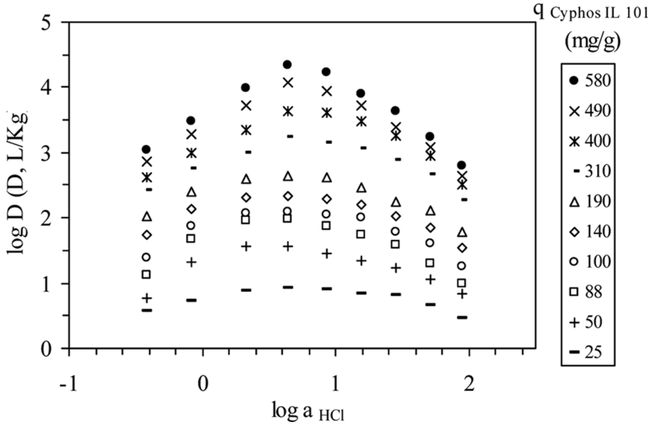


Figure 5. Influence of HCl activity on the Zn(II) distribution coefficient for different extractant loadings. (C_0: 20 mg Zn L^{-1}; m/V: 4 g L^{-1}; T: 20°C).

In the 3–8 M HCl concentration range (log a_{HCl}: 0.647–1.953), the plot of log D versus log a_{HCl} shows linear trends with slopes varying between -0.32 and -1.2. However, it is important to observe the strong decrease of the slope with high HCl concentrations, which was probably due to the co-existence of a number of different chloro-complexes of Zn(II) under selected experimental conditions. Under less concentrated HCl solutions the slope was close to -1, since the predominating Zn(II) species is $ZnCl_3^-$ and based on the contribution of two molecules of Cyphos IL 101 the reaction can be modeled according to:

$$ZnCl_3^- + 2L^+Cl^- \rightleftarrows (L^+)_2ZnCl_4^{2-} + Cl^- \qquad (4)$$

In the case of highly acidic solutions ([HCl] > 6 M), the predominance of $ZnCl_4^{2-}$ and the release of 2 molecules of Cl^- (slope close to -2) allows proposing the following reaction:

$$ZnCl_4^{2-} + 2L^+Cl^- \rightleftarrows (L^+)_2ZnCl_4^{2-} + 2Cl^- \qquad (5)$$

Regardless of HCl concentration range, it appears that the extracted Zn(II) species is $(L^+)_2ZnCl_4^{2-}$.

Further studies (currently in progress) have shown that other metal ions (Fe(III), Au(III), Hg(II), Pd(II), Pt(IV) ..) can be also extracted as chlorocomplexes. Competitive sorption of this kind of metal ions can affect the selectivity properties of Cyphos IL 101 impregnated in the resin. However, in some cases, selectivity can be improved controlling chloride concentration. Cationic metal ions are not extracted.

Sorption Isotherms

Influence of Cyphos IL 101 Loading on Zn(II) Sorption Isotherms

(Figure 6a) compares Zn(II) sorption isotherms for EIRs with different Cyphos IL 101 loadings. As expected, increasing the loading of Cyphos IL 101 on the resin increased its sorption capacity. The shape of the curve was the same, characterized by a sharp initial slope followed by a plateau. The sorption isotherms were modeled using the Langmuir equation:

