On the selective separation of metal ions from hydrochloride aqueous solution by pertraction through supported ionic liquid membranes

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ABSTRACT

Previously, we reported the use of imidazolium and ammonium based ionic liquids in the absence of chelating agents for the selective liquid–liquid extraction of Zn(II), Cd(II), Cu(II), and Fe(III) from hydrochloride aqueous solutions. It was found that the ionic liquid methyltrioctylammonium chloride, $[MTOA^+][Cl^-]$, allowed the almost complete removal of Zn(II), Cd(II), Fe(III) and Cu(II) from the aqueous solutions. In this work, supported ionic liquid membranes based on methyltrioctylammonium chloride were used in an pertraction process for the selective extraction of Fe(III), Zn(II), Cd(II) and Cu(II). The influence of the composition of the receiving phase (milliQ water or Na_2CO_3, 0.1 M; or NH_3,6 M) in the pertraction process was analyzed. It was found that Milli-Q water and Na_2CO_3 allowed the recovery of Zn (II), Fe(III), reaching pertraction factors (*PFs*), defined as the ratio between the concentration of the target metal ion in the receiving and the feed phase, of up to 373 for Zn(II), using Na_2CO_3 as receiving phase at 48 h and 9 for Fe(III), using Milli-Q water at 31 h. The use of NH_3 (6 M) allowed the recovery of Cd(II), with a PF of 15.1 at 24 h. Therefore, by modifying the stripping composition, the selective separation of the target metal ions can be reached. It is worthy to highlight the remarkable stability of the obtained supported ionic liquid membranes.

1. Introduction

Current industrial and academic researchers are focusing on promoting wastes recycling for their re-use in some industrial applications. Some of these wastes have a metallic nature. For instance, the galvanic industry produces a spent pickling hydro-chloric acid effluent with a high concentration of Zn(II), Fe(III) and traces of other heavy metals [1]. Electronic devices are another source of metallic wastes. Their incineration is risky for the environment and human health. In the European Union, the emissions derived from electronic wastes incineration are quanti- fied in 36 t per year of mercury and 16 t per year of cadmium [2]. On the other hand, the major component of solid wastes of metallurgical zinc industries is copper. The process gives a sludge, which contains copper as main component together with other metal ions such as cadmium, lead, nickel, cobalt and iron. The selective extraction and separation of these metal ions from their mixed solutions is of great interest in hydrometallurgical processes because of the possibility of recovering the valuable metals, as well as addressing the environmental pollution problems [1,2].

Several technologies can be used to remove toxic metals from liquid effluents, including precipitation, solvent extraction, ion exchange, etc. [3,4]. Most of these methods are technically demand- ing, involve considerable energy cost and/or result in large amounts

of waste solvents. Membrane-based separation processes have been recognized as a promising alternative to overcome these drawbacks, since they do not require high energy consumption for their operation and because they can be conducted under moderate operating conditions and sequential operation. Among membrane- based separation processes, the use of supported liquid membranes (SLMs) has received growing attention during recent decades [5]. In supported liquid membranes (SLMs), usually an organic liquid is imbedded in small pores of a polymeric support and is kept there by capillary forces. The advantages of this technology are a relatively small volume of the organic solvent and carrier in the membrane, which make possible to use expensive carrier, simultaneous extrac- tion and re-extraction steps, high separation factors, easy scale-up, low energy requirements, modest operation conditions and low capital and operating costs [6,7]. However, despite all these advantages, the SLM technique is not fully utilized commercially at high scale, primarily due to its progressive performance decay with time. Various mechanisms have been proposed to explain the SLM instability: the loss of organic phase from the membrane through evaporation or dis- solution into the surrounding liquids, liquid migration due to pressure differences or osmotic pressure gradients [8,9] and emulsion formation [10] or attrition of the organic film [10–12] due to lateral shear forces. Consequently, the SLM stability may also be affected by the chemical nature and textural properties of polymeric support, the type of organic solvent used in the studied process, the preparation method [13,14], etc., while the time periods for observed instability varies from a few hours to several months depending on the system [8,9]. Many research groups have achieved SLMs with improved stability by a variety of means, including polymerization of the top layers [15], gelation of a liquid membrane [9,16], and interposition of a highly permeable material [17].

A new approach to improve the stability of supported liquid membranes is to use the ionic liquid as liquid phase in supported liquid [18,19]. Ionic liquids (ILs) are organic salts remaining as liquids under room temperature. They normally consist of an organic cation (e.g. imidazolium, pyridinium, pyrrolidinium,phos- phonium, ammonium), and a monoatomic or polyatomic inorganic anion (e.g. chloride, tetrafluoroborate, hexafluorophosphate) or, more and more current, an organic anion (e.g. trifluoromethylsul- fonate, bis[(trifluoromethyl)sulfonyl]imide) [20]. The main advan- tage of these media over organic solvents are their near-zero vapor pressure, their good chemical and thermal stabilities, their typical high viscosity and the fact that their solubility in the surrounding phases can be controlled by adequate selection of the cation and anion. All these unique properties of ionic liquids result in a more stable membrane phases [19,21]. Indeed, the application of ionic liquid membrane technology has received growing attention during the last decade [22], being applied to the selective trans- port of organic compounds such as amines, alcohols, organic acids, ketones, ethers, and aromatic hydrocarbons[23–28] mixed gases [29,30] and metal ions [31–36].

In a previous work, the liquid–liquid extraction of Zn(II), Cd(II), Fe(III) and Cu(II) from aqueous hydrochloride solutions using ionic liquids in the absence of chelating agents was analyzed [37]. It was found that the ionic liquid methyltrioctylammonium chloride, [MTOA$^+$][Cl$^-$], allowed almost complete removal of Zn(II), Cd(II), Fe(III) (extraction percentage4 94) and Cu(II)(extraction percentage∼80) from the aqueous solutions. These results indicate that the use of ionic liquids as an alternative to traditional extraction agents in liquid/liquid extraction of heavy metal ions is very promising. The present work aims to carried out the selective separation of Fe(III), Zn(II), Cd(II) and Cu(II) from hydrochloride aqueous solution by pertraction through a flat sheet supported ionic liquid membranes in the absence of a chelating agent. For this study, the ionic liquid

methyltrioctylammonium chloride was used as ionic liquid phase. The influence of the pH and the composition of feed and received phases on the metal ions separation were analyzed.

2. Experimental

2.1. Chemicals

A polymeric membrane of 25 mm diameter from Millipore S.A. (Madrid, Spain) was used as support with the following specifica- tions: Nylons HNWP -hydrophilic polyamide membrane- with a pore size of 0.45 mm, thickness of 170 mm and weight 0.0256 g. The ionic liquid methyltrioctylammonium chloride, [MTOA+][Cl−] (purity 497%, water content 31% mass) was purchased from Sigma-Aldrich-Fluka Chemical Co. (Madrid, Spain). Solvents and other chemicals were purchased from Sigma-Aldrich-Fluka Che- mical Co. (Madrid, Spain), and were of the highest purity available.

2.2. Preparation of supported liquid membranes

The preparation of supported liquid membranes was described in detail previously [38]. In brief, immobilization involved placing the membrane in a 10 mL AmiconTH ultrafiltration unit, to which 3 mL of ionic liquid was added before applying a nitrogen pressure of 2 bar. Pressure was released once a thin layer of ionic liquid appeared on other side of membrane, indicating that all the pores were presumably full. Then, the membrane was left overnight in vertical position to remove by gravity all the excess ionic liquid located from the membrane surface. The IL content in the resulting SLMs was aprox. 151.5 g m−2 and the thickness was aprox. 191 mm.

2.3. Transport studies

The transport of Zn(II), Cd(II), Cu(II), and Fe(III) through the SLMs at 303.15 K was evaluated using the experimental setup shown in Fig. 1. The experimental setup consisted on a glass diffusion cell with two independent compartments, 30 mL each, separated by the SLM. O-rings were inserted on each side of the SLM. The entire assembly was held together by a threaded connector. Both compartments were mechanically stirred. In each experiment, the initial solute concentrations in the feed phase were 0.1 g/l of Fe(III), Zn(II), Cd(II) and/or Cu(II), in hydro- chloric acid (1 M). Either MilliQ-water or sodium carbonate (0.1 M) or ammonia (6 M) was used as receiving phase. The transport experiment was begun by adding 30 mL of each solution to their respective compartments. The solute concentrations were mon- itored by atomic absorption spectrophotometry, sampling 100 mL of each compartment at regular time intervals as described in the section 2.4. Sampling ceased when the metal ion concentrations in both phases were stabilized. The efficiency of the pertraction was evaluated by the pertrac- tion factor (PF), which was calculated by the following equation Eq. (1):

$$PF = \frac{C_{rM}}{C_{fM}} \qquad (1)$$

where C_{rM} and C_{fM} refer to concentration of the metal ion M in the receiving phase and in the feed phases, respectively. Determi- nations were made in triplicate to ensure the repeatability of the tests and mean values are reported. The repeatability of the assay, measured by the relative standard deviation, was 3% or less. Furthermore, a separation factor ($\alpha_{M1/M2}$) was determined as a numerical criterion to compare the ability of the ionic liquids to separate the target metal ions Eq. (2).

$$\alpha_{M1/M2} = \frac{C_{rM1}/C_{fM1}}{C_{rM2}/C_{fM2}} \qquad (2)$$
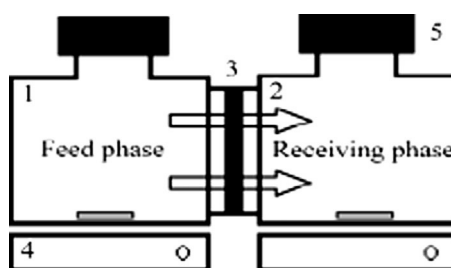

Fig. 1. Schematic illustration of the glass diffusion cell set up with two independent compartments used for experiments: (1) feed solution containing solutes; (2) receiving solution containing fresh solvent; (3) supported liquid membrane; (4) magnetic stirrer; and (5) septum.

where $C_{r,M1}$ and $C_{r,M2}$ are the concentration of the metal ions M_1 and M_2 in the receiving phase, respectively, and $C_{f,M1}$ and $C_{f,M2}$ are the concentration of the metal ions M_1 and M_2 in the feed phase, respectively. This parameter indicates the process efficiency in separating the metal ions: the higher $\alpha_{M1/M2}$, the more selective it is in separating the target metal ions.

