

Recovery and enrichment of heavy metals using new hybrid Donnan dialysis systems combining cation exchange textile and solvent impregnated resin

Dalila Berdous[†] and Djamal-Eddine Akretche

Chemistry Faculty, Hydrometallurgy and Inorganic Molecular Chemistry Laboratory,
University of Sciences and Technology (USTHB), BP 32, El-Alia, 16111 Bab Ezzouar, Algiers, Algeria
(Received 30 March 2013 • accepted 21 May 2013)

Abstract—The purpose of this work is to apply Donnan dialysis coupled with the cation exchange membrane (CMX), the cation exchange grafted textile (CET) and the solvent impregnated resin (SIR) for recovery and enrichment of heavy metal ions from dilute solutions. The influence of some analytical parameters was investigated. The transport results show that the three barriers enhance the diffusion of silver, lead and copper, but the osmosis phenomenon is limited when the transport is carried out through CET and the SIR. The results of enrichments indicate that SIR and CET increase the enrichment factor of less hydrated ions. For instance, and for a volume ratio equal to 10, the values of silver enrichment factor obtained for (CMX/CMX/CMX), (CMX/CET/CMX) and (CMX/SIR/CMX) are equal to 2.5, 8.92 and 4.98, respectively. In addition, the use of SIR improves the enrichment of lead, whereas the CET improves the silver's one.

Key words: Heavy Metals, Enrichment, Donnan Dialysis, Hybrid System, Cation Exchange Grafted Textile, Solvent Impregnated Resin, Extractant, D2EHPA, TOPO, DPTU

INTRODUCTION

Human activities have been considered to be responsible for environmental pollution by large amounts of toxic elements. Exposure to these toxic elements imposes risks not only to human health, but also to plants, animals and microorganisms [1]. Consequently, the accurate determination of metals at trace levels in environmental water samples is a subject of great concern. Donnan dialysis has been demonstrated to be a useful technique for the preconcentration and recovery of metal ions. Most researchers have employed an ion exchange membrane indicating the process as diffusion [2] or Donnan dialysis [3-5]. The process is based on the Donnan equilibrium principle [6] with the usual aim being the separation of ions or charged species. The transport in the Donnan dialysis is a function of two phenomena: diffusion due to the concentration gradient, and migration due to the potential gradient arising from the difference in ionic concentrations across the membrane [5]. Another important parameter affecting the permeation of ions is the membrane charge [7], which depends on the pH, and the electrolytes in the bulk solution. Dialysis is able to solve two important industrial problems: recovery of valuable materials and removal of undesired ions from waste streams [8]. Many studies have reported the economic and technical contributions of the cation exchange textile (CET) on the electrodialysis for diluted aqueous media (production of ultra-pure water [9,10] and micro-extraction [11,12]). The introduction of the ion exchanger textile between two ion exchange membranes (IEM) increases the conductivity of the solution to be treated and the amount of metals extracted. Lacour Stella et al. [13,14] have used the ion exchange textile for the electrowinning of metals (Zn,

Ag, Cd, Ni, Cu) from an aqueous solution in order to extract and focus. K. Basta et al. [15] have studied the extraction of lead from dilute solutions combining the cation exchange membranes (CMX) and the cation exchanger textile by application of an electric field. The solvent impregnated resins (SIR) have been shown to be effective sorbents for the selective recovery of metal ions from aqueous solutions [16]. They combine not only the advantages of ion exchange resin for dilute processing with specific properties of the extractants, but also, a high distribution ratio, and a high selectivity of the extractants dissolved in a liquid organic phase with the simplicity of equipment and operation characteristic of solid ion-exchange technology [17]. SIR was introduced in hydrometallurgical applications by Warshawsky [17,18]. The Amberlite XAD is resin widely used to develop several chelating materials for pre-concentration procedures due to its good physical and chemical properties such as porosity, high surface area, durability, and purity [19-21]. Amberlite XAD-4 has been often used as a solid sorbent to prepare a ligand-loaded resin. Wang and al. [22] have used an extractant resin, with styrene-divinyl benzene copolymer as support and (HEH [EHP]) as the extractant, and its performance in separating rare earth, such as gadolinium and terbium. Many papers on the adsorption of metal ions have focused on the use of resins containing organo-phosphorus acids as extractants [23,24].

In the present work, a preconcentration of metal ions has been investigated by means of Donnan dialysis combining membrane to a cationic exchange textile and solvent impregnated resin (SIR). Before the application of the hybrid system to the concentration of these metals, the separation and the enrichment of lead, copper and silver, knowing that they are often associated in ores and industrial wastewater, were investigated. The obtained results have shown a reduction of the osmosis phenomenon and good yield for the metal concentration.