$$q = \frac{q_m bC}{1 + bC} \qquad (6)$$

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

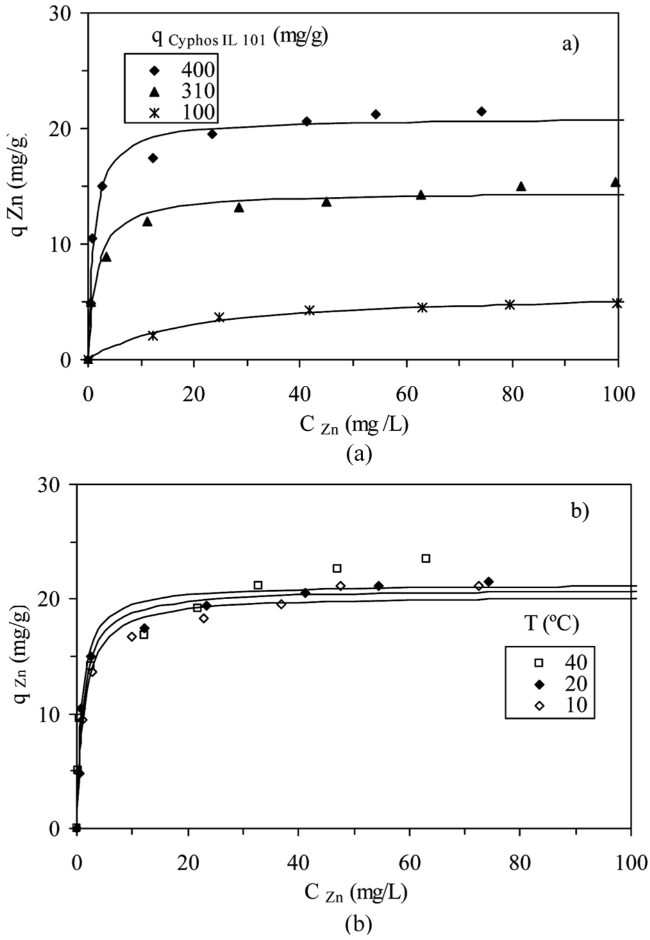


Figure 6. Zn(II) sorption isotherm. Line: modeling of experimental data using the Langmuir equation. (a) Influence of Cyphos IL 101 loading of the EIR [HCl]: 3M; T: 20°C; m/V: 4 g L^{-1}). (b) Influence of temperature [HCl]: 3M; m/V: 4 g L^{-1}; $q_{\mathrm{Cyphos\ IL\ 101}}$: 400 mg g^{-1}).

Table 3 gives the parameters of the model obtained for various extractant loadings at 20°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 Cyphos IL 101 loadings of 400 mg g^{-1} EIR (i.e. 0.771 mmol Cyphos IL 101 g^{-1} EIR), 310 mg g^{-1} EIR (i.e. 0.598 mmol Cyphos IL 101 g^{-1} EIR) and 100 mg g^{-1} EIR (i.e. 0.193 mmol Cyphos IL 101 g^{-1} EIR) were 20.9 mg Zn g^{-1} EIR (i.e. 0.320 mmol Zn g^{-1} EIR), 14.5 mg Zn g^{-1} EIR

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

T (°C)	$q_{Cyphos\ IL\ 101}$ (mg g^{-1})	q_m (mg g^{-1})	b (mg g^{-1})	R^2
20	100	5.84	0.056	0.990
20	310	14.5	0.647	0.969
20	400	20.9	0.912	0.977
10	400	20.3	0.797	0.974
40	400	21.3	1.13	0.954

(i.e. 0.222 mmol Zn g^{-1} EIR), and 5.84 mg Zn g^{-1} EIR (i.e. 0.089 mmol Zn g^{-1} EIR), respectively. The saturation of the extractant immobilized on the resin was similar for the 3 cases of EIRs. The stoichiometric molar ratios between Zn and Cyphos IL 101 at saturation on EIRs were 0.42, 0.37, and 0.46, respectively. This result is consistent with the stoichiometric ratio proposed for the extracted species (i.e. $(L^+)_2ZnCl_4$).

Influence of Temperature on Zn(II) Sorption Isotherms

The sorption isotherms were determined at different temperatures (10°C, 20°C and 40°C) under selected experimental conditions ([HCl]: 3 M; m/V: 4 g $L^{-1;}$ $q_{Cyphos\ IL\ 101}$: 400 mg Cyphos IL 101 g^{-1} EIR). Figure 6b shows Zn(II) sorption isotherms obtained under selected experimental conditions. The superimposition of the isotherms clearly demonstrates the poor impact of temperature on sorption performance. This result is consistent with the proposed ion exchange mechanism; indeed ion exchange processes are generally characterized by low ion exchange energies.

Uptake Kinetics

Uptake kinetics may be controlled by several steps including:

(a) film diffusion (external diffusion),
(b) intraparticle diffusion, or
(c) chemical reaction.