2.4. Analytical method

The uptake of metal ions was monitored by removing samples of the aqueous solutions periodically for analysis. Atomic absorp- tion spectrophotometry (Varian spectra AA model) was used for the determination of metals (Zn(II), Cd(II), Cu(II), and Fe(III)). All aqueous solutions were prepared using deionised water.

3. Results and discussion

3.1. Pertraction of Fe(III), Zn(II), Cd(II) and Cu(II) from a HCl 1 M solution with a SILM using milli-Q water as receiving phase

As commented above, it has been demonstrated in liquid–liquid extraction experiments that the ionic liquid [MTOA+] [Cl−] allowed almost complete removal of Zn(II), Cd(II), Cu(II), and Fe(III) [37]. For this reason, this ionic liquid has been chosen as liquid phase in supported liquid membranes and the resulting membranes has been used for analyzing the selective separation of Fe(III), of Zn(II), Cd(II) and Cu(II). In the first set of experiments the feed phase consists in a solution of each metal ion (100 ppm) in HCl 1 M and the receiving phase was milliQ-water with a pH= 6. Fig. 2 shows the metal ions concentration and pH profiles in feed and receiving phases in the transport of Fe(III), Zn(II), Cd(II) and Cu(II) through a SILM based on [MTOA$^+$] [Cl$^-$]. As can be seen in Fig. 2a, the concentration of Fe(III) in the feed phase continuously decrease until a minimum value of about 10 ppm, reached at 31 h. Thereafter, the metal ion concentration in this phase increased until about 40 ppm. In the receiving phase, initially the concentration of

Fe(III) increased up to a concentration of about 90 ppm, reached at 31 h, which is concomitant to the decreasing of the concentration of this metal ion in the feed phase. Then the maximum metal ion concentration decreases to 40 ppm, equaling the concentration in the feed phase. The results are therefore very satisfactory because the supported liquid membrane based on the ionic liquid [MTOA$^+$] [Cl$^-$] allows the separation of Fe(III) almost entirely in receiving phase at 31 h.

The aim of the pertraction process is to separate the metal ions in the receiving phase. To evaluate the metal ions recovery in the receiving phase the pertraction factor (PF) parameter is used, defined as the ratio between the concentration of a given metal ion in the feed phase and the concentration of this metal ion in the receiving phase. Therefore, the higher this parameter is, the higher efficiency in the recovery of this metal ion in the receiving phase is. Fig. 3 shows the evolution of this parameter with time for Fe(III), Zn(II), Cd(II) and Cu(II). The maximum of this representa- tion indicates the time at which the experiment should be stopped to achieve the greatest efficiency in the recovery of this metal ion. As can be seen in Fig. 3a, the pertraction factor of Fe(III) increases with time reaching a maximum value at 31 h (PF= 8.9), after which it decreases to values approaching to PF= 1, therefore, equaling the concentrations the metal ion in the feed and receiving phases.
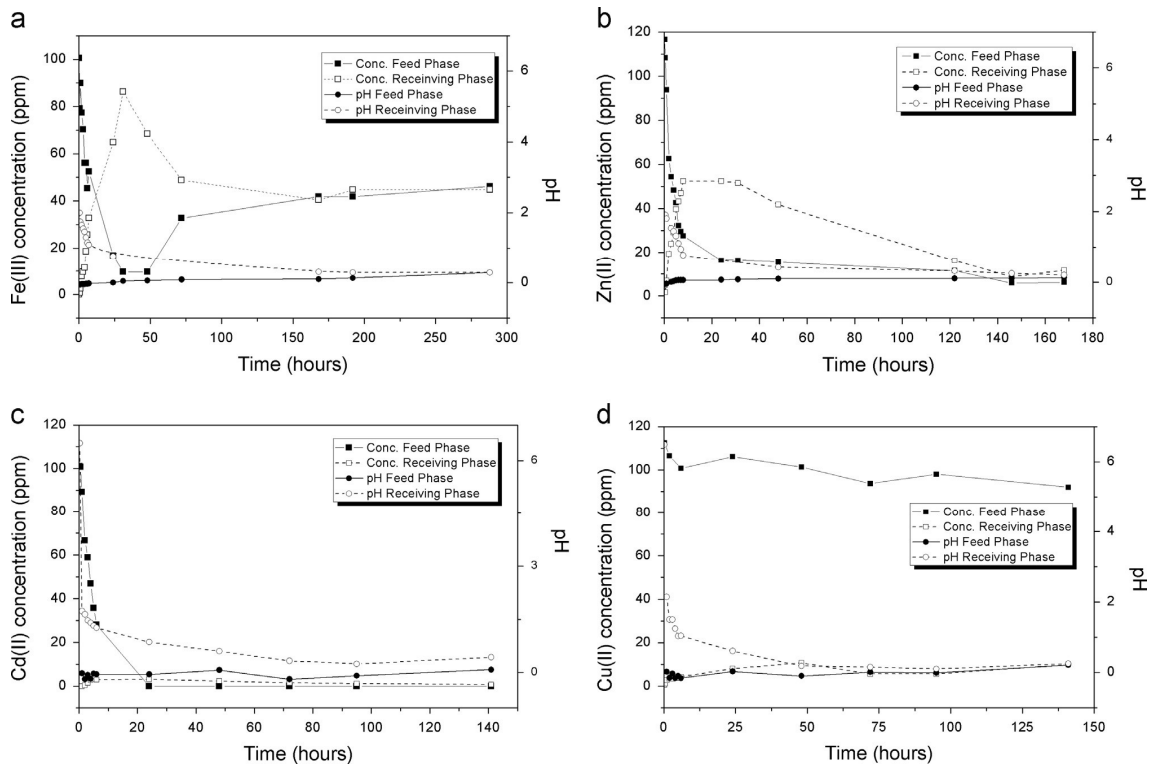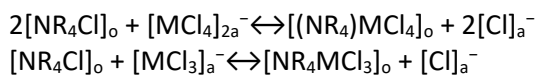

Fig. 2. Metal ions concentration (square symbols) and pH (circle symbols) profiles in the feed (full symbol) and receiving (empty symbol) phases in the transport of (a) Fe(III), (b) Zn(II), (c) Cd(II) and (d) Cu(II) through a supported liquid membrane based on [MTOA$^+$][Cl$^-$]. The initial concentration of metal ions in the feed phase was 0.1 g/L in HCl 1 M. Receiving phase was milli-Q water.

In the case of [MTOA+][Cl-], which is a quaternary amine, the extraction mechanism could be ion exchange, as proposed by Juang et al. [39] for the extraction as Zn(II) and Cd(II) from chloride solutions with Aliquat 336. The proposed mechanism is given by the following equations:

$$2[NR_4Cl]_o + [MCl_4]_{2a}^- \leftrightarrow [(NR_4)MCl_4]_o + 2[Cl]_a^-$$
$$[NR_4Cl]_o + [MCl_3]_a^- \leftrightarrow [NR_4MCl_3]_o + [Cl]_a^-$$

On the other hand, it was found that for imidazolium-based ionic liquids, specifically [omim$^+$][PF$_6^-$], an increase in HCl con- centration leads to an improvement in the extraction

efficiency for Zn(II), Fe(III) and Cd(II) but not for Cu(II). This fact suggests that, in the case of imidazolium-based ionic liquids, hydrochloric acid could be involved in the extraction of the metal ions [37]. In the present experiments, having in mind that the pertraction process of Fe(III) by using a membrane based on [MTOA$^+$][Cl$^-$] is achieved using a hydrochloric acid solution in the feed phase and a more basic solution (milli-Q water) in the receiving phase, the difference in HCl concentration between the feed and receiving phase allows that the concentration of the metal ion in the receiving phase was higher than the equilibrium concentration (50% of the initial concentration of the metal ion in the feed phase). For that, the extraction process in the membrane could involve the action of hydrochloric acid while in the stripping phase could take places the breakup of the compound based on the metal ions/IL/ hydrochloric acid formed. Therefore, the transport driving forces are the difference ion metal concentration and HCl concentration between feed and receiving phase.