[†]To whom correspondence should be addressed.
E-mail: gebesadz@gmail.com

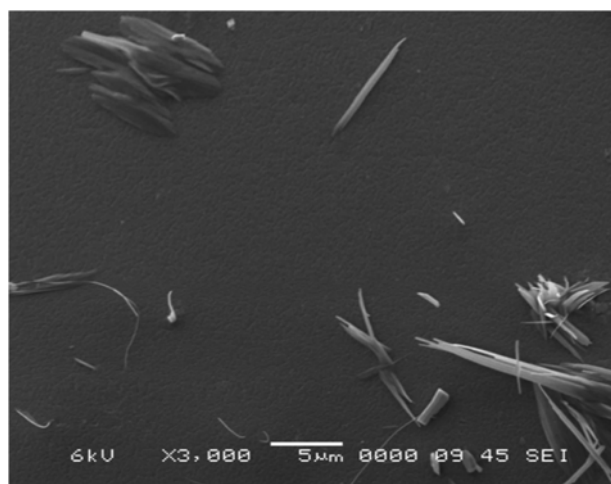


Fig. 1. SEM micrograph of Amberlite (XAD-4) resin.

EXPERIMENTAL PART

1. Membranes and Products

The cation exchange membrane used is the CMX membrane containing polysulfonated groups and furnished by Tokuyama Soda co Ltd. Its exchange capacity is $1.62 \text{ meq} \cdot \text{g}^{-1}$ and a thickness of $175 \times 10^{-6} \text{ m}$.

The used cation exchange textile (CET) is manufactured by Institut des Textiles de France; its exchange capacity is $0.45 \text{ meq} \cdot \text{g}^{-1}$.

The Amberlite XAD-4 macroporous resin (styrene-divinylbenzene copolymer), for which SEM micrograph and physical properties are given in Fig. 1 and Table 1, respectively, is a polymeric adsorbent supplied as white insoluble beads. It's a non ionic crosslinked polymer which derives its adsorptive properties from its patented macroporous structure (containing both a continuous polymer phase and a continuous pore phase). This structure gives Amberlite XAD-4 polymeric adsorbent excellent physical, chemical and thermal stability. Purchased from Rohm and Haas as a water wet product imbibed with sodium chloride (NaCl) and sodium carbonate (Na_2CO_3) salts to retard bacterial growth. These salts must be washed from the adsorbent prior to use and it is suggested that this be achieved by washing with water. Prior to impregnation, the resin was washed with deionized water and NaCl several times to remove inorganic impurities, and then let to dry.

2. Reagents and Solutions

Copper(II) nitrate, lead(II) nitrate and silver(I) nitrate (analytical grade reagents) were purchased from Fluka. All reagents were used as received without further purification. The aqueous phases were prepared by dissolving the different reagents in deionized water.

Di(2-ethylhexyl)phosphoric acid (D2EHPA) was the product of Sigma. It had a purity of about 95% and was used without further purification. Trioctyl phosphin oxide (TOPO) was product of Fluka;

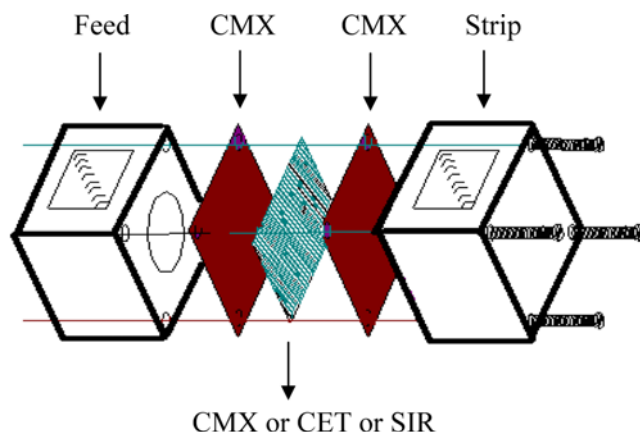


Fig. 2. Schematic diagram of the Donnan dialysis cell.

it had a purity of about 95%. Diphenyl-thiourea (DPTU) was the product of Aldrich and its purity is 98%. Metal nitrates, n-hexane and chloro-form as a solvent, and other inorganic chemicals were supplied by Fluka as analytical reagent grade and used as received.

3. Impregnation Procedure

SIR can be modelled as “a liquid complexing agent dispersed homogeneously in a solid polymeric medium.” The impregnated agent should have strong affinity to the matrix. The Amberlite XAD resins are widely-used. The attractiveness of SIR lies in the possibility of selecting an existing extractant and adapting it to solve a pressing problem. Naturally, most of the SIR studies so far have been concerned with immediate problems, and the extractants chosen have been mostly commercial. They include acidic organophosphorous extractant.

The SIR were prepared as dry method most widely used, the extractant, diluted by a solvent, is placed in contact with the polymer, and the solvent is removed by slow evaporation under vacuum. This method is most successful in the impregnation of hydrophilic extractant, such as amines, ethers, and esters.

