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Abstract: This is a report on the separation and recovery of zinc ions from an acidic mine drainage using a stirred transfer cell-type emulsion liquid membrane contactor. Di(2-ethylhexyl) phosphoric acid was used as a highly selective carrier for the transport of zinc ions through the emulsified liquid membrane. A study was made of the effect on the extraction extent and initial extraction rate of the following variables: pH and initial metal concentration of the feed phase, carrier content in the organic solution, a stripping agent concentration in the receiving phase, and stirring speed in the transfer cell. The content of sulfuric acid as a stripping agent did not show in the studied range any significant influence on metal permeation through the SLM, although a minimum hydrogen ion concentration of 100 g/L is suggested in the internal aqueous solution to ensure an acidity gradient between both aqueous phases to promote the permeation of metal ions toward the strip liquor. Results show

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that using a pH of 4.0 in the feed acid solution, a concentration of 3% w/w_o of phosphoric carrier in the organic phase and a H_2SO_4 content of 100 g/L in the strip liquor, the extent and rate of extraction through the liquid membrane can be highly favored, pointing to the potential of this method for extracting heavy metals from many kinds of dilute aqueous solutions.

Keywords: Zinc, acid drainage, liquid membrane, separation

INTRODUCTION

In recent years important progress has been reported by many researchers on the removal or recovery of metal ions from acid aqueous solutions by emulsion liquid membranes (ELM) (1–4). It is clear that this method is a very useful option especially for the treatment of dilute solutions, since the volume ratio between the receiving solution and the metal-donor phase can be greatly decreased. When compared with other conventional methods for metal separation such as ion exchange resins, liquid solvent extraction and precipitation, ELM generally allows higher metal concentration in fewer steps and improved selectivity is easily achieved through the use of specific extractant compounds dissolved in suitable organic diluents.

Among the potential practical applications of ELM we may mention the treatment of many kinds of industrial waste waters (5, 6) and the removal of different pollutants, particularly heavy metals, from contaminated waters from mining activities, including residual solutions from hydrometallurgical processes such as leaching, flotation, or solvent extraction (7, 8). Another possible application of this technology is in acid mine drainage (AMD). They constitute one of the most complex problems inherent to ferrous and non-ferrous metal mining operations. AMDs occurs naturally when sulfide ores, mainly copper and iron, are slowly but continuously oxidized in the presence of air and water, resulting in a highly acidic solution that contains dissolved metals, becoming a pollution problem that is difficult to assess and remediate.

However, the metal ion content in AMDs is normally low, mainly due to dilution by natural ground and surface water, turning impractical the recovery or removal of the metals by using conventional methods which are economically inapplicable (9–11). For example, the metals precipitate only when the pH of these solutions is increased, making this alternative impractical due to problems such as dissolution of precipitates, the use of large inventories of expensive chemicals, and the generation of huge volumes of sludge that is not easily disposable.

Therefore, it becomes necessary to apply alternative technologies for metal removal that are economically attractive for solutions containing low levels of metal ions. In this relation, the use of ELMs has been shown to be an effective technology (12–17). ELMs correspond to a membrane-based solvent extraction process which would be very adequate for uptaking heavy metal ions from acidic aqueous solutions using a reduced inventory of organic solvents in processes with high capacity for extraction. Until now, numerous papers concerning the practical application of ELM have been published for the recovery of metals from hydrometallurgical leach solutions and the removal of other metallic ions from acid waste streams (18–29).

However, we have not found in the technical literature reports on the treatment of these acid mine drainages using this membrane technique. We have studied the use of an emulsion liquid membrane contactor for zinc uptake from an acidic aqueous effluent. The liquid membrane was prepared by dissolving an alkylphosphonic extractant used as a mobile carrier, and Span-80, a surfactant, in kerosene. The liquid membrane allowed selective and efficient metal permeation, under the experimental conditions used in the study (30). In another paper related to this field, we published a communication about the kinetics of copper removal from an acidic mine drainage by a liquid emulsion membrane in a stirred transfer cell, as an approach to understanding the metal permeation mechanism in the ELM (31).