Although, initially the concentration of HCl in the feed phase is 1 M (pH= 0) and in the receiving phase (pH= 6) no HCl is present, with time the hydrochloric acid of the feed phase passes to the receiving phase until the pH was equalized in both phases resulting the same pH in both phases (pH= 0.3). This fact would explain the equalization of the concentrations of Fe(III) in the feed in and receiving phases at the end of the experiment. On the other hand, it is worthy to note that if a mass balance between the feed or receiving phase is made, the amount of metal ion is lower than the initial amount of metal ion in the feed phase.
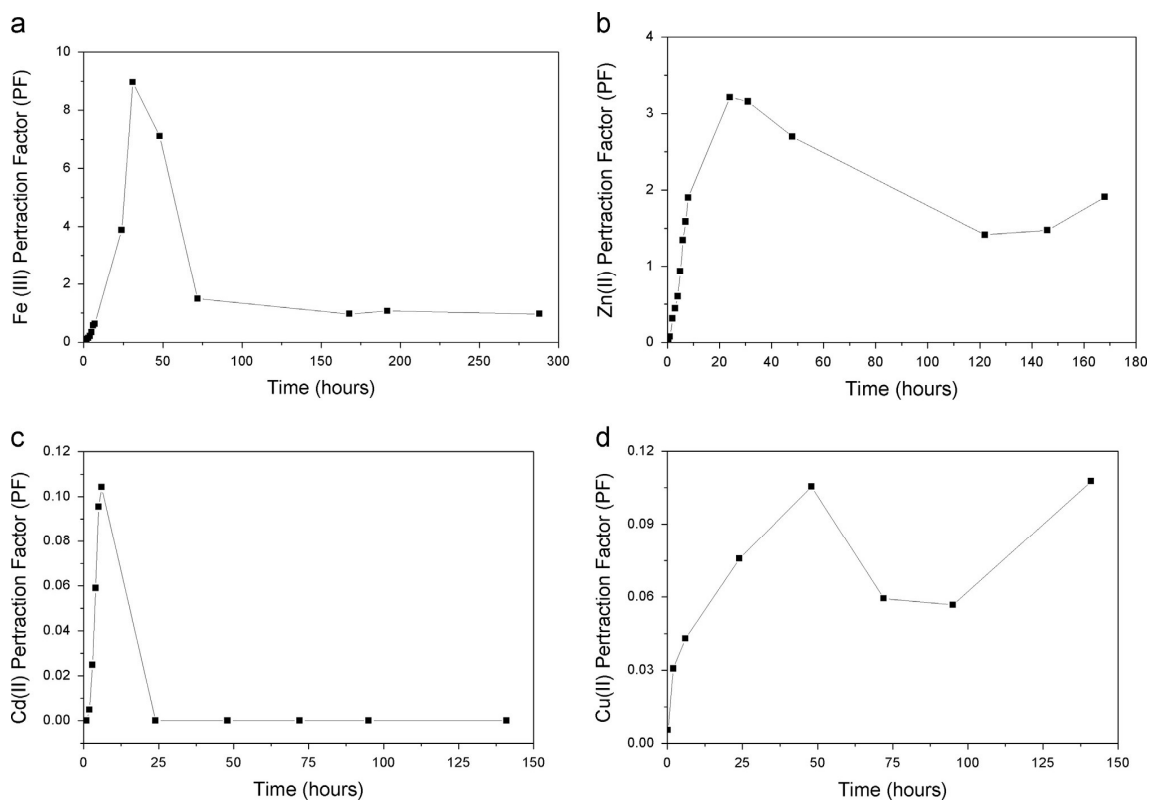

Fig. 3. Evolution over time of the Pertraction Factor (PF) of (a) Fe(III), (b) Zn(II), (c) Cd(II) and (d) Cu(II) using the Nylons®-[MTOA$^+$][Cl$^-$] supported ionic liquid membrane.

The reduction of amount of metal ions could be explained by two reasons: (i) because part of the metal ion remains absorbed in the ionic liquid phase immobilized in the membrane or (ii) because part of the Fe (III) ion has been precipitated in the feed or receiving phase. In order to evaluate those hypotheses, the software "medusa" (⟨http://www.kemi.kth.se/medusa/⟩) has

been used. This software determines the predominant species as a function of the pH and the metal ion concentration in the medium. Fig. 4a shows the predominant area diagram for Fe(III) in which reflects the predominant species of this metal ion as a function of pH (in the pH range −1 to 13) and metal ion concentration in the medium. The concentration range studied was from log [Fe(III)] =−7 (in which case the concentration of Fe(III) is equivalent to zero) until log [Fe(III)] =−2, since the logarithm of the initial concentration of Fe(III) is log [Fe(III)] =log [0.0018] =−2.74., which is the maximum concentration reached in the feed or receiving phase.

As can be seen in Fig. 4a, the ion Fe(III) precipitates as Fe_2O_3 (hematite, a red precipitate) at pH > 1 for high Fe(III) concentrations and at pH > 2.5 for low Fe(III) concentrations. Since the final pH in the feed and receiving at the end of the experiment was pH= 0.3, Fe(III) would be found in solution. Therefore, the deviation from the compliance of the mass balance would be due to the absorption Fe(III) in the supported ionic liquid membrane. Fig. 2b shows the evolution of the concentration of Zn(II) and the pH in the feed and receiving phases in the same operating conditions as the previous assay and using a supported liquid membrane based on [MTOA$^+$][Cl$^-$]. It was found that the metal ion Zn(II) presented the same behavior that Fe(III) (Fig. 2a). Initially, the metal ion decreases in the feed phase and increases in the receiving phase. Attending the value of the pertraction factor (PF) shown in Fig. 3b, the optimal operation time for Zn(II) recovery is about 24 h, which corresponds with the highest value for the pertraction factor (PF = 3.2). After this maximum, metal ion concentrations in both compartments tend to equalize due to the equalization of the HCl concentration in both compartments.

The mass balance of Zn(II) in the feed and receiving phase shows a decrease in the metal ion concentration with time. As can be seen in the Zn(II) predominant area diagram (Fig. 4b), Zn(II) begins to precipitate at pH >7, never reached in this assay. Therefore, the loose of Zn(II) detected with the mass balance is not due to the precipitation of the metal ion but to retention of the metal ion in the supported ionic liquid membrane. The transport of Cd(II) was also analyzed through a Nylons®- [MTOA$^+$][Cl$^-$] supported ionic liquid membrane. Fig. 2c shows the concentration profiles of this metal ion in feed and receiving phases, and the pH profile. As can be seen in Fig. 2c, Cd(II) concentration in the feed compartment continuously decrease until near zero at 24 h. Nevertheless, the concentration of this metal ion in the receiving phase only reached a maximum of 3 ppm. In a previous work [40], it was proved that [MTOA$^+$][Cl$^-$] allows the entire extraction of Cd(II) in the same conditions.

Furthermore, having into account the pH profile showed in Fig. 2c and the predominant area diagram for this metal ion (Fig. 4c), the decrease in Cd(II) concentration was not due to precipitates formation in the receiving phase. Therefore, we conclude that Cd(II) is retained in the supported ionic liquid membrane. Fig. 2d shows that almost no Cu(II) was extracted from the feed phase using the same conditions assayed for the other three metal ions. Pertraction Factor (PF) increased slightly from the beginning of the experiment, reaching a maximum value of 0.1 (see Fig. 3d). Mass balance was also practically constant during the entire assay, no observing Cu(II) accumulation in the liquid membrane. The behavior of pH was similar to the other experiments. It increased in the feed phase and decreased in the receiving phase due to the transport of HCl, reaching the same pH in both compartment at the end of the experiment. The results found in the case of Cu(II) was unexpected, having in mind that in a previous work [37] the extraction of Cu(II) with [MTOA$^+$][Cl$^-$]was around 80% at the same conditions assayed in this paper. It could be due to the fact that the amount of ionic liquid immobilized in the membrane is not enough for an effective extraction of the Cu(II) contained in the feed phase.
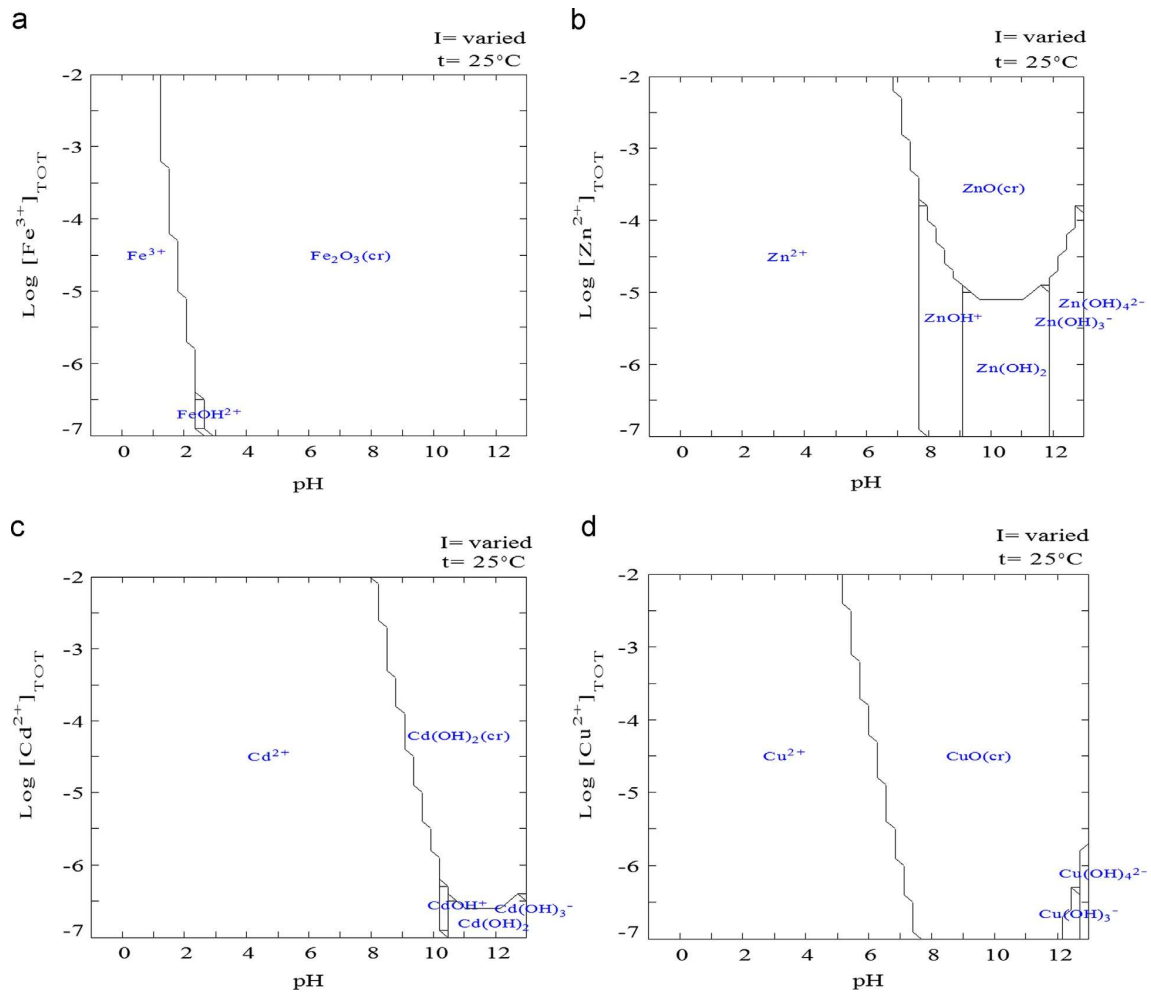
Fig. 4. Predominant area diagram for (a) Fe(III), (b) Zn(II), (c) Cd(II) and (d) Cu(II) (⟨http://www.kemi.kth.se/medusa/⟩).