4. Donnan Dialysis Cell and Procedure

Dialysis was carried out in a stirred cell represented in Fig. 2. The cell consisted of two compartments made of Teflon. The membrane (or membrane and textile, or membrane and SIR) was sandwiched between the two half cells. The effective volume of each cell was $140 \times 10^{-3} \text{ l}$. The feed compartment contained the metal solution at a concentration of 10^{-3} M of metal salt; the other compartment noted strip contained variable concentrations of nitric acid. Each compartment was provided with a vertical mechanical stirrer at stirring speed 600 rpm which was previously determined as high enough to minimize the thickness of the boundary layer. The experiments began when starting the stirring motors in the two compartments of the cell. The exposed membrane area was 7 cm^2 . All the experiments were performed in a thermostat at the temperature $T = 25^\circ \text{C}$. The experiment duration was fixed to six hours and $1 \times 10^{-3} \text{ l}$

Table 1. Physical properties of macroporous Amberlite (XAD-4) resin

Polymeric resin	Porosity ($\text{cm}^3 \cdot \text{cm}^{-3}$)	Pore volume (cm^3/g)	Specific surface (m^2/g)	Average pore diameter (nm)
1-Styrene-divinyl benzene, aromatic (hydrophobic) XAD-4	0.513	0.974	780	5

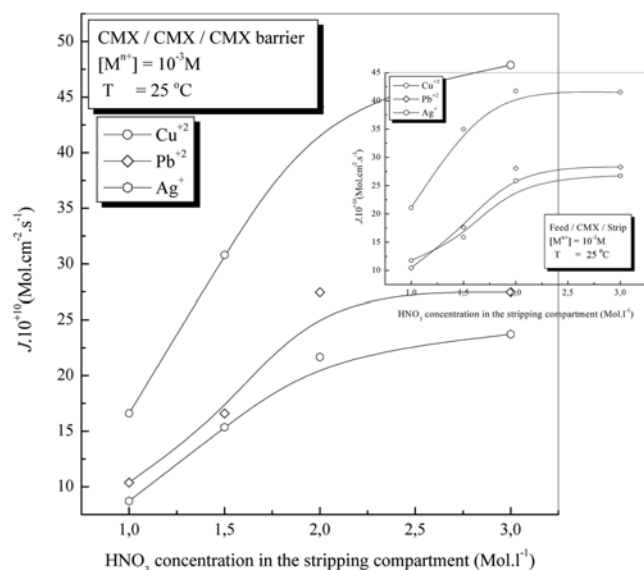


Fig. 3. Ions flux versus the nitric acid concentration inside the stripping compartment.

of solution was taken up in the regular time (1 hour) from the feed and strip compartments in the order of the determination of metal ions flux through the membrane.

RESULTS AND DISCUSSION

1. Recovery of Cu(II), Pb(II) and Ag(I) Using Different Systems

For all experiments, the concentration of metals (M^{n+}) was fixed to 10^{-3} M and that of nitric acid (HNO_3) varied from 1 M to 3 M.

1-1. Donnan Dialysis Using CMX/CMX/CMX Barrier

Fig. 3 shows the evolution of metal fluxes versus nitric acid concentration in the stripping compartment. The flux values of ions were calculated from the slope of the amount of the ion transported quantity as a function of time curves.

It is noticed that, a difference of flux values appears between copper, which was well hydrated, lead and silver, which were less hydrated. This result was observed also in the case where one CMX membrane was used as indicated in Fig. 3. In addition, the curves show that the quantity of the transported ions increases gradually with the acid concentration inside the stripping compartment and attains a limit after 2 M of HNO_3 concentration. It is due to the increasing of the osmosis phenomenon which, compared to the use of one CMX, is observed when the difference of concentration between the two compartments increases, which we consider that H^+ ions are transferred by the proton jump mechanism. This means that when ions reach the swollen region in the membrane, they are exchanged with metal ions and simultaneously the membrane contracts.

It appears that H^+ ions play the role of the driving force and transport caused by the pH difference between both sides. Thus, the fixed membrane charge will play an important role in the transport of electrolytes. In our case, we can assume that bivalent ions (Cu, and Pb) are well transferred regarding the fact that they need only two fixed charge ions. To explain the unexpected flux value of silver ion, we

should consider its low hydration, which decreases the distance between the ion charge and the membrane charge. This situation gives rise to the creation of a repulsion strength, which decreases the ion exchange. This explanation is confirmed by the result obtained in the previous work [6] when the CMV membrane was used. In effect, CMV is more charged than CMX and the silver flux was lower in the same experimental conditions. This transport system induces a competition between the ion jump mechanism and the coulomb strength effect. The influence of the electrostatic effect is reduced for the hydrated ions, knowing that one layer of water molecules at least separates the exchangeable cations.

1-2. Donnan Dialysis Using CMX/CET/CMX Barrier

Knowing that the hydration has an effect on the osmosis phenomenon and that other materials can modify the behavior of some ions particularly during an enrichment test, we performed Donnan dialysis using two cation exchange membranes CMX combined with a cation exchange grafted textile CET as a permselective barrier. In Fig. 4, the flux of both silver and lead is enhanced by the presence of the cation exchange textile. So, according to previous works [6-8], this result confirms the hypothesis of hydrophilic character of the cation exchange textile, which retains both water and ions that are well hydrated [25-49]. As it has been shown before, hydration enthalpies of the studied ions indicate that copper is more easily hydrated and consequently retained inside the cation exchange textile, while lead and silver cross through all barriers by means of fast ion exchange with the textile and with the following cation exchange membrane (thermodynamic data represented by the hydration enthalpies of copper, lead and silver are respectively, -502 kcal.

