Emulsion Pertraction Technology In Hollow Fiber Modules: Application To Metallic Valorisation From Wastewater

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Nowadays, polluted wastewater containing heavy metals is an environmental problem that should be solved due to the high environmental impact of these wastes. In order to fullfill the “zero discharge” strategy, the recovery of the valuable compounds from these solutions is an important economical and environmental objective. One of the technologies in agreement with this strategy is the Emulsion Pertraction Technology that is a new membrane-based solvent extraction technology able to remove metals from aqueous streams in a selective way and simultaneously, to concentrate them making possible metallic valorisation.

In this work two specific applications are discussed: i) the removal of zinc contained in spent hydrochloric acid solutions from zinc hot galvanizing plants and, ii) the removal of hexavalent chromium from surface and groundwaters as a result of the widespread use of this metal in industrial applications. In both cases, after proving the viability of the separation-concentration processes, the influence of the operation variables on the process efficiency is analysed.

1. Introduction

The presence of metals in wastewaters, is an environmental problem that is necessary to solve due to the high toxicity of most of these compounds. On the other hand, the valorisation of these compounds -for reuse in some industrial applications- is an interesting alternative in order to minimize the environmental impact and to compensate the costs associated to the cleaning processes. Therefore, the development of “near zero discharge” technologies which also permit the recovery of the valuable compounds is a sustainable alternative to the traditional treatment processes.

The difficulty in the development of recovery processes is associated to physico-chemical complexity usually encountered in waste effluents, where the target species are present in a heterogeneous mixture with different amounts of non-desirable compounds. Membrane-based solvent extraction technologies and in particular Emulsion Pertraction Technology (EPT) are promising alternatives for the treatment of aqueous streams containing metallic pollutants.

EPT allows the simultaneous extraction (EX) and back-extraction (BEX) of metallic pollutants using hollow fiber modules as membrane contactors. In EPT, the aqueous phase with the target species is put in contact in one hollow fiber module with an emulsion formed by stripping phase dispersion into the organic phase that contains a selective extractant. The solute is transferred from the aqueous feed solution to the organic phase, and then it is transported to the internal back-extraction solution. Thus, in the EPT technology, extraction and back-extraction operations are efficiently combined in a single membrane contactor unit. Therefore, the use of EPT is in agreement with the process intensification strategy that aims at the replacement of large, expensive and energy-intensive equipment with alternatives that are less costly, more efficient or that combine multiple operations into a single apparatus (Charpentier, 2002).

Emulsion pertraction has been applied to the selective recovery of different heavy metals such as Zn, Hg, Fe, Pb, Cd, Cu, Cr, and Ni. EPT is specially suitable for selective removal of these metals from low concentration levels and their simultaneous concentration to a much higher level. Effluents coming from galvanic processes, nuclear industries, zinc-containing wastewaters from the rayon industry, etc. have been successfully treated by means of this technology (Ortiz et al., 2003).

In this work, two different applications have been considered: i) separation and recovery of zinc chlorocomplexes contained in spent pickling solutions and, ii) separation and concentration of hexavalent chromium anions contained in groundwater reservoirs.

2. Experimental set up

Valorisation experiments were done at laboratory scale using one microporous hollow fiber module (Liqui-Cel® Extra-Flow 2.5 x 8, Hoechst Celanese) as contactor, with an effective contact area of 1.4 m^2 and an effective mass transfer length of 0.15 m. These contactors contained 10200 fibers of polypropylene (X-30 fibers) with a nominal porosity of 40% and had an internal diameter of 240 μm with a wall thickness of 30 μm. The tortuosity factor was 2.6.

Figure 1 presents a flow diagram describing the experimental set-up. The aqueous feed solution flows through the inner side of the hollow fiber, while the emulsion phase runs counter currently through the shell of the module. The differential pressure between the aqueous phase and the emulsion phase allows the stabilization of the interface between both phases at the hydrophobic membrane pores (Urtiaga et al., 2005).

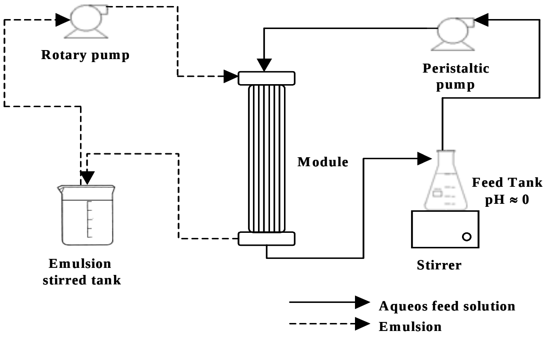

Figure 1. Experimental set-up.

Table 1 shows the physicochemical characteristics of the aqueous streams used to carry out the experimental work. In the case of zinc recovery, the system under study has a very high chloride concentration and consequently zinc ions form chlorocomplex species (Regel, 2001; Cierpiszewski, 2002). In the second case study, synthetic solutions that simulate the composition of groundwater containing chromium(VI) were employed. These solutions contain other competitive species, mainly sulphate and chloride anions due to the specific location of the groundwater reservoir.