The fluxes of the metal ions through the membranes were calculated from the initial slope of the metal ion concentration profiles (see Table 1). As can been seen the higher flux were reached by Fe (III) and Zn(II) (2.62 and 3.73 g m^{-2} s^{-1}, respectively), while much lower fluxes were reached in the case of Cd(II) and Cu (II) (0.37 and 0.32 g m^{-2} s^{-1}, respectively). Once studied the pertraction processes for the metal ions Fe(III), Zn(II), Cd(II) and Cu(II) separately, an assay was carried out with a mixture of the four metal ions (0.1 g/L of each) in HCl 1 M at the same operation conditions using the same SILM. This experiment was carried out to check if the presence of other metal ions in the medium could significantly affect the extraction of a given metal ion. Fig. 5 shows separately the concentration profiles of the four metal ions and the pH profiles in both the feeding and receiving phase.

Table 1. Initial fluxes of metal ions through supported liquid membranes based on [MTOA⁺] [Cl⁻] using different receiving phases.

Metals ion	Initial flux ($\times 10^3$) (g m^{-2} s^{-1})					
	MilliQ-water individual	Na$_2$CO$_3$ (0.1 M)		NH$_3$ (6 M)		
		mixture	individual	mixture	individual	mixture
Fe(III)	2.62	1.20	2.11*	2.38*	–	0*
Zn(II)	3.73	2.78	0.95*	0.81*	–	0.54
Cd(II)	0.37	0.32	0.41	0.36	2.27	1.77
Cu(II)	0.32	0.03	0.47	0.46	–	0.76

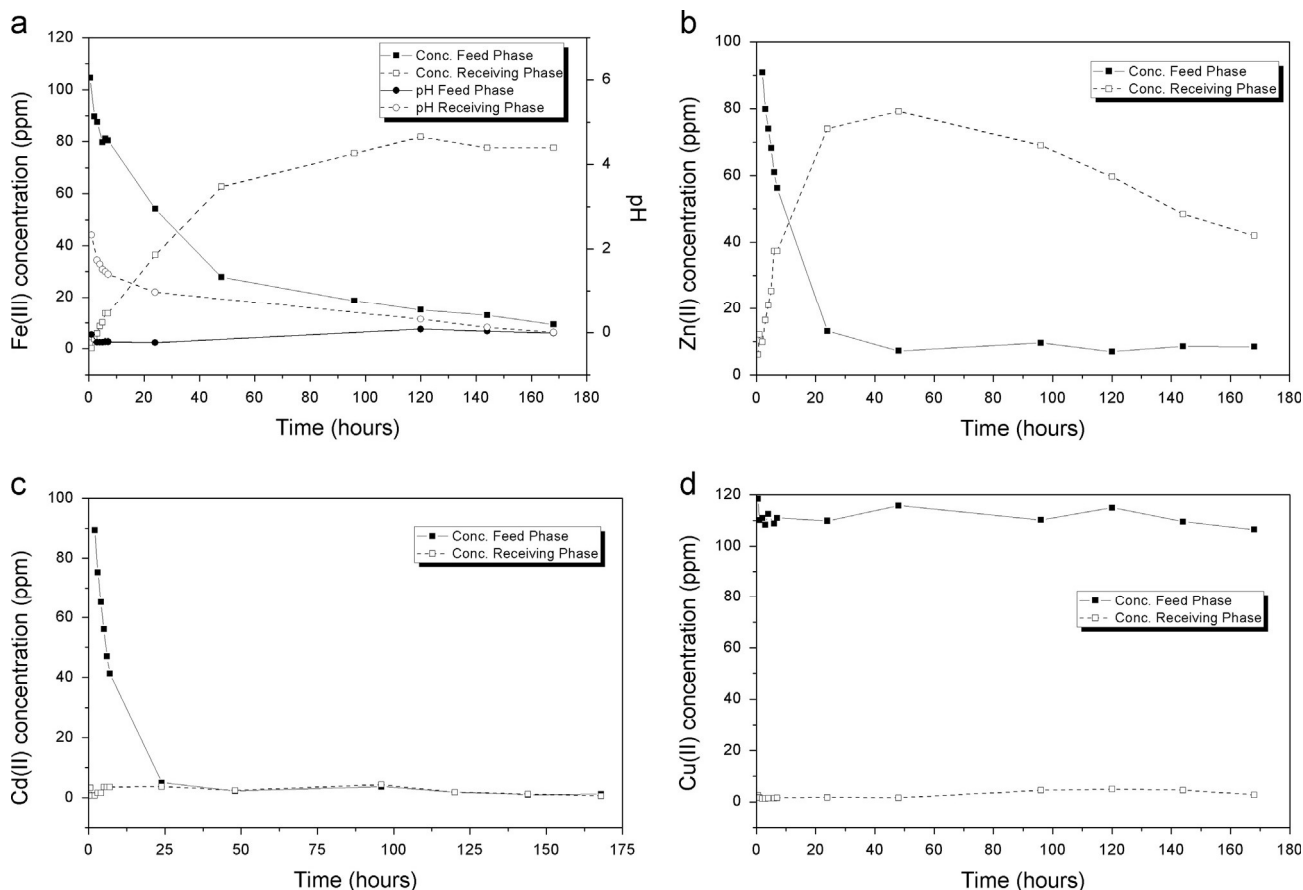* Precipitation of metal ion has been observed.

Fig. 5. Metal ions concentration (square symbols) and pH profiles (circle symbols) in the feed (full symbol) and receiving phases (empty symbol) in the transport of (a) Fe(III), (b) Zn(II), (c) Cd(II) and (d) Cu(II) through a supported liquid membrane based on [MTOA⁺][Cl⁻]. The feed phase consisted in a mixture of the four metal ions with an initial concentration in each of 0,1 g/L in HCl (1 M). Receiving phase was milliQ water.

By comparing Fig. 2 and Fig. 5, it is worthy to note that, with a few exceptions which will be commented below, no significant differences between the transport of a given metal ion in absence or presence of other metal ions were found. Therefore, not significant interferences exist between metal ions in their trans- port through supported ionic liquid membranes. For the metal ion Fe(III), a continuous removal from feed phase is observed throughout the entire