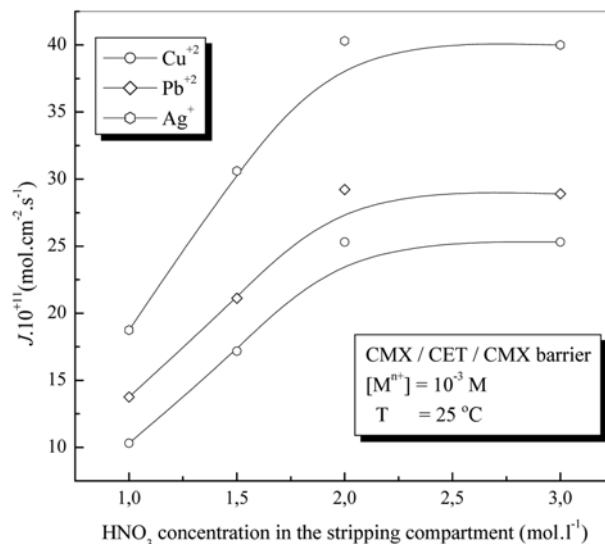


Fig. 4. Ions flux versus the nitric acid concentration inside the stripping compartment.

Table 2. The variation of the amount of metal ions retained in the textile according to the acid concentration

[HNO_3] in strip ($Mol \cdot l^{-1}$)	1	2	3
[Cu^{2+}] 10^4 ($Mol \cdot l^{-1}$)	8.6	8.9	8.1
[Ag^+] 10^4 ($Mol \cdot l^{-1}$)	1.6	1.1	0.9
[Pb^{2+}] 10^4 ($Mol \cdot l^{-1}$)	3.9	2.6	2.5

mol^{-1} , $-353.7 \text{ kcal}\cdot\text{mol}^{-1}$ and $-101 \text{ kcal}\cdot\text{mol}^{-1}$ are showing the ability of each ion to be hydrated).

Complementary experiences have confirmed that the more hydrated ions are retained inside the grafted textile by means of the measurement of the quantity of ion fixed in the CET after six hours of Donnan dialysis experiment. In effect, Table 2 shows a good correlation with the hydration enthalpies and confirms both the hydrophilic properties of the textile and great affinity for the high hydrated ions. 1-3. Donnan Dialysis Using CMX/SIR/CMX Barrier

Here, the different concentrations of nitric acid were used in the stripping compartment with $[\text{Extractant}] = 10^{-2} \text{ M}$.

Figs. 5 and 6, which give the variation of the ion fluxes as function of concentration of nitric acid in the stripping compartment, in the case of TOPO and DPTU extractant, respectively, show that the quantity of the transported ions increases gradually with the acid

concentration inside the stripping compartment; however, it attains a limit after 2.5 M of HNO_3 . This is due to the osmosis phenomenon, which is observed when the difference of the concentration between the two compartments increases, so in order to limit the osmosis phenomenon we work at 2 M concentration of HNO_3 in the stripping compartment.

To confirm these results, other experiments were conducted by the examination of the metals adsorption onto XAD-4 impregnated by TOPO and DPTU towards extractant concentration and pH of metal solution, as indicated in the following study.

2. Study of the Metal Adsorption onto SIR

2-1. Effect of Extractant Concentration Adsorbed onto the XAD-4 Resin

For the three metals used, in our previous work [50], we studied the effect of the concentration of the extractant impregnated on the

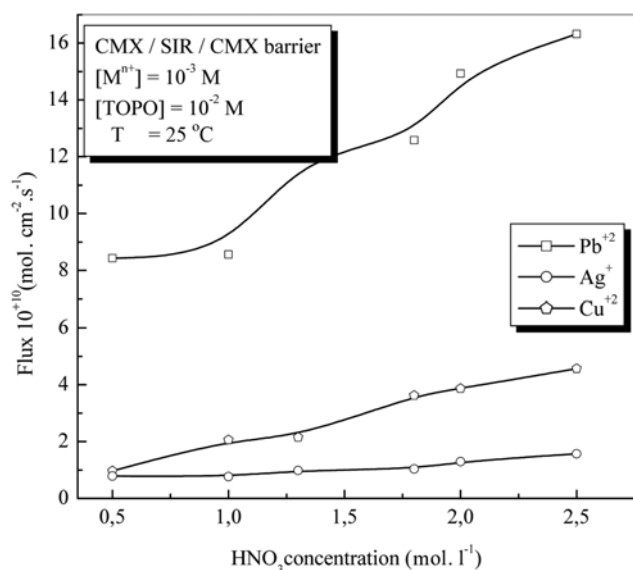


Fig. 5. Ions fluxes as a function of concentration of nitric acid in the stripping compartment.