In most cases, binding in sorbents is controlled by diffusion mechanisms rather than the reaction rate; though some systems are 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 the 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) 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

Film Diffusion: $$F_1(X) = -\ln(1 - X) = f(t) \tag{7}$$

Particle Diffusion: $$F_2(X) = -\ln(1 - X^2) = f(t) \tag{8}$$

Shrinking Core Model

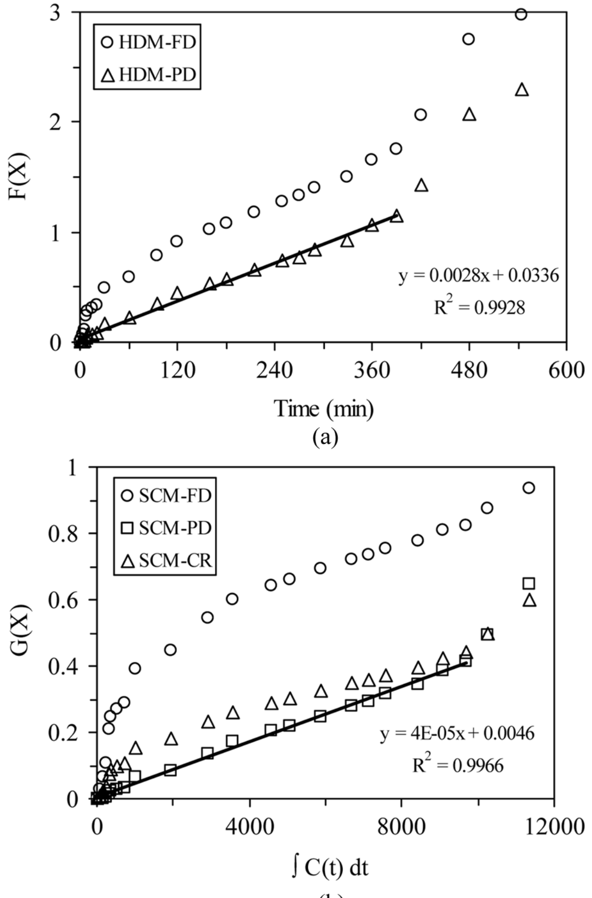
Film Diffusion: $$G_1(X) = X = g\left(\int_0^t C(t)dt\right) \tag{9}$$

Particle Diffusion: $$G_2(X) = 3 - 3(1 - X)^{2/3} - 2X = g\left(\int_0^t C(t)dt\right) \tag{10}$$

Chemical Reaction Rate: $$G_3(X) = 1 - (1 - X)^{1/3} = g\left(\int_0^t C(t)dt\right) \tag{11}$$

where X is the fractional approach to 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 considered the predominant limiting step.

Figure 7 shows an example of the modeling of experimental data according Equations (7–11). This figure clearly shows that the models based on film diffusion and chemical reaction limitations did not fit experimental data. In the case of the model based on intraparticle diffusion, the equation fitted well experimental data at low contact time



(a)

(b)

Figure 7. Testing of controlling diffusion mechanisms – Models of kinetics controlled by film diffusion, intraparticle diffusion and chemical reaction under homogeneous diffusion model (a) or shrinking core model (b) (C_0: 40 mg Zn L^{-1}; $q_{\text{Cyphos IL 101}}$: 190 mg g^{-1} EIR; v: 150 rpm, T: 20°C, [HCl]: 3M, m/V: 4 g L^{-1}).

(i.e. 6–8 hours) but some discrepancies were observed at longer contact times. A combination of resistance mechanisms would probably be more appropriate for simulating experimental data; however, in a first approximation the intraparticle diffusion model allows the comparison of diffusion properties in function of experimental parameters. Figure 8 shows the time course of residual concentration, varying the content of Cyphos IL 101 in the resin, the temperature and the initial concentration of Zn(II). The solid line on the figures shows the modeling of intraparticle diffusion model according the so-called Crank's equation, assuming that the resistance to film diffusion is negligible and that the solid is initially free of Zn(II) ions (46):

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

q(t) and q_{eq} are the concentrations of the metal in the resin at time t and equilibrium respectively. D_e is the intraparticle diffusion coefficient ($M^2\,min^{-1}$), r is the mean radius of resin particle (M), and q_n non-zero roots of the equation:

$$\tan q_n = \frac{3q_n}{3 + \alpha\, {q_n}^2} \tag{13}$$

$$\text{with} \quad \frac{q}{VC_o} = \frac{1}{1+\alpha} \tag{14}$$

These simplified model equations fitted well experimental data (Fig. 8). Twelve to fourteen hours of contact were necessary to reach equilibrium. This long contact time is significantly greater than the time required to reach equilibrium for liquid-liquid extraction with other metal systems (tetrachloroaurate) (47): 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).