experiment. In consequence, there was a continuous rising in the PF which reached a maximum of PF= 8.3 at 168 h (Fig. 6a). When tested separately this metal ion, PF was 9 at 31 h and subsequently fell to 1 at the end of the experiment. In the mixture experiment, the mass balance was constant throughout the experience, accumulating less than 10% of the metal ion in the membrane. In the case of Zn(II) Fig. 6b, a higher pertraction factor was reached with the mixture of metal ions (PF=11 at 48 h) than with the sole metal ion (PF=3.2 at 24 h). After this maximum, the separation factor decreased, being its final value in the case of the mixture of metal ions (PF=5 at 168 h) also higher than the final value reached in the assay with the sole metal ion (PF=1.9 at 168 h). On the other hand, the amount of Zn(II) in the feed and receiving solutions in the case of the mixture of metal ions was reduced to approximately 60% at the end of the experiment due to the accumulating of the ionic liquid in the membrane, while in the case of the transport of this metal ion assayed alone was higher (approximately 80%).
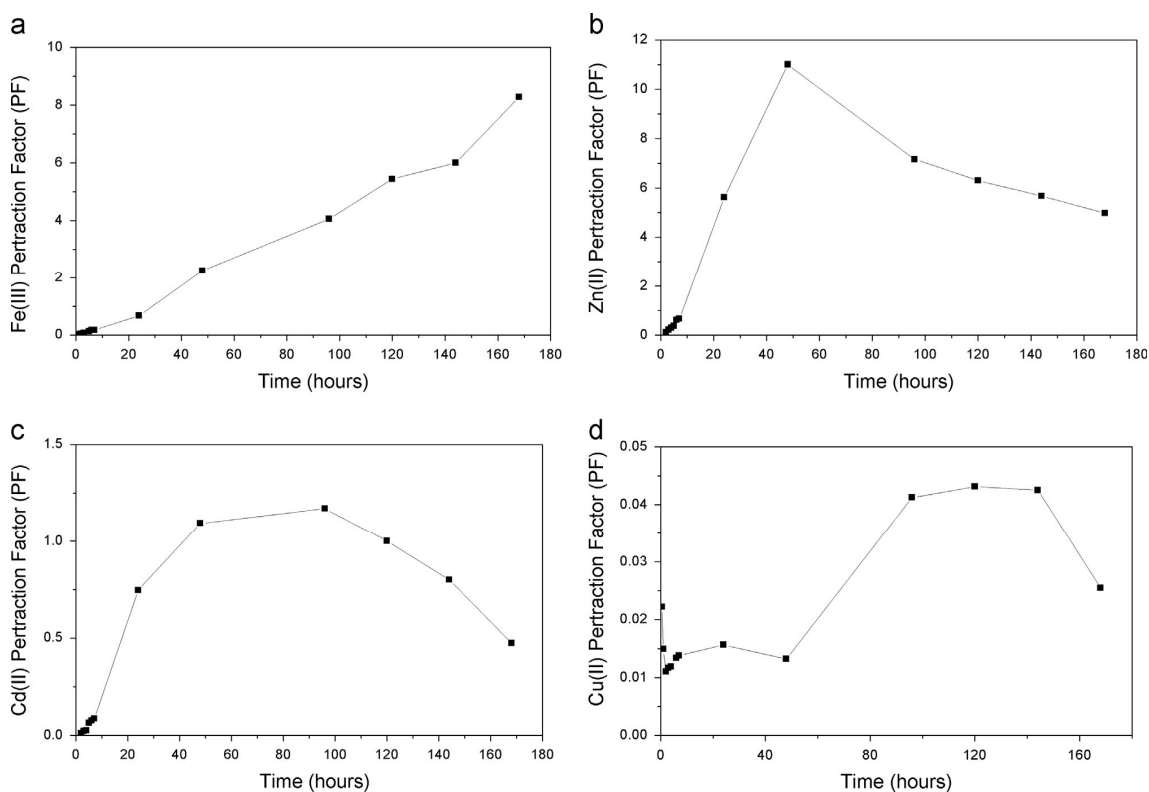

Fig. 6. Evolution over time of the Pertraction Factor (PF) of (a) Fe(III), (b) Zn(II), (c) Cd(II) and (d)Cu(II) using the Nylons-[MTOA$^+$][Cl$^-$] supported ionic liquid membrane, a mixture of the four metal ions with an initial concentration in each of 0,1 g/L in HCl (1 M) as feed phase and milliQ water as receiving phase.

Cd(II) behavior in the experiment carried out with a mixture of metal ions was also similar than that observed in absence of other metal ions. It is removed from feed phase and retained in the SILM, with a minimum stripping. The only difference observed is that the disappearance of Cd(II) in the feed phase in the mixture experiment was slower than that observed in the experiment in absence of other metal ions. In the latter case Cd(II) completely disappeared at 24 h while in the former case it does not take place until 168 h. The extraction of Cu(II) showed no significant differences in both sole and mixture assays. In both cases Cu(II) concentration decreases slightly in the feed phase and it also increases slightly in the receiving phase, keeping constant the mass balance through- out the experiment. That is, no accumulation of the metal ion in the SILM was observed. Differences in behavior between the separation of individual metals and the separation of a mixture of them can be explained considering that the ionic liquid contained in the membrane gets saturated earlier when a higher metal ion concentration is present in the feed phase. For that reason, Cd(II) needs more time to get completely absorbed in the

membrane. This also implies that HCl transport through the membrane is slower, thus maintaining the pH differences between the two chambers which improves the efficiency of the pertraction process. This is the case of Zn(II) and Fe(III) in the metal ions mixture experiments. Once the metal ions Zn(II) and Fe(III) are in the receiving phase, they have more difficulty in getting back to the feed phase due to the higher HCl concentration difference between chambers. Consequently, as it was observed, Zn(II) and Fe(III) concentration in feed and receiving phase were not equal at the end of the mixture experiment. The higher saturation of the membrane could also explain the lower metal ions fluxes in the case of the mixed metal ions assays (see Table 1).

To get a better understanding of the separation efficiency of a mixture of the metal ions Zn(II), Cd(II), Cu(II) and Fe(III), the separation factors (α) of the six possible pairs of metal ions that can be established between Zn(II), Cd(II), Cu(II) and Fe(III) were calculated. The enrichment factor (α), defined in the Materials and Methods Section, indicates the separation efficiency of a mixture of two metals between the feed and receiving phases. A high enrichment factor indicates that one of the metals has remained in the feed phase and the other has passed to the receiving phase in a high extent. Fig. 7 shows the evolution of the enrichment factors of the different pairs of metal ions over time. As can be seen in Fig. 7, enrichment factor for the mixture Zn (II)/Fe(III) reaches a value of $\alpha Zn/Fe= 8.4$, with a follow decrease to 0.6 at 168 h. It is due to the fact that Zn(II) is transported to the receiving phase faster than Fe(III), although as time passes, concentration of these two metal ions get equal in the feed and the receiving phases. Enrichment factor for Zn(II) and Cd(II) quickly take values around $\alpha Zn/Cd= 10$ during all the experiment. Although these two metal ions get extracted from feed phase, Cd(II) remains in the membrane while Zn(II) is stripped to the receiving phase. These results evidence the possibility of separating Zn(II) from Cd(II).

For the couple Zn(II) and Cu(II), enrichment factor reach a maximum of $\alpha_{Zn/Cu} = 833$ a t 48 h, falling down, until around 200 at 96 h, when it stabilizes. This behavior could be explained by the fact that Cu(II) is not extracted from the feed phase. For the same reason, the pair Fe(III)/Cu(II) could be also successfully separated, the enrichment factor increasing continuously along the entire experiment up to $\alpha Fe/Cu= 325$.

High values of enrichment factor were also obtained for the couple Cd(II) y Cu(II) ($\alpha_{Cd/Cu}= 82$ at 48 h). In this case, a separation does not occur by pertraction, but for the retention of Cd(II) in the supported ionic liquid membrane. The case of Fe(III) and Cd(II) is similar to that of Zn(II)/Cd(II) and Cd(II)/Cu(II). A high value of enrichment factor ($\alpha Fe/Cd= 17.5$ at 168 h) was obtained, due to the fact that Fe(III) is stripped in the receiving phase while Cd(II) is retained in the membrane.

3.2. Effect of the receiving phase composition on the pertraction of Fe (III), Zn(II), Cd(II) and Cu(II) from hydrochloride aqueous solution by using a supported ionic liquid membrane based on [MTOA⁺][Cl⁻]

As commented above, the metal ion extraction by using ionic liquids take place by a mechanism which involves HCl. Hence, stripping of metal ions from the ionic liquid phase immobilized in the membrane could be improved by using a more basic receiving phase, capable to break the compound based on the metal ions/IL/ hydrochloric acid formed. For that, the pH of the receiving phase has been increased by using sodium carbonate or ammonia.
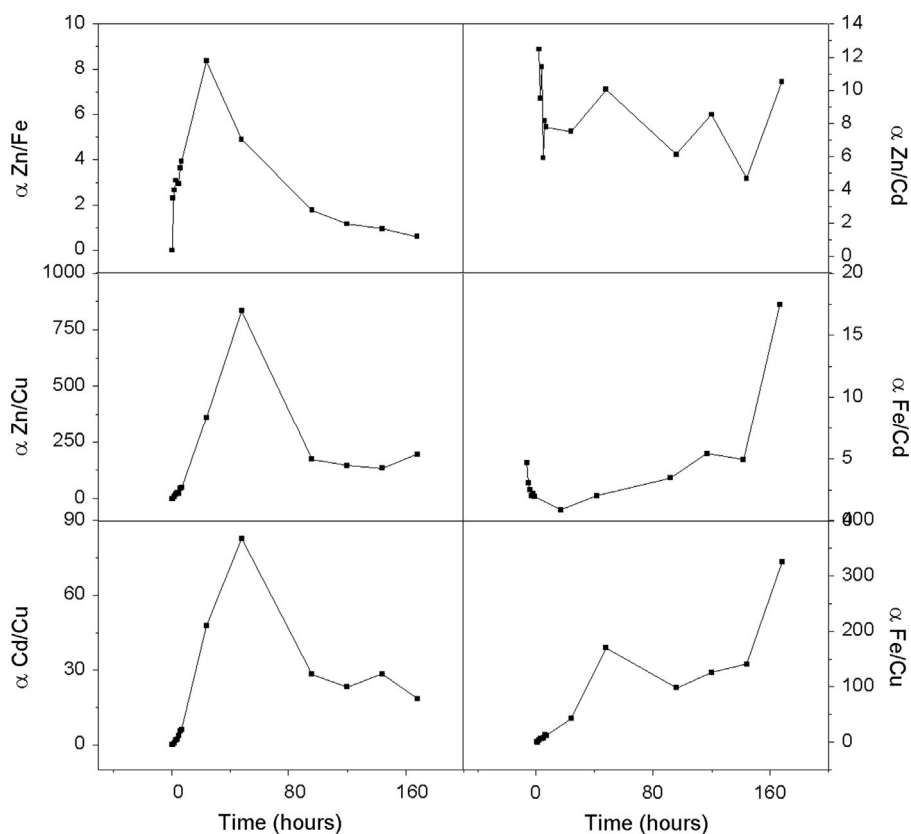
Fig. 7. Evolution over time of the separation factors for the six possible pairs of metal ions that can be established between Fe(III), Zn(II), Cd(II) and Cu(II). The feed phase consisted in a mixture of the four metal ions with an initial concentration in each of 0,1 g/L in HCl (1 M). Receiving phase was milliQ water.