The present study deals with the extraction of zinc ions from an acidic mine drainage using the commercially available D2EHPA alkylphosphoric extractant dissolved in aviation kerosene, using a stirred transfer cell-type surfactant membrane contactor. The stirred transfer cell allows determination of the interfacial area, and reduces drastically some operational problems such as emulsion breakdown and swelling. This way it is possible to measure the initial extraction rate of metal what represents a first approach to know the kinetics of process.

EXPERIMENTAL

Materials

A sample of an acidic mine drainage from a copper mine was used as the feed solution (external aqueous phase). It had a pH in the range of 2 to 4, a variable sulfate concentration averaging 5 g/L, and a specific gravity of 1.06 at 20°C. The AMD sample used in this study had the following average chemical composition: 250 mg/L Cu(II), 80 mg/L Fe, 60 mg/L Zn. Minor amounts of other metals like Ca, Mg, Al, As, Cd, Pb were detected which did not affect the zinc ion extraction. The pH of AMD samples were adjusted by using sulfuric acid and sodium hydroxide solutions. Concentrated sulfuric acid solutions were used as stripping agents, henceforth called the internal aqueous phase, acting as metal-acceptor solutions.

Di(2-ethylhexyl)-phosphoric acid, $C_{16}H_{35}PO_4$, (D2EHPA) (Sigma Co.), a nonspecific alkylphosphoric compound, which is a light-yellowish transparent liquid with a molar mass of 322.4 g/mol and a specific gravity of 0.96 at 20°C, was used as carrier extractant for zinc. Span-80 (sorbitan monooleate), a well-known nonionic commercial surfactant whose structure has been described in a previous paper (30), was used for stabilizing the membrane. Industrial grade aviation kerosene (Esso-Chile, 81% aliphatic compounds) was used without further purification as organic diluent for both the extractant and the surfactant molecules. It has a low volatility that makes possible its use as solvent without loss by evaporation at the high stirring speeds required to prepare the emulsion system. All the other reagents used were of analytical grade.

PROCEDURE

All transport experiments were carried out at 30°C. The membrane contactor consisted of a stirred transfer cell with two compartments, the bottom one for the external aqueous solution of the AMD sample, over which a volume of the primary emulsion phase was added carefully taking care not to disturb the interface. The transfer cell had two turbine-blade stirrers turning in opposite directions. The AMD feed phase zone volume was 170 mL, the compartment for the primary emulsion had a volume of 50 mL, and the interfacial area was 27.34 cm^2. The primary emulsion was prepared by stirring vigorously the internal aqueous stripping solution with the organic phase consisting of the alkylphosphoric extractant and the surfactant dissolved in kerosene, following the experimental procedure described in detail in a previous paper (31). The stirring was done with an OMNI ultrasonic agitator, which allowed dispersion of the internal aqueous solution in the organic phase, producing an emulsion with small droplets.

Both phases, previously conditioned, in their compartments, were stirred gently in opposite directions at constant speed with an Ika-Ruhrwerke RW20 stirrer, keeping a neat interface throughout the experiment.

With the purpose of measuring the concentration drop profile of zinc and other metals in the external aqueous raffinate, samples of it were taken at fixed intervals through a sampling tube connected directly to the lower phase. Metals content in all raffinate samples were measured directly by atomic absorption on a Perkin Elmer Model 3110 spectrophotometer. An Oakton-500 pH meter with a Ag/AgCl glass pH electrode was used for measuring the acidity of the AMD. All other experimental procedures were the same as in a previous paper (31).

RESULTS AND DISCUSSION

It is clear that the transport of metallic ions through an emulsion liquid membrane is largely dependent on the chemical variables that affect the extraction and back-extraction reactions on both sides of the membrane. The extraction of Zn(II) using D2EHPA as carrier corresponds to a typical cation-exchange reaction where the organophosphoric compound is a common weak-acid extractant that forms complexes with metals following different stoichiometry according to its concentration and that of the metal, as has been reported by many authors (32–34). However, first it was necessary to find the appropriate stirring speed conditions in the transfer cell used in this study. As mentioned above, no complete mixing between the aqueous feed and the emulsion phases must occur in order to achieve a clear interface between them. In this way the interfacial area can be calculated and emulsion breakdown is avoided. Stirring speeds in the range 0–80 rpm were examined, the same for both compartments. It was seen that under the experimental conditions tested in this study, a stirring speed of 50 rpm is required to overcome the natural resistance in the outer aqueous phase which is the controlling one, particularly when the metal content in it is as low as the 60 mg/L of Zn(II) measured in the AMD sample used in this study. Below 50 rpm the contact of primary emulsion and acid feed solution was not good enough and no extraction was observed. Above this stirring speed threshold the extraction becomes independent of it, changing only as a function of processing time. However, when stirring speeds faster that 80 rpm were used, it was found that the interface between the emulsion and the raffinate (zinc unloading feed) tended to become unstable and a certain degree of emulsion breaking occurred. Then, in subsequent experiments, a stirring speed of 80 rpm was used which assured good metal extraction and a stable interface.