As expected increasing Cyphos IL 101 content in the resin increased the volumetric density of reactive groups, which in turn decreased zinc residual concentration in the solution (Fig. 8a). The intraparticle diffusion coefficient slightly increased when increasing the content of Cyphos IL 101 from 88 to 190 mg Cyphos IL 101 g^{-1} EIR, before significantly decreasing when the Cyphos IL 101 content was increased to 400 mg Cyphos IL 101 g^{-1} EIR (Table 4). At high Cyphos IL 101 content, the saturation of the porous resin with Cyphos IL 101 may contribute to steric hindrance due to possible phenomena of aggregation of the Cyphos IL 101. The density of reactive groups allowed increasing the

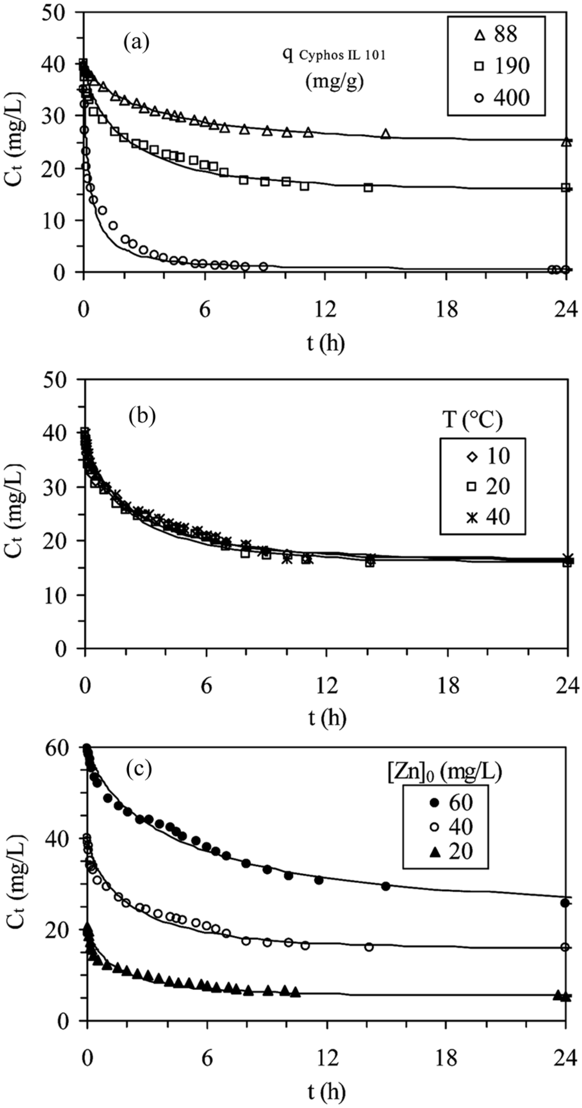


Figure 8. Modeling of extraction kinetics using the intraparticle diffusion equation: (a) Influence of Cyphos IL 101 loading of the EIR (T: 20°C; C_0: 40 mg L^{-1}); (b): Influence of temperature ($q_{\text{Cyphos IL 101}}$: 190 mg g^{-1}, C_0: 40 mg L^{-1}); (c): Influence of Zn(II) concentration ($q_{\text{Cyphos IL 101}}$: 190 mg g^{-1}, T: 20°C). [HCk]: 3M, m/V: 4 g L^{-1})

amount of metal to be sorbed but at the expense of a relative limitation of their accessibility.

Changing the temperature did not affect equilibrium distribution of Zn(II) between solution and solid phase as shown on Fig. 6b, this parameter did not affect the kinetic profile. The superimposition of the time course of residual concentration proves that the sorption process was not driven by temperature effects. The intraparticle diffusion coefficients remained in the same range of values (5.3 10^{-11}–5.8 $10^{-11}\,m^2\,min^{-1}$, see Table 4).