3.2.1. Receiving phase: sodium carbonate 0.1 M

The transport of Fe(III), Zn(II), Cd(II) and Cu(II) through a supported ionic liquid membrane based on [MTOA$^+$][Cl$^-$] was analyzed using Na$_2$CO$_3$ 0.1 M as receiving phase. These studies has been carried out using as feed phases (i) 0.1 g/L solution of each metal ion in HCl 1 M and (ii) a mixture of the four metal ions (0.1 g/L in each) in HCl 1 M. Fig. 8 shows the evolution over time of Fe(III), Zn(II), Cd(II) and Cu(II) concentrations in the feed and the receiving phases in both experiments, in absence or presence of the others metal ions under study.

As can be seen in Fig. 8a, the concentration profiles of Fe(III) in the feed and receiving phases using Na$_2$CO$_3$ as receiving phase is slightly different to that obtained using milli-Q water. Specifically, the use of Na$_2$CO$_3$ (0.1 M) as receiving phase maintain the pH difference between the feed and the receiving phases for longer times. It is because HCl is neutralized by Na$_2$CO$_3$ in the received phase. For that reason, the concentration of Fe(III) in both phases at the end of the experiment are not equal. Furthermore, a lower concentration of Fe(III) in the receiving phase was reached (67 ppm at 48 h) using Na$_2$CO$_3$ as receiving phase compared to that obtained with milli-Q water (90 ppm at 31 h). As be also seen in Fig. 8a, the concentration of Fe(III) was reduced approximately 50% in the first 6 h, however no concentration of Fe(III) was detected in the receiving phase. Considering the mass balance, the total concentration of Fe(III) ion decreased with time until 6 h of experiment and subsequently it increased to values close to the initial concentration. As comment above, the pH of the receiving phase decreases slowly being higher than 8 at 10 h. As is apparent from the Fe(III) predominant area diagram (Fig. 4a), the ion Fe(III) precipitates as Fe$_2$O$_3$ (red precipitate hematite) at pH > 1 for high concentrations of Fe(III) and at pH > 2.5 for low concentrations of the metal ion. Therefore, considering the high alkaline pH

of the receiving phase at the beginning of the experiment, the fact that the mass balance does not fit at this point could be explained by the precipitation of Fe(III) as Fe_2O_3 in the receiving phase (visually observed) and its absorption in the membrane. The precipitation of Fe(III) can also explain the lower maximum concentration of Fe (III) reached in the receiving phase using Na_2CO_3 as receiving phase respect to that obtained using milli-Q water. Once the pH of the receiving phase decreases until pH= 0.72 (at 24 h), due to the transport of HCl from the feed to the receiving phase, and to the transport of Na_2CO_3 from the receiving phase to the feed phase, the precipitate of Fe2O3 starts redissolving and the concentration of Fe(III) increases quickly in the receiving phase from 0 to 67 mM after 48 h. The phenomenon of precipitation and redissolution was also observed visually since a yellow-red precipitate was observed in the receiving phase which subsequently redissolves. The maximum pertraction factor for Fe(III) reached during this experiment was PF = 4 (data non shown). The pertraction factor was lower in that case than that obtained in the experiment using milli-Q water as receiving phase (PF = 9), which could be due to the precipitation of Fe_2O_3 in the former case.

Fig. 8b shows the pertraction process for Zn(II) using 0.1 M sodium carbonate aqueous solution as receiving phase. The behavior found for this metal ion is very similar to that found for Fe(III). Initially, the Zn(II) concentration decreased continuously in the feed phase, while it was not increased in the receiving phase until 8 h. At 24 h, there was a significant increase in the concentration of Zn(II) in the receiving phase, which continued increasing in the receiving phase moderately until 48 h. These results can be also explained considering the variation of pH in the receiving and feed phase throughout the experiment. As can be observed in the area diagram for predominant ion for Zn(II) (Fig. 4b) at relatively high metal ion concentrations and alkaline pH, Zn(II) can precipitates as ZnO. In this context, the ion Zn(II) starts crossing the membrane and its concentration is reduced in the feed phase. In the receiving phase, Zn(II) is putted into contact with the alkaline solution (pH >9) and it starts to precipitate as ZnO.
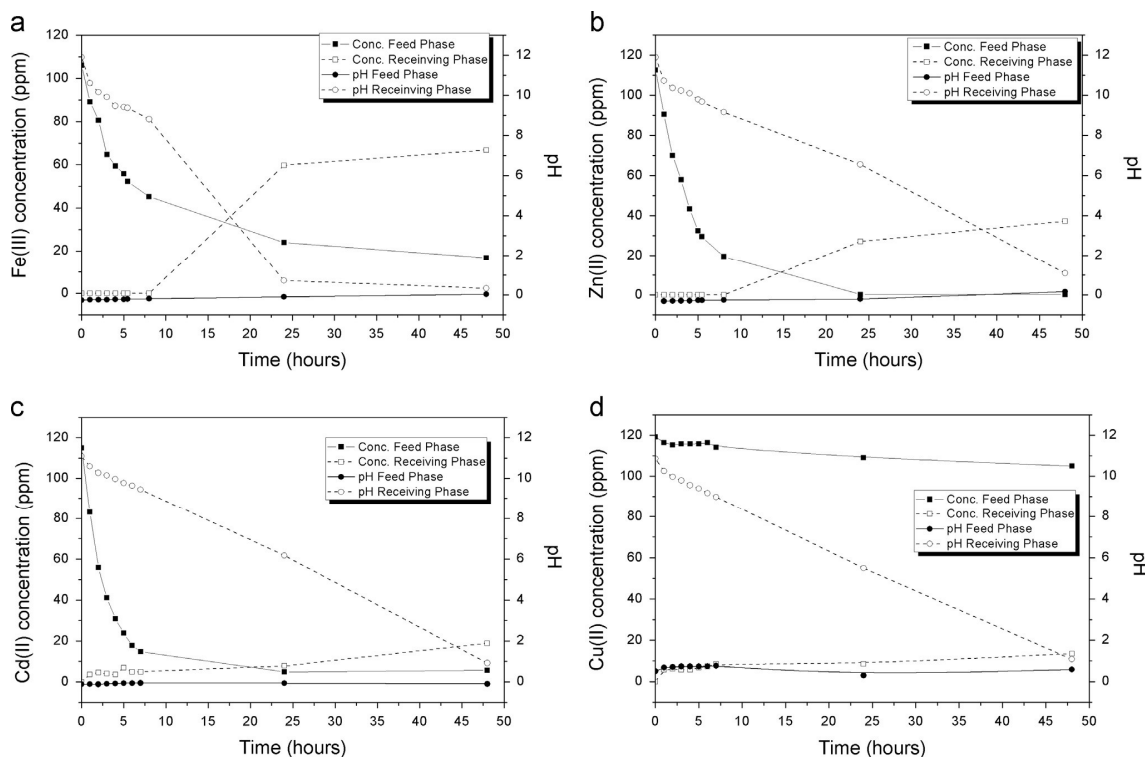

Fig. 8. Metal ions concentration (square symbols) and pH profiles (circle symbols) in the feed (full symbol) and receiving phases (empty symbol) in the transport of (a) Fe(III), (b) Zn(II), (c) Cd(II), and (d) Cu(II) through a supported liquid membrane based on [MTOA$^+$][Cl$^-$]. Initial concentration of a given metal ion in the feed phase was 1 g/L in HCl (1 M). Receiving phase was Na_2CO_3 (0.1 M).

At 24 h, the pH decreased to 6.5 in the receiving phase and, therefore, ZnO start redissolving, with the consequent increase of the Zn(II) concentration in this phase. Although the maximum concentration of Zn(II) in the receiving phase was much higher in the milli-Q experiment respect to the experiment using Na_2CO_3, the maximum pertraction factor was reach in the latter case (PF = 373 at 48 h) due to the higher Zn(II) concentration differences between the feed and receiving phase reached when the alkaline receiving phase was employed. Regarding Cd(II) ion, as can be seen in Fig. 8c, there was a continuous reduction of Cd(II) concentration in the feed phase due to the extraction of the metal ion in the membrane, while the concentration in the receiving phase slightly increased. The mass balance thus showed a continuous decrease of Cd(II) over time. In this case, the decrease of the total metal ion concentration cannot be explained by the precipitation of Cd(II) ion at high pH, as in the previous cases. As shown in the predominant area diagram for Cd(II) (Fig. 4c), at pH < 9 Cd(II) hydroxide is redissolved. Therefore, if the decrease of the concentration of Cd(II) was due to the precipitation as hydroxide, it should have redissolved in the receiving phase at 24 h since the pH was 6.2 and Cd(II) should have increased sharply in that phase. As this behavior was not found, the concentration profiles can be explained by absorption of the metal ion Cd(II) in the ionic liquid phase of the membrane. The sodium carbonate solution used as receiving phase was not able to efficiently reextract the Cd(II) absorbed in the membrane. However, the results were improved over those obtained using milli-Q water as receiving phase since the concentration of Cd(II) in the receiving phase increases until 20 ppm, reaching a maximum value of PF= 3.3 at 48 h (data non shown) while this value was significantly lower using milli-Q water (PF= 0.1).This fact could be explained by the higher pH gradient between the feed and receiving phase reached in the experiment with the alkaline receiving phase, which allows an easier stripping of the metal ion from the membrane to the receiving phase.