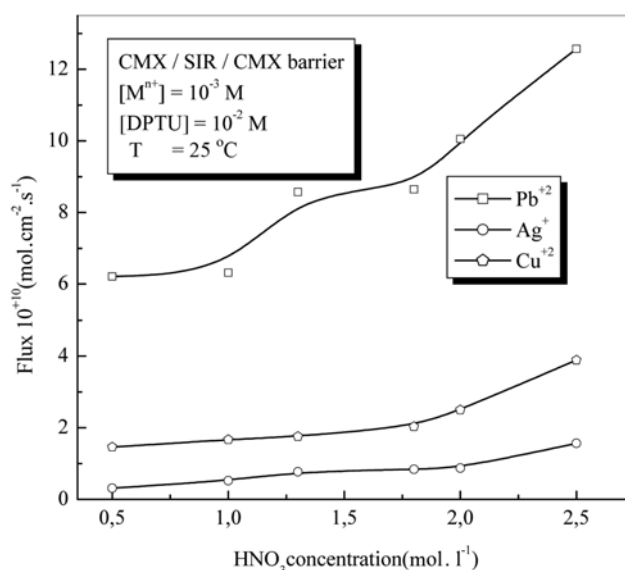


Fig. 6. Ion fluxes as a function of concentration of nitric acid in the stripping compartment.

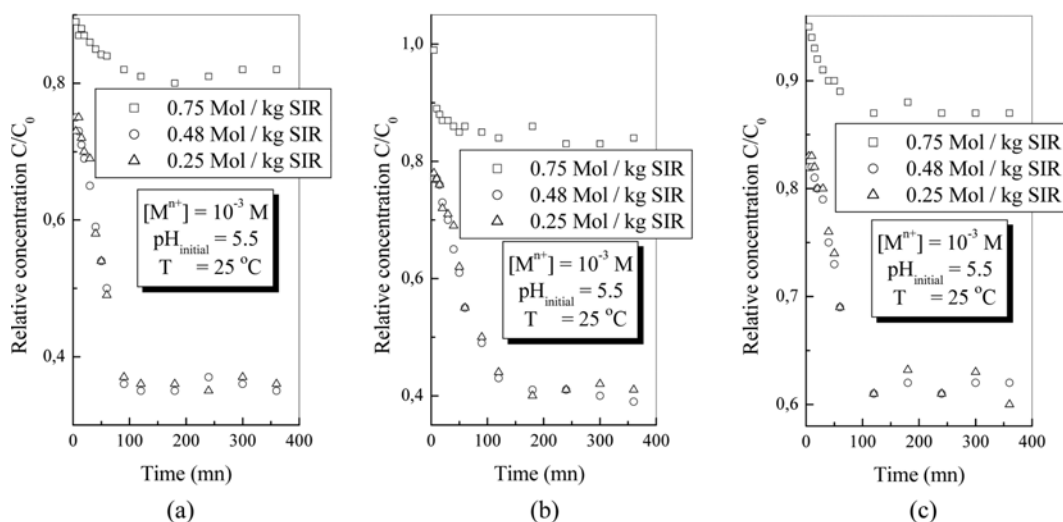


Fig. 7. The variation of the relative concentration of metal ion at different concentrations of the TOPO extractant: (a) Lead, (b) Copper, (c) Silver.

XAD-4 Amberlite resin. We have found that the flux of metals increases with the increasing of the concentration of TOPO and DPTU extractants in the resin; however it attains a limit, due to the saturation of the pores of the resin impregnated with the extractant. In addition, for each extractant concentration, unlike DPTU the use of TOPO as extractant improves the metal ion transport. To explain this result, other experiments were conducted in glass columns of 10 cm long with an inside diameter equal to 4 mm. The experimental procedure has been described in previous studies [51]. Each experiment consists to the introduction of 0.2 g of impregnated resin in the column; then it was kept packed with two pieces of glass wool. A volume of 80 ml of solution at various concentrations metal flows along the column at a rate equal to 0.4 ml/min. The outgoing metal solution is recycled to the column, so that the concentration of metal in the tank remains constant. 2 ml samples were taken every five minutes from the tank. The pH of the aqueous solution recovered was measured with a pH meter. For each extractant we used three concentrations and studied the extraction of silver, copper and lead for six hours to keep the operating conditions above. Samples were taken at regular time intervals. The obtained results are given in Figs. 7 and 8, which present the time variation of the relative concentration for lead, copper and silver, respectively.

These figures show that the increasing of the amount of extractant impregnated on the XAD-4 resin, improves the extraction of metals for the two extractants. This is due to the kinetics of extraction which is controlled by the saturation of the extractant impregnated in the resin. These results are in perfect agreement with those obtained by other authors [52-55].