The last panel of Fig. 8 shows the impact of Zn(II) concentration on kinetic profiles. Increasing the initial concentration increased the time required to reach equilibrium due to the decrease of the molar ratio between reactive groups and metal ions. This is confirmed by the progressive decrease of the intraparticle diffusion coefficient when increasing metal concentration (Table 4). While the differences for intraparticle diffusion coefficients between 20 and 40 mg Zn L^{-1} were negligible (5.9 10^{-11} and 5.8 $10^{-11}\,m^2\,min^{-1}$), when increasing initial metal concentration to 60 mg Zn L^{-1}, the drop of the intraparticle diffusion coefficient was more significant (down to 2.7 $10^{-11}\,m^2\,min^{-1}$). Juang and Lin investigated the recovery of Zn(II) from acidic solutions using Amberlite XAD-2 and Amberlite XAD-4 resins impregnated with bis(2-ethylhexyl)-phosphoric acid (D2EHPA): they found intraparticle diffusion coefficient in the range 1 10^{-10}–1.9 $10^{-11}\,m^2\,min^{-1}$, this means 5 to 10 times greater than in the present system (48,49). Serarols et al. used Amberlite XAD-2 resin impregnated with DEHPA for the binding of zinc from HCl solutions; they obtained intraparticle diffusion coefficients in the range 1.2 10^{-11}–8.4 $10^{-11}\,m^2\,min^{-1}$ (50). These values are consistent with those obtained with Cyphos IL 101-impregnated resin.

Table 4. Intraparticle diffusion coefficients of Zn (II) on the XAD-7 resin impregnated with Cyphos IL 101 ([HCl]: 3M, m/V: 4 g L^{-1}).

$q_{Cyphos\ IL\ 101}$ (mg g^{-1})	T (°C)	C_0 (mg L^{-1})	Diffusion coeff. $D_e{}^{*}10^{11}$ ($m^2\ min^{-1}$)
88	20	40	4.9
190	20	40	5.8
400	20	40	1.2
190	10	40	5.3
190	40	40	5.5
190	20	20	5.9
190	20	60	2.7

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 HNO_3, 0.1 M H_2SO_4, and 0.1 M Na_2SO_4. These solutions allowed a significant recovery of Zn(II) from loaded resins. The desorption was probably due to the destabilization of zinc chlorocomplexes when the loaded resin was immersed into chloride-free solutions. However, in most cases zinc recovery was not complete during the first desorption step, probably due to the presence of residual chloride ions in the matrix of the resin. During the second step of the desorption process (the resin being completely washed off from chloride ions), it was possible to completely remove the metal from the EIR. At each sorption/desorption cycle, the sorption step (S) was followed by two desorption steps (DI and DII) and the results obtained over five cycles are reported on Fig. 9. The figure shows that