Fig. 8d shows the concentration of Cu(II) and pHs profiles in the feed phase and receiving when sodium carbonate was use as receiving phase. As can be seen, the behavior was similar to that found when milli-Q water was used as receiving phase. Therefore, the use of 0.1 M sodium carbonate as reextrantant agent for Cu(II) not improve is achieved in the pertraction this ion metal. Once studied the pertraction process for the metal ions separately using 0.1 M sodium carbonate as receiving phase, the process was analyzed using a mixture of the four metal ions Fe(III), Zn(II), Cd(II) and Cu(II) (0.1 g/L each) (Fig. 9). It is worthy to note that the transport of metal ions separately and in the mixture was pretty similar. The main difference found was the higher extent of reextraction reached in the mixture experiment, which could be explained by the fact that the pH of the receiving phase decrease more slowly and consequently the pH gradient between both phases along the experiment was higher in that case than that in the experiments of metal ions separately. The increase found in the pH gradient in the experiment with a mixture of metal ions could be explained by the fact that in that case, the higher saturation of the membranes makes more difficult the transport of HCl from the feed to the receiving phase. It is noteworthy that higher separation factors were reached using 0.1 M sodium carbonate compared with milliQ-water. A very high separation factor was found for the pair of metal ions Zn(II)/Cu(II) (α = 2633 at 94 h). This high value can be explained by the fact that the reextraction of Zn(II) in the receiving phase takes place to a great extent while most of the Cu(II) ion remains in the feed phase during most of the experiment. The enrichment factor was also very high for the pair Zn(II)/Cd(II) (α = 298 for 94 h), although in this case the Cd(II) was not reextracted in the receiving phase but absorbed in the liquid membrane. Significant enrichment factors were also obtained for the couples Zn(II)/Fe(III) (α = 110 to 94 h) and Fe(III)/Cu(II) (α = 24 to 94 h).
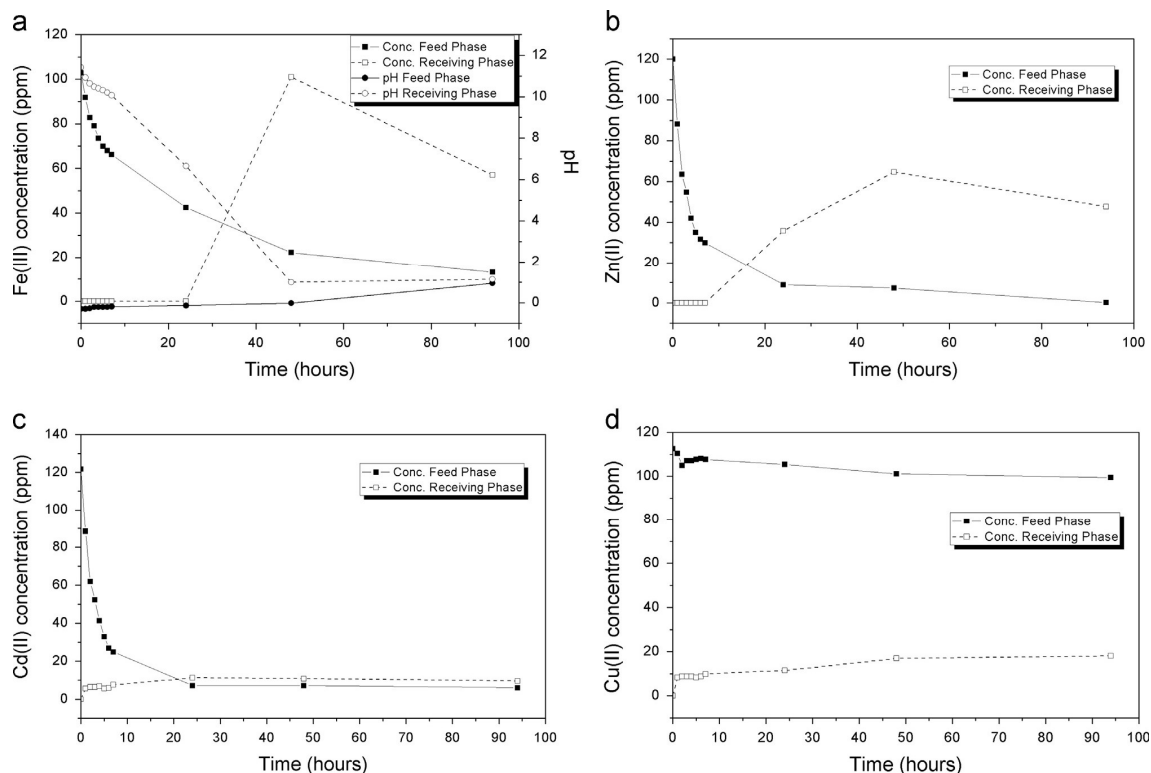
Fig. 9. Metal ions concentration (square symbols) and pH profiles (circle symbols) in the feed (full symbol) and receiving phases (empty symbol) in the transport of (a) Fe (III), (b) Zn(II), (c) Cd(II), and (d) Cu(II) through a supported liquid membrane based on [MTOA$^+$][Cl$^-$]. The feed phase consisted in a mixture of the four metal ions with an initial concentration in each of 0.1 g/L in HCl (1 M). Receiving phase was Na$_2$CO$_3$ (0.1 M).

3.2.2. Receiving phase: ammonia 6 M.

The transport of a mixture of the metal ions Fe(III), Zn(II), Cd(II) and Cu(II) (0.1 g/L in each) in HCl (1 M) through a supported ionic liquid membrane based on [MTOA$^+$][Cl$^-$] was analyzed using ammonia 6 M as receiving phase. Fig. 10 shows the concentration of the four metal ions in the feed and the receiving phases and the pH profiles. As can be observed in Fig. 10, the pH in the receiving phase is maintained much higher than in the previous experiments using milli-Q water and Na$_2$CO$_3$, the pH being higher than 10 during all the experiment. In the feed phase, the pH also increased faster than in the previous experiments (pH~9 at 9 h) due to the transport of ammonia from the receiving to the feed phase. As can be seen, the concentration of Fe(III) began to decrease continuously in the feed phase being null at 24 h. However, no Fe(III) was detected in the receiving phase during all the experiment. Fe(III) starts being transported from the feed to the receiving phase and, according with the predominant area diagram for Fe(III) (Fig. 4a), it precipitates when reach the receiving phase due to the high pH value. Fe(III) also precipitates in the feed phase when the pH in this phase is higher than 2.5.

In the case of Zn(II) (see Fig. 10b), the concentration of this metal ion decreased in the feed phase until a value of around 60 ppm but it did not increase significantly in the receiving phase. Therefore, the mass balance of Zn(II) is not satisfied, which could be explain by the absorption of this metal ion in the membrane. As can be observed in Fig. 10b, Zn(II) remains in solution at pHs 49, contrary to what would be expected from Fig. 4b. This fact could be explained by the formation of complex of this metal ion with NH$_3$ which are soluble at basic pHs. The pertraction factor for Zn(II) was consistently lower in this case (PF <0.2 at 94 h) than that found using 0.1 M sodium carbonate as receiving phase (PF = 477 to 94 h). The concentration of Cu(II) decreased in the feed phase until 80 ppm and it increased slightly in the receiving phase. After 24 h the pH

of the feed phase reached a value higher than 8, and therefore, according to the predominant area diagram of this metal ion (Fig. 4d), Cu(II) should precipitates as CuO. Contrary to what it was expected, Cu(II) remain in solution in the feed and receiving phases due to the formation of NH_3-complexes.
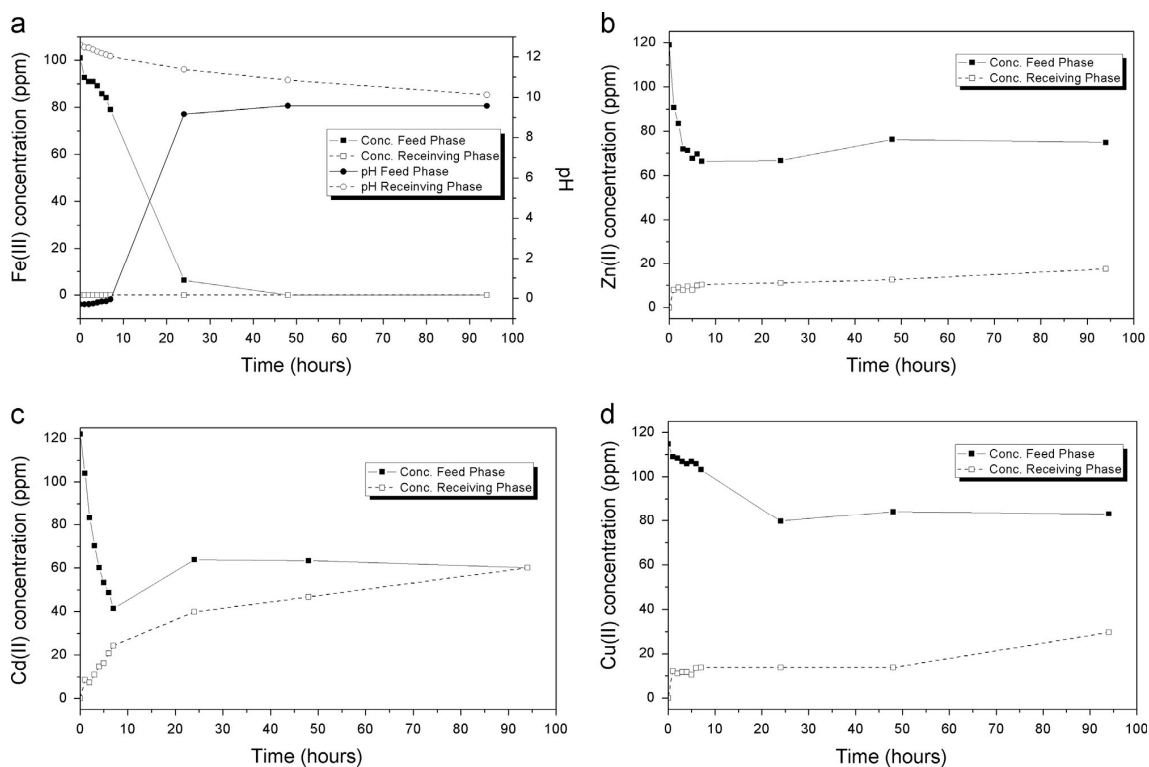