On the other hand, the evolution of the relative concentration of metals versus the time, given in Figs. 9 and 10, with maintaining constant the concentration of the extractant, the metal concentration and the initial pH of the metal solutions, shows that lead is the most extracted by the XAD-4/ligand resin compared to silver and copper. 2-2. Effect of pH Solution on the Phenomenon of Extraction

The initial values of pH were fixed as 2.6, 3.6 and 6.6. The con-

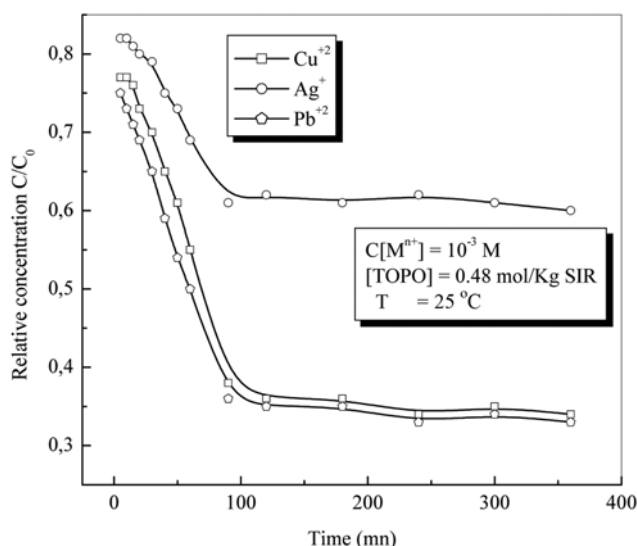


Fig. 9. The time variation of the relative concentration of metal.

centrations of the metal ions and the extractant are equals to 10^{-3} M and to 10^{-2} M, respectively. The samples were taken at regular times. pH value and concentration are given for each solution. Figs. 11 and 12 show the variation of the amount of metal adsorbed on the resin XAD-4 as a function of time for different extractants and at different initial pH values of the metal solution.

The pH of the solution has a great influence on the adsorption kinetics at the equilibrium; it was recognized that this importance is related to the shape of the metal in solution and also to the functional groupings of the extractant adsorbed on the resin. The more the pH value is important, the more H^+ ions move functional groups of different ligands, leading to the fixing of the metal ions on the resin. In effect, from Figs. 11 and 12, when the pH varies from 2.6 to 6.6, the kinetics of extraction becomes faster. This indicates that the pH

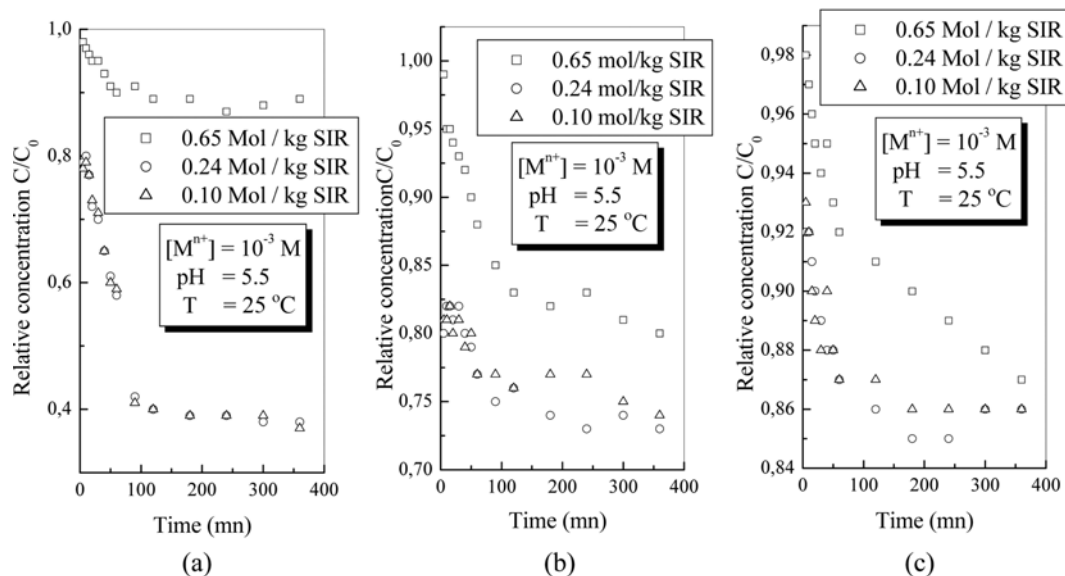


Fig. 8. The variation of the relative concentration of metal ion at different concentrations of the DPTU extractant: (a) Lead, (b) Copper, (c) Silver.