Table 1. Feed solutions characteristics.

	Zinc Solution (Real effluent)	**Chromium Solution** (Synthetic solutions)
Compounds	**[Zn] =1254 mol/m^3** [Fe^{+2}] = 1719 mol/m^3 [Cl^-] = 6403 mol/m^3 Traces: Mn, Pb, Al, Cr, etc.	**[Cr^{+6}] = 9.6 mol/m^3** [SO_4^{2-}] = 10.4 mol/m^3 [Cl^-] =8.5 mol/m^3
pH	≈ 0	Adjusted to 1.5 (H_2SO_4)

Emulsion was prepared by dispersing the aqueous stripping solution into the organic phase which contains the selective carrier. For this purpose an emulsifier Ultraturrax T25 (IKA A.G.) able to provide high stirring speed, (8000 - 20500 rpm) was used.

For zinc extraction, pure TBP (Tributyl Phosphate, MERCK) and service water were the solvating extractant and the stripping phase respectively. The organic phase used for chromium (VI) extraction was prepared using 10% v/v of tri – octyl/decyl amine (Alamine® 336, COGNIS) as anionic extractant, Isopar L Fluid (EXXONMOBILE CHEMICAL), that is an isoparaffinic hydrocarbon, as solvent, 3% v/v of Pluronic PE 3100 (block copolymer of ethylene oxide and propylene oxide, BASF) as surfactant and 1% v/v of 1-Dodecanol (MERCK) as modifier. The BEX step was performed using NaOH (PANREAC) in a concentration range of 3000 – 6000 mol/m^3.

Chromium and zinc concentrations were analysed using an atomic absorption spectrophotometer Perkin Elmer 3110. The sulphate and chloride determination was carried out with an ion chromatograph, Dionex Dx-120.

3. Results

In both cases, the viability of the separation-concentration process from the solutions with the compositions given in Table 1 was analyzed. The results concerning to the viability of the separation-concentration of zinc and chromium has been reported in previous works (Samaniego et al., 2007; Bringas et al., 2006).

After having tested the process viability, different kinetic experiments were performed in order to analyze the influence of both, the initial zinc concentration and the emulsion volume ratio (TBP/water) in the kinetics of EX and BEX steps. In the case of chromium the influence of sodium hydroxide concentration in the EX and BEX kinetics was analysed. In order to define the operation conditions that maximize the process selectivity the influence of the chromium concentration in the extraction of sulphate and chloride anions was studied. Experiments were duplicated so that the results presented here are average values of the metal concentration, obtained in both experiments.

3.1 Zinc

Starting with the effluent with an initial concentration of zinc of 1200 mol/m^3 (Experiment I), two different feed batches were prepared by dilution of the effluent to obtain initial zinc concentrations of 600 and 300 mol/m^3 (Experiments II and III). The 80/20, 60/40, 50/50 TBP/water volume ratio in the emulsion was studied (Experiments IV, V y VI). In this case initial zinc concentration -1200 mol/m^3- was used. Figure 2 shows the kinetic results of extraction and back-extraction in Experiments I-III. The dimensionless concentration of zinc is given in order to facilitate the comparison between the results obtained at different initial zinc concentrations.

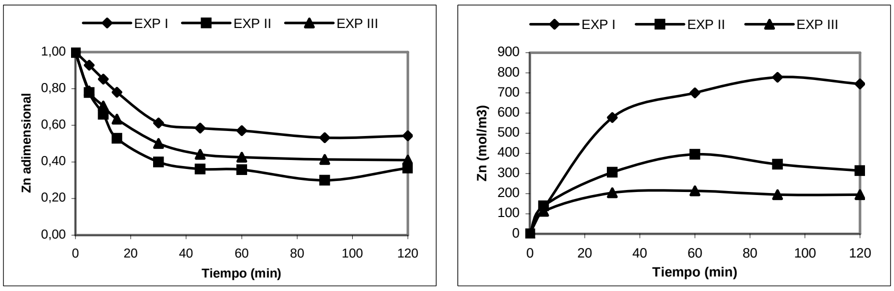

Figure 2. Evolution of zinc concentration in the extraction and stripping phases.

As shown in Figure 2, the concentration of zinc in the aqueous feed phase down to the range between 40-60% of the initial value after 2 hours of experimental running, indicating that the extraction of zinc is achieved with a satisfactory rate, whereas the concentration of zinc chloride in the stripping phase achieved maximum values around 700 mol/m^3. Figure 3 shows the evolution with time of zinc concentration in the aqueous feed phase and mass in the stripping phase in Experiments IV to VI.