Fig. 10. Metal ions concentration (square symbols) and pH profiles (circle symbols) in the feed (full symbol) and receiving phases (empty symbol) in the transport of (a) Fe(III), (b) Zn(II), (c) Cd(II), and (d) Cu(II) through a supported liquid membrane based on [MTOA$^+$][Cl$^-$]. The feed phase consisted in a mixture of the four metal ions with an initial concentration in each of 0,1 g/L in HCl (1 M). Receiving phase was NH_3 (6 M).

Regarding to the transport of Cd(II), unlike it occurred by using the previous receiving phases tested (milli-Q water and Na_2CO_3 0.1 M), the new receiving phase (ammonia) allows the stripping of the Cd(II) adsorbed into the liquid membrane. This could be due to the fact that for the reextraction of this metal ion from the ionic liquid immobilized in the membrane it is highly necessary to maintain a basic pH in the receiving phase during the whole experiment. Cd(II) remains also soluble in the feed and receiving phase at basic pH due to the formation of NH_3-complexes.

As can been seen from Table 1, the use the ammonium solution allows an important increase in the initial flux of Cd (II) through the membrane. The same behavior was found for Cu(II), while in the case of Zn(II) and Fe(III) the fluxes of these metal ions were reduced. Regarding the enrichment factors obtained for the different metal ions pairs, it were greater than the unity for the couples containing Cd(II) (i.e. Cd(II)/Zn(II), α= 4.5 at 48 h; Cd(II)/Cu(II), α = 4.5 at 48 h). For getting a better understanding of the transport of Cd(II) using ammonia 6 M as receiving phase, a new experiment was performed using as feed phase a solution of Cd(II) (0.1 g/L) in HCl 1 M. Fig. 11 shows the pH and the concentration profiles in the feed and receiving phase for this experiment. As can be seen in this figure, the highest stripping for Cd(II) was reached in this experiment, being the maximum Cd(II) concentration in the receiving phase of around 90 ppm. The total concentration of Cd(II) in the feed and receiving phase (mass balance) decreases initially but after 6 h of experiment the stripping of Cd(II) in the receiving takes place, which allows to fit the mass balance and to achieve the initial values of the metal ion concentration.
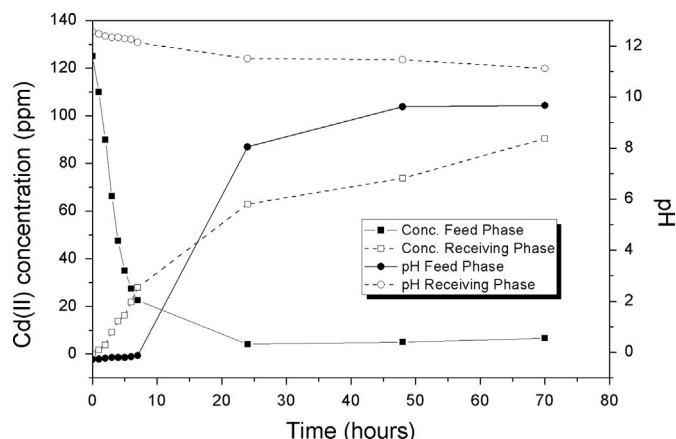
Fig. 11. Metal ions concentration (square symbols) and pH profiles (circle symbols) in the feed (full symbol) and receiving phases (empty symbol) in the transport of Cd(II) through a supported liquid membrane based on [MTOA$^+$][Cl$^-$]. Initial concentration of Cd(II) in the feed phase was 1 g/L in HCl (1 M). Receiving phase was NH$_3$ (6 M).

As it happens in the previous experiments with milli-Q water, the stripping of Cd(II) was higher in the individual test than in the mixture with other metal ions. Furthermore, the initial metal ion flux was higher (2.27 g m^{-2} s^{-1}) than that reached in the experiment with the mixture of different metal ions (1.77 g m^{-2} s^{-1}). This behavior can be attributed to the fact that the higher saturation of the membrane in the assay with the mixture of metal ions make difficult the transport of Cd(II) ions through the ionic liquid immobilized therein. Therefore, the use of NH$_3$ as receiving phase allows the maximum pertraction factor found for Cd (II) in all conditions assayed in the work (PF = 15.1 to24 h).

3.3. Stability of supported ionic liquid membranes based on [MTOA$^+$] [Cl$^-$] to aqueous medium

As discussed above, one of the most important advantages when using supported liquid membranes based on ionic liquids is that the membrane can be stabilized against loss of liquid phase thereof by adequately selection of the ionic liquid [41]. Since the ionic liquid [MTOA$^+$][Cl$^-$] has a low solubility in water (0.02%v/v), it would be expected that the supported liquid membrane based on this ionic liquid is very stable. Table 2 shows the percentage of ionic liquid remaining in the polymeric membrane after the pertraction assays. As can be seen in Table 1, a high stability was observed in all cases even after 456 h of assay. The percentage of retained ionic liquid ranges from 75% to 89%, and in most membranes was higher than 80%. It is worthy to highlight that although the solubility of the ionic liquid in water is low, the water solubility in [MTOA$^+$] [Cl$^-$] is high (40 mass %). Therefore, since the ionic liquid used was not completely water-saturated (31 mass %), the volume of IL in pores could increased due to saturation with water and part of membrane liquid could leak from pores due to this effect more than to the leaching IL from membrane. In a previous work [19] we observed a limited stability of supported liquid membranes based on imidazolium ionic liquid against high polar solvent (i.e. water). In the present work, the ionic liquid [MTOA$^+$][Cl$^-$] has been chosen as liquid phase due to its higher hydrophobicity in comparison with the imidazolium ionic liquids previously tested in polar solvents. The use of this type of ionic liquids has allowed the preparation of very stable supported ionic liquid membranes against high polar media, like water.

Table 2 Percentage of remaining [MTOA⁺][Cl⁻] after pertraction assays

Metal ion/ receiving phase	Time assayed (h)	Initial weight (g)	Final weight (g)	Remaining IL (% mass)
Zn(II)/H$_2$O pH=6	168	0.0986	0.0897	87.6
Fe(III)/H$_2$O pH=6	456	0.0988	0.0886	85.8
Cu(II)/H$_2$O pH=6	141	0.1006	0.0834	76.0
Cd(II)/H$_2$O pH=6	141	0.1013	0.0897	83.8
Zn(II)/Na$_2$CO$_3$ 0.1 M	48	0.1007	0.0925	88.6
Fe(III)/Na$_2$CO$_3$ 0.1 M	48	0.0998	0.0815	74.5
Cu(II)/Na$_2$CO$_3$ 0.1 M	48	0.1007	0.0850	78.1
Cd(II)/Na$_2$CO$_3$ 0.1 M	48	0.1001	0.0905	86.6
Cd(II)/NH$_3$ 6 M	70	0.1003	0.0885	83.6

4. Conclusions

In this study we outlined the possibility of using supported liquid membranes based on ionic liquids for the selective separation of metal ions. Specifically, a supported ionic liquid membrane based on methyltrioctylammonium chloride was used in a pertraction process for the selective extraction of Zn(II), Cd(II), Fe(III) and Cu(II) using stripping phases of different compositions, such as milli-Q water, Na$_2$CO$_3$ (0.1 M) or NH$_3$ (6 M). Fe(III) was recovered using milli-Q water as receiving phase, with an PF= 9 at 31 h. Sodium carbonate (0.1 M) allowed the recovery of Zn(II), reaching extraction factors of up to 373 at 48 h. The use of NH$_3$ (6 M) as receiving phase allowed the recovery of Cd(II) with a PF=15.1 at 24 h. Furthermore, it was found that by modifying the stripping phase composition, the selective separation of the target metal ions can be reached. Based on these studies, a new continuous process could be design for the selective separation of the target metal ions by using the obtained supported ionic liquid membrane, which has been found to be very stable in contact with aqueous solutions and varying the phase pH of the feed and receiving phases along the experiment. This process is now under study in our labs.

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