The extent of zinc extraction, E_{ext} [–], was determined by measuring the metal concentration in the feed solution as follows:

$$E_{ext} = [(C_{Zno} - C_{Zn})/C_{Zno}], \tag{1}$$

where C_{ZnO} and C_{Zn} denote the initial zinc content in the acid mine drainage feed sample and the metal concentration in the raffinate, respectively.

With the purpose of getting a neat interface between the primary emulsion and the aqueous feed phase when the stirring transfer cell is employed, it is important to use an appropriate volume ratio of the organic solution to the internal aqueous solution (Vor/Vaq) to prepare the emulsion phase. Based on the experience obtained in previous experiments related to copper transport using this membrane method, a Vor/Vaq of 2.0 was set in all these experiments (31). This ratio assures a good degree of extraction and an adequate interface with suitable mobility of the stripping aqueous phase droplets in the emulsion. It has been found that metal extraction is independent of the Vor/Vaq ratio when a value greater than 2.0 is used. In contrast, the behavior of the emulsion was poor when a ratio close to 1.0 was used, probably due to reduced motion of the internal aqueous phase droplets within the emulsion. Furthermore, an increase in the emulsion's drop diameter is expected when the organic volume in it is reduced. This fact would cause a reduction of the interfacial contact area between the feed phase and the emulsion at the interface in the transfer cell, thereby bringing about a decreased metal transport across the membrane.

In order to determine the effect of the sulfuric acid content in the internal aqueous stripping phase on zinc extraction, several experimental runs of metal transport through the organic liquid membrane were carried out, changing the concentration of this acid in a range between 10 to 300 g/L (0.10–3.0 mol-g/L). Samples of raffinate were taken at different time intervals. The results are shown in Fig. 1. In all these experimental runs the carrier content in the organic phase was 3% w/w$_o$ D2EHPA and the pH of AMD sample was adjusted at a value of 3.0.

The extraction of Zn(II) is practically constant regardless of the acid content in the strip liquor, indicating the reduced effect of the back-extraction step on the overall process rate. The stripping reaction is very fast and constant in the acid concentration range tested in these experiments. It would be the extraction reaction step—i.e. the chemical reaction of the metal with the carrier extractant in the interface between the external aqueous phase and the emulsion globule—that would have an important influence on the overall process rate, as confirmed by the results shown below. Considering that the extraction of zinc by D2EHPA proceeds by cation-exchange and that to produce the reverse reaction, i.e. the breaking of the metal-extractant complex, a minimum acid content in the strip liquor is needed, in subsequent experiments a H_2SO_4 concentration of about 100 g/L was used in this phase. This level of acid ensures an acidity gradient between both aqueous phases enough to promote the permeation of metal ions toward the receiving solution. This acidity gradient constitutes the chemical driving-force that produces the coupled-transport of metal in the SLM. In this way the metal is stripped and the carrier is regenerated and pumped back to the extraction interface.

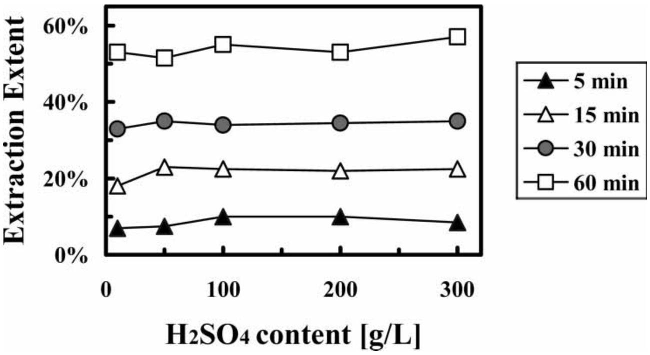

Figure 1. Influence of sulfuric acid content in internal aqueous solution on extraction extent of zinc. Feed solution: 60 mg/L Zn, initial pH 3.0. Organic solution 3% (w/w$_o$) D2EHPA in kerosene.