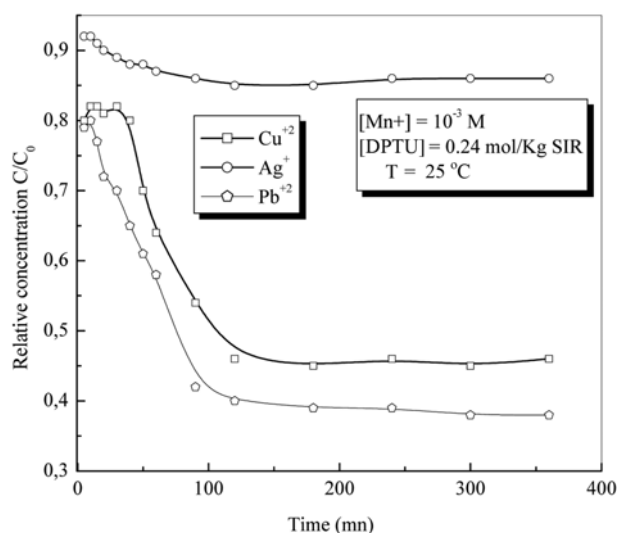


Fig. 10. The time variation of the relative concentration of metal.

improves the extraction of metals. These results agree with those obtained in other works [56,57]. In addition, Cortina et al. showed that metal extraction is pH dependent with the general low: the important extraction of metals is induced by an increase in pH [58].

3. Efficiency of a Hybrid System

We next compare the diffusion fluxes of lead, copper and silver, given versus nitric acid concentration, from the feed compartment to the receiver one, in order to determine an efficient system to the recovery of heavy metals. The obtained results are in Table 3.

From this Table, when we compare the three systems investigated, the diffusion fluxes of metals are generally important in the case of CMX/CMX/CMX system. This result is due to the fact that the thickness of this barrier is lower than others [6]. But when we compare just between the two hybrid systems used, the SIR improves the transport of metal ions from the feed compartment to the strip compartment. This can be explained by the influence of the extractant impregnated on the XAD-4 resin. In addition, we deduce from Table 3, the versatility of the hybrid system, which explains the inverse

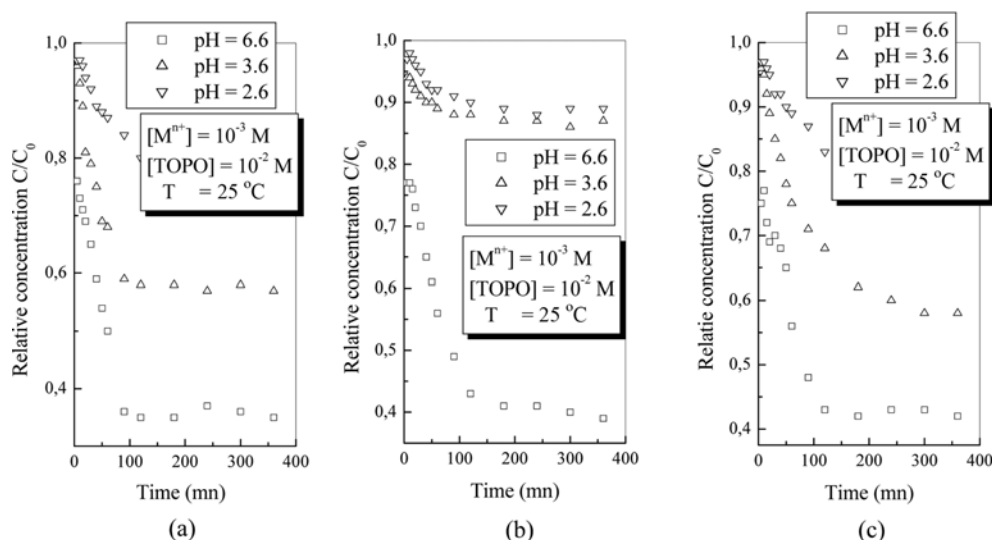


Fig. 11. The time variation of the relative concentration of metal at different pH in the case of TOPO extractant. (a) Lead, (b) Copper, (c) Silver.

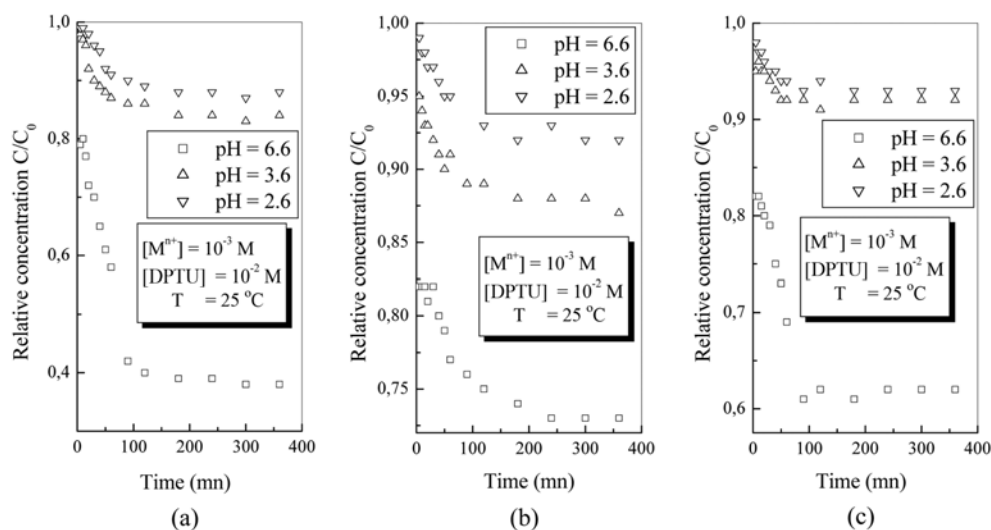


Fig. 12. The time variation of the relative concentration of metal at different pH in the case of DPTU extractant. (a) Lead, (b) Copper, (c) Silver.