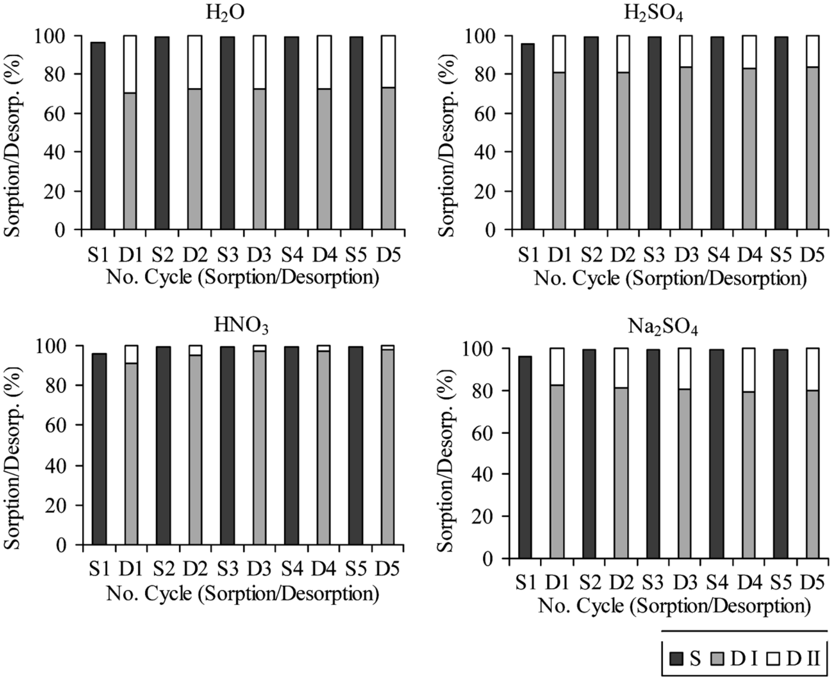


Figure 9. Sorption and desorption of Zn(II) from loaded EIR using water, 0.1 M H_2SO_4, 0.1 M HNO_3, and 0.1 M Na_2SO_4, over 5 sorption/desorption cycles.

Table 5. Sorption (S) and desorption (DI, D II and D_t) of Zn(II) from loaded EIR using water, 0.1 M HNO_3, 0.1 M H_2SO_4, and 0.1 M Na_2SO_4. Average of 5 sorption/desorption cycles

Eluent	S (%)	D I (%)	D II (%)	D_t (%)
H_2O	98.6	72.2	27.7	99.9
H_2SO_4 0.1 M	98.6	82.7	17.2	99.9
HNO_3 0.1 M	98.6	95.7	4.3	100.0
Na_2SO_4 0.1 M	98.4	80.7	19.3	99.9

except in the case of nitric acid, for which the first desorption step recovered more than 95% of zinc previously adsorbed, the second step represented about 20% of the total metal removal. The eluents can be ranked according the following scale:

$$HNO_3 >> H_2SO_4 \approx Na_2SO_4 > H_2O$$

Despite the less efficient desorption of water compared to other eluent it is important to observe that after two desorption steps it was also possible to reach a complete recovery of the metal. This figure also shows that sorption and desorption performances were maintained without significant difference over 5 cycles. Table 5 shows the percentage of sorption (S) and the percentages of desorption at step 1 and 2 (DI and DII) as well as the total desorption (D_t); the values presented on this table represent the average values obtained over the five cycles. The mean value for sorption was systematically higher than 98%, though some differences can be detected between the different eluents as pointed out above, after the second desorption step the desorption was complete, regardless of the eluent.

CONCLUSION

The impregnation of Amberlite XAD-7 with Cyphos IL 101 enables the preparation of an efficient EIR for Zn(II) recovery from HCl solutions. The Zn(II) was extracted as anion chlorocomplex ($ZnCl_4^{2-}$) by ion exchange mechanism. Under selected experimental conditions (Cyphos IL 101 content greater than 300 mg g^{-1} EIR), removal yields greater than 60% were obtained for HCl concentrations ranging between 1 and 7 M, with maximum extraction in the range 2–4 M HCl. The maximum sorption capacity was close to 20 mg Zn(II) g^{-1} EIR (i.e. 0.40 mol Zn(II) mol^{-1} Cyphos IL 101). The maximum sorption capacity and the affinity coefficient in the Langmuir equation that best fitted experimental data increased with Cyphos IL 101 content, while these parameters were almost not affected by the temperature.

The impact of the content of Cyphos IL 101 in the resin, the temperature, and the zinc concentration on kinetic profiles were studied. Temperature (in the range 10–40°C) did not affect sorption kinetics. The intraparticle diffusion coefficients ranged between $1.2\ 10^{-11}$ and $6\ 10^{-11}\ m^2\ min^{-1}$ for selected experimental conditions. Increasing the amount of Cyphos IL 101 in the resin from 190 to 400 mg Cyphos IL 101 g^{-1} EIR decreased the diffusion coefficient from $5.8\ 10^{-11}$ to $1.2\ 10^{-11}\ m^2\ min^{-1}$.

Zinc(II) was very efficiently desorbed from loaded EIR using 0.1 molar solutions of Na_2SO_4, H_2SO_4 or HNO_3 and even water. Desorption greater than 99% were obtained and sorption and desorption efficiencies were maintained almost constant over five sorption/desorption cycles.

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