Figure 2 shows the change in extraction extent of zinc with pH of the acid mine drainage. These experiments were carried out at different carrier extractant concentrations in the organic phase, using in all runs a surfactant concentration of 2% w/w_o and a sulfuric acid concentration of 100 g/L in the strip liquor. The pH of the feed solution used to be a very important variable in solvent extraction processes, especially when the extractants act by an ion-exchange mechanism.

In Fig. 2 it is seen that the highest Zn(II) extraction was achieved in the pH range between 4 and 5. Metal extraction decreases as the pH of the aqueous feed solution decreases. This must be attributed to the fact that ionic zinc species form preferably a stable complex with the alkylphosphoric compound under weakly acidic conditions, in agreement with the experimental data of the extraction equilibrium reported before (30). When at the interface the extraction reaction starts and its rate increases, the zinc-D2EHPA complex diffuses towards the organic phase driven by the favored mass transfer of this species through the W/O interface. The results also show that the extent of transport of metal through the membrane is enhanced as the content of the carrier compound in the organic membrane film is increased. It is clear that the extraction chemical reaction takes place around the interface between the AMD solution and the primary emulsion phase.

From previous studies made to test the potential capacity of ELM to recover or remove heavy metal ions from aqueous solutions, it was clearly seen that the coupled transport process of the ions through membranes retains the characteristics of conventional solvent extraction processes in mixer-settler reactors. Therefore, ELM corresponds to a process of mass transfer with chemical reactions whose equilibrium and kinetics aspects are fundamental. In this sense, the content of carrier extractant in the organic

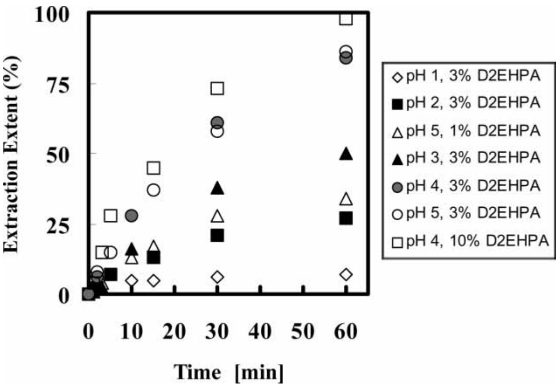

Figure 2. Effect of feed initial pH and carrier extractant concentration on the extraction extent of zinc. Feed solution: 60 mg/L Zn; Stripping solution: 100 g/L H_2SO_4.

phase would affect the chemical extraction reaction at the interface as well as the diffusion process through the membrane

If it is assumed that the extraction chemical reaction between metal and extractant occurs at the external interface of the organic liquid membrane, and that as reported previously (35) the carrier in a kerosene-like aliphatic diluent is normally dimerized, the extraction reaction would proceed according to one of the following two most probable equations:

$$Zn^{2+}_{aq} + 2(HR)_{2org} \longleftrightarrow ZnR_2 \cdot 2HR_{org} + 2H^{+}_{aq} \quad (2)$$

$$Zn^{2+}_{aq} + (3/2)(HR)_{2org} \longleftrightarrow ZnR_2 \cdot HR_{org} + 2H^{+}_{aq} \quad (3)$$

where HR denotes the acid alkylphosphonic extractant, $(HR)_2$ is its dimer, and the subscripts “aq” and “org” denote aqueous and organic solutions adjacent to the interface. Both extraction equations have been proposed, each of them prevailing according to the extractant concentration in the organic phase and the ratio of the metal and the carrier content in the outer interface (36, 37). The higher the carrier/metal concentration ratio the greater is the possibility that the chemical equilibrium be governed by equation 2. These equations confirm that the acid content of the aqueous solution is one of the controlling parameters of the reaction.

Figure 3 shows the influence of the pH of the feed aqueous solution on the initial extraction rate, R_{in}, calculated using the following equation:

$$R_{in} = C_{Mo}(V_{aq}/A)(dE/dt) \quad (4)$$

where V_{aq} and A denote the volume of feed solution and the area of the interface, respectively, (dE/dt) represents the change in the extent of metal extraction with time, and R_i is expressed in [mol-g/cm^2 · sec].