Table 3. The diffusion fluxes of metal ion determined through the three systems used

[HNO ₃] (Mol·l ⁻¹)	J _i 10 ¹⁰ (mol·cm ⁻² ·s ⁻¹)			J _i 10 ¹¹ (mol·cm ⁻² ·s ⁻¹)			J _i 10 ¹⁰ (mol·cm ⁻² ·s ⁻¹)		
	CMX/CMX/CMX			CMX/CET/CMX			CMX/SIR/CMX		
	Ag ⁺	Cu ⁺²	Pb ⁺²	Ag ⁺	Cu ⁺²	Pb ⁺²	Ag ⁺	Cu ⁺²	Pb ⁺²
1	10.60	16.21	8.67	26.25	10.36	23.55	4.36	12.58	24.21
2	18.01	48.17	23.67	39.28	21.3	32.62	8.89	18.54	27.89

Table 4. Enrichment factors according to the volume ratio

Volume ratio (feed/strip)	CMX/CMX/CMX			CMX/CET/CMX			CMX/SIR/CMX		
	F _{Ag⁺}	F _{Cu²⁺}	F _{Pb²⁺}	F _{Ag⁺}	F _{Cu²⁺}	F _{Pb²⁺}	F _{Ag⁺}	F _{Cu²⁺}	F _{Pb²⁺}
2	0.79	1.67	1.04	1.96	1.21	1.88	0.51	1.23	1.65
4	1.85	2.40	2.05	3.91	2.30	3.62	1.80	2.03	2.23
10	2.50	2.88	2.50	8.92	4.67	7.98	4.98	6.23	7.52

of its selectivity towards silver and lead. To confirm all these results we proceed to study the enrichment factor F.

4. Enrichment

The various effects of the textile and SIR with D2EHPA as extractant on the osmosis phenomenon according to the considered ion can induce a modification in the selectivity of the operation. To examine this effect, we performed experiments using a feed compartment with three components at the same concentration (10⁻³ M) and a stripping compartment with various concentrations of nitric acid. Enrichment factors were examined by using a circulating cell and by means of reducing volume of the stripping compartment and were calculated according the following relation:

$$F = \frac{C_t}{C_0} \quad (1)$$

Where [C]₀ and [C]_t are, respectively, the initial concentration of M in the feed compartment and the concentrations in the stripping compartment at an instant t of the dialysis.

Experiments for each ion were performed during six hours and the concentration of acid in the stripping compartment was fixed initially to 2 M. Volume ratios between the feed compartment and the stripping compartment were varied from 2 to 10. Table 4 shows that enrichment factors increase with the volume. However, both cation exchange textile and solvent impregnated resin greatly reduce this phenomenon for the less hydrated ions (silver and lead) that have higher enrichment factors values (8.92 and 7.98 for silver and lead, respectively, in case of CET, and 7.52 and 6.23 for lead and copper, respectively, in the case of SIR). This result shows the efficiency of hybrid system, which combines ion exchange membrane to ion exchange textile and solvent impregnated resin to obtain a concentrated solution. This fact is not possible through the three cation exchange membrane (CMX) as we can see for a volume ratio equal to 10 where the higher enrichment factor is 2.88 for copper ion; this is explained by the high water transport which is induced by the great difference between the compartment volumes.

CONCLUSION

We studied the recovery and enrichment of heavy metals, by using classic and hybrid systems, in which the Donnan dialysis is cou-

pled to different membranes. The experiments carried out through three types of barrier containing, respectively, the cation exchange membrane CMX, the cation exchange textile CET and the solvent impregnated resin SIR, sandwiched between two cation exchange membranes, have showed the important role which can play the selective barrier and the properties of CET and SIR on the efficiency of Donnan dialysis process and on the ionic enrichment, respectively. We have noted that the use of the (CMX/CMX/CMX) barrier increases the diffusion fluxes of the metal ions, due to its thin thickness. Also, we noticed that metal ions diffused better through the barrier with solvent impregnated resin than the barrier with the cation exchange textile. This explains the influence of the extractant on the transport phenomenon. The results of our study have showed that the enrichment factor increases with the volume ratio, which becomes important with the use of the CMX/SIR/CMX and the CMX/CET/CMX barriers. In addition, we noted that the use of the SIR and the CET gives rise to high values of the enrichment factor for the less hydrated metallic ions. We have observed that the barrier CMX/SIR/CMX promotes lead enrichment (Pb(II)), and the barrier CMX/SIR/CMX promotes silver enrichment (Ag(I)).

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