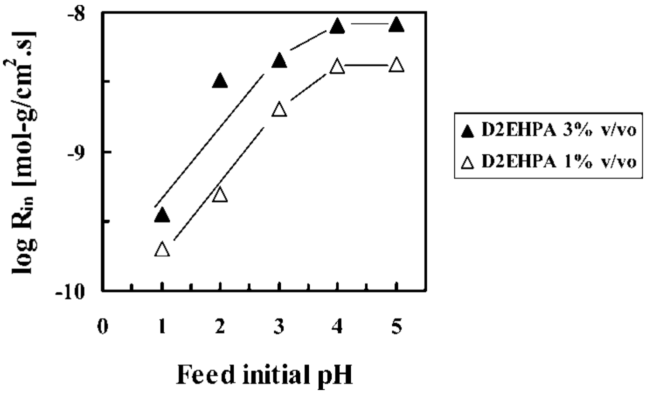

Figure 3. Effect of feed initial pH on initial extraction rate. Feed solution: 60 mg/L Zn; Stripping solution: 100 g/L H_2SO_4.

It is seen that the initial extraction rate is proportional to the pH of the acid mine drainage. A maximum rate is reached in the pH range greater than 4.0, which agrees with the results shown in Fig. 2. These results would indicate that at higher pH values the rate would be controlled by the diffusion of metal species in the external aqueous phase film. However, at lower pH the overall rate of the process would be controlled by the chemical reaction between the metal and the extractant at the external interface of the liquid membrane, since in this acidity range the rate is affected by the extractant, the metal and the hydrogen-ion concentration at the interface.

Figure 4 shows the dependence of initial extraction rate on carrier content in the organic solution. It is seen that the initial extraction rate is proportional to the extractant content in the primary emulsion. However, a larger effect was seen in experimental runs made at higher pH values, where the chemical activity of the carrier is favored. An excess of extractant will not change dramatically the extent and the rate of metal extraction due probably to the stoichiometry of formed zinc-carrier complexes, as is shown in the extraction chemical equations. Moreover, as is well-known, an unnecessarily higher extractant molecule content in the organic phase can produce an increase in the viscosity of the liquid membrane affecting the diffusion of the species and thereby the mass transfer process. Besides, the surface active properties of the carrier and its metal complexes at higher D2EHPA concentrations could destabilize the emulsion.

Figure 5 shows the change in the extent of zinc extraction as a function of metal concentration in the aqueous feed solution, in experimental runs carried out at two different pH values. In all the experiments a 3% w/w$_o$ carrier content in the organic phase was employed. As expected, metal extraction decreases as the zinc content in the AMD sample increases, which is consistent with the fixed stoichiometry to form the Zn-D2EHPA complex. The higher

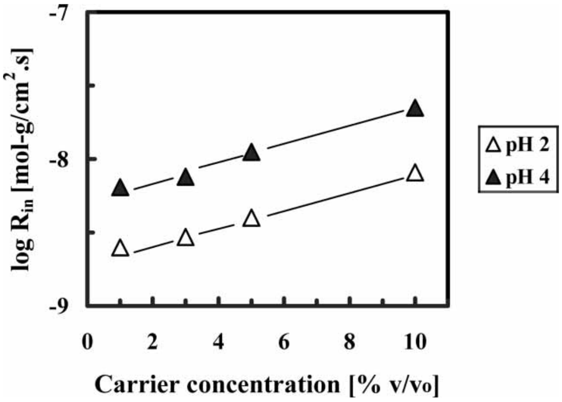

Figure 4. Dependence of initial extraction rate on carrier content in organic solution. Feed solution: 60 mg/L Zn; Stripping solution: 100 g/L H_2SO_4.

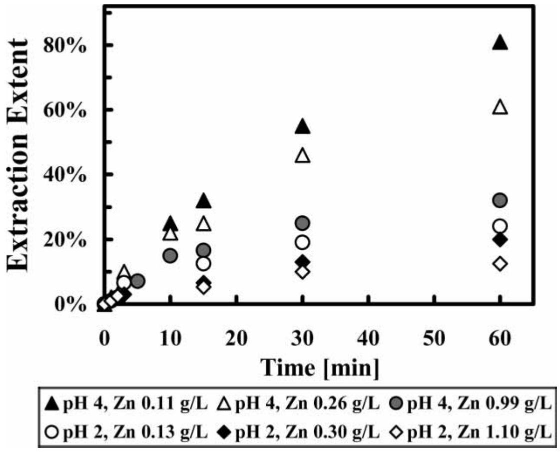

Figure 5. Zinc extraction extent as a function of feed metal concentration. Organic solution 3% (w/w$_o$) D2EHPA in kerosene. Stripping solution: 100 g/L H_2SO_4.

the metal content in the feed solution, the higher must be the concentration of the carrier in the liquid membrane.

Figure 5 also shows that the extraction of metal is enhanced when the acidity of the acid drainage is lower, confirming the results described before. However, more important is the measurement of the influence of metal concentration in the feed solution on the initial extraction rate. Figure 6 shows the dependence of the initial metal extraction rate with the change in zinc content in the AMD sample. The carrier content in the liquid membrane was the same as in Fig. 5. It is seen that under the experimental condition studied there was a clear proportionality between the initial rate and the metal concentration in the feed solution. However, a higher metal

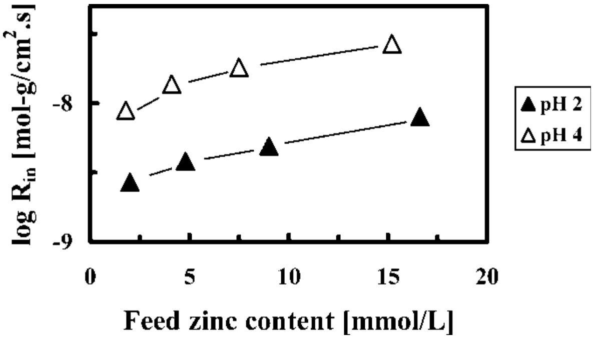

Figure 6. Influence of feed zinc content on initial extraction rate. Organic solution 3% (w/w$_o$) D2EHPA in kerosene. Stripping solution: 100 g/L H_2SO_4.

extraction rate was found in the experiments carried out at higher pH values, in agreement with the extraction extent data.

In short, from the results presented in this study it is possible to indicate that the pH of the AMD and the carrier extractant concentration in the organic phase affect the extraction equilibrium, and that both variables as well as the metal content in the acid drainage showed a dependence on the initial extraction rate of metal in the stirred transfer cell. This fact confirms that the extraction chemical reaction has an important role in the control of the metal permeation process through the membrane. Neither the stripping step nor the diffusion of species in the different phases of the system had a significant influence on metal transport.

Figure 7 shows schematically the interfacial chemical reactions for zinc permeation through the ELM, with the alkylphosphoric acid as carrier. The transport of zinc through the membrane is considered to be composed of the following elementary steps:

1. diffusion of zinc ions through the stagnant layer of AMD solution
2. at the external interface of emulsion globules, zinc ions react with the dimer of the extractant D2EHPA (represented as HR)
3. the zinc-extractant complex diffuses into the emulsion droplet, crossing the organic phase
4. an interfacial stripping reaction occurs at the internal interface of the emulsion globule, where breaking of the metal complex by the stripping agent takes place, and
5. zinc ions diffuse through the stagnant layer of internal strip liquor where they are concentrated.

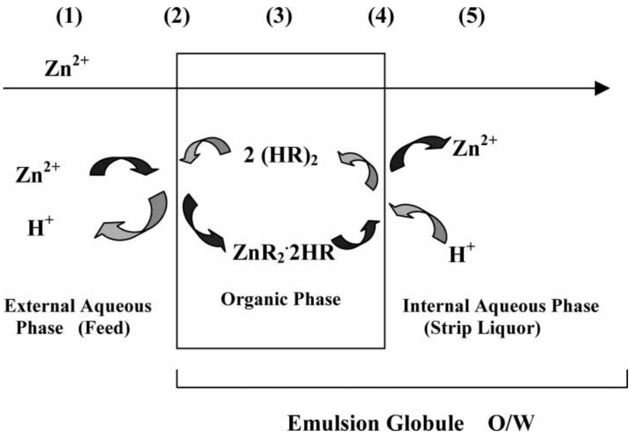

Figure 7. Schematic representation of zinc transport through the surfactant liquid membrane.

Then, step 2, i.e. the interfacial extraction reaction, would be the rate-controlling step, with the diffusional resistance in the membrane and aqueous phases being negligibly small. This assumption, validated by the experimental results, makes it possible to consider the equilibrium at any point inside the membrane, and therefore the concentration of metal species—as free ions or complexed with carrier—at the interfaces can be estimated from the equilibrium reactions proposed in Eqs (2) and (3). Furthermore, although in the range studied the acid concentration in the stripping solution did not have an important influence on the extent of metal extraction, a minimum content of it is required to break the Zn(II)-D2EHPA complex, allowing the zinc ions in the inner aqueous solution to concentrate and regenerating the carrier, which back-diffuses again to the outer interface for a new extraction-stripping cycle.

A maximum value of 98% for the extraction extent of Zn(II) was measured under the most appropriate experimental conditions tested in this study: a pH of 4.0 in the AMD solution, a 3% w/w_o of phosphoric carrier in the organic solution and a H_2SO_4 content of 100 g/L in the strip liquor. Although copper ions may be extracted by the alkylphosphoric extractant at a pH value higher than 3.0, when both metals, zinc and copper, are present together in an aqueous solution, the competition to form the metal-extractant complex is easily won by zinc, explaining why the extent of Cu(II) extraction did not exceed a value of 2–4%. No other ions were cotransported at all under the optimal conditions for zinc uptake. It is more critical to carry out the experiments under suitable acidity conditions in the feed solution. As measured in these experiments, the stability of the zinc complex with the weak acid carrier increases as the hydrogen-ion concentration in the external interface decreases. This is probably due to the fact that under those conditions there are fewer hydrogen-ions which could compete with zinc ions for the available site at the interface.

An ELM is normally unstable, with emulsion breakdown caused by the coalescence of dispersed drops being one of the most complicated problems. Another common operational problem of ELM is the appearance of a swelling phenomenon due to the transfer by osmosis of water from the external aqueous phase toward the strip liquor. Both problems were evaluated by measuring the volume change of the internal and external aqueous solutions. For that reason a surfactant which causes a decrease of the interfacial tension of the system, is required, generating smaller globules that help stabilize the emulsion. The widely known compound Span-80 was used as emulsifying agent at a concentration of 2% w/w_o in the organic phase. This surfactant content was appropriate to keep the emulsion stable under the experimental conditions examined in this study. The use of an unnecessarily higher concentration of Span-80 can affect the metal transport efficiency in the membrane, as a greater interfacial resistance would be generated. On the other hand, although the carrier presents a certain degree of interfacial activity because of its chemical structure, it was found that, regardless of the carrier concentration in the liquid organic membrane, the primary emulsion is not formed if a surfactant with concentrations below 1.5% w/w_o is used to prepare the organic solution.

CONCLUSIONS

The separation of zinc ions from acidic mine drainage by a stirred transfer cell-type liquid membrane contactor was carried out in a batch operation. This contactor allowed to measure the initial extraction rate of metal which permitted to obtain information about the kinetics of process. The experimental results provided the following information:

The D2EHPA carrier, containing a phosphorus atom, had a high affinity for zinc removal. The transport of metal was enhanced by an increasing content of alkylphosphoric extractant in the organic phase and a decreasing acidity of the aqueous feed solution, indicating that the extraction chemical reaction between the metal and the carrier would occur at the interface that separates the external aqueous solution and the droplet of the primary emulsion. Furthermore, the initial extraction rate was affected by both variables (carrier content and pH) and also by the increase in metal concentration in the acidic drainage.

However, the results indicate that at higher pH values the rate would be controlled by the diffusion of metal species in the external aqueous phase film, and at lower pH values the overall rate of the process would be controlled by the chemical reaction between the metal and the extractant at the external interface of the ELM.

The high degree of selectivity for zinc transport shown by the ELM system reveals its promising potential for the recovery or selective removal of zinc ions from waste aqueous solutions. The information obtained in this study will be of great value in subsequent steps of a research related with the use of batch-type stirred tanks in which a double emulsion is fully formed, which is the preliminary stage required to operate the ELM process efficiently on an industrial scale.

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