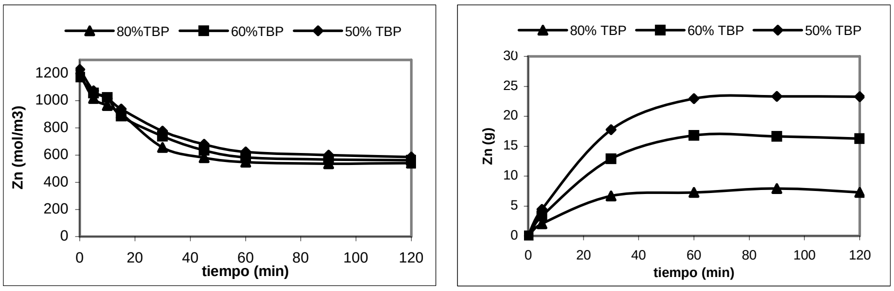

Figure 3. Influence of TBP/Water volume ratio in the stripping phase.

As shown in Figure 3 the influence of the TBP/water volume ratio in the extraction kinetics can be considered negligible, due to in all the experiments the carrier concentration is higher than the stoichiometric one required for the total extraction of zinc. In relation to the BEX step, it is observed that the lower volume ratio TBP/Water, the higher mass of back-extracted zinc. Therefore, the back-extraction percentage referred to the mass of zinc in the aqueous feed solution, increases from 10-15% to 30-40% when the TBP/Water volume ratio changes from 80/20 to 50/50. This behaviour can be explained by two phenomena: i) working with lower extractant concentration the BEX reaction is shifted to the right and, ii) high volume of water in the emulsion leads to lower values of zinc concentration and consequently to a higher driving force when compared to the solubility limit.

3.2 Chromium

The experiments were carried out working with the aqueous feed solution flowing in a single-pass mode whereas the emulsion phase recycled itself in order to achieve a high concentrated stripping solution.

Two different experiments were performed in order to analyse the influence of the BEX agent concentration on the separation kinetics working with synthetic solutions with the characteristics shown in Table 1: Experiment I, [NaOH] = 3000 mol/m^3 and Experiment II, [NaOH] = 6000 mol/m^3. Figure 4 shows a comparison of the kinetic results of the EX and BEX of chromium (VI)), sulphate and chloride.

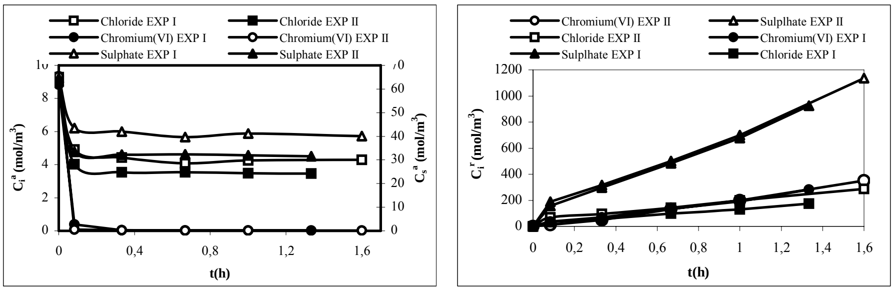

Figure 4. Evolution with time of the solutes concentration in the aqueous feed and back-extraction solutions

From Figure 4 it can be noticed that in the studied range of variables, 3000 mol/m^3 ≤ NaOH ≤ 6000 mol/m^3, and working with excess of OH^- ions there is no influence of the NaOH concentration in the BEX step. Furthermore, the BEX process is not selective because all the species are totally back – extracted from the organic phase. For this reason the selectivity has to be controlled in the EX step. The operation variables that affect the process selectivity are the initial chromium concentration, pH and flowrate of the aqueous feed solution. Different experiments were performed in order to study the influence of those operation variables in the extraction of sulphate and chloride. Figure 5 shows the evolution of the sulphate flux and chloride flux with the initial chromium concentration.

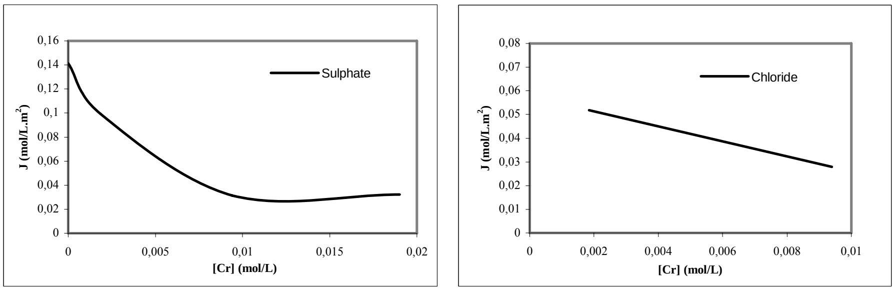

Figure 5. Evolution of the sulphate and chloride fluxes

From these results it can be confirmed that the higher chromium concentration in the aqueous feed solution, the lower sulphate and chloride extraction fluxes and consequently a higher process selectivity is achieved. The influence of the pH and flowrate of the aqueous feed solution will be analysed in a further work.

4. Conclusions

This work reports the viability of using the emulsion pertraction technology for the separation and recovery of i) zinc contained in spent hydrochloric acid solutions from zinc hot galvanizing plants and, ii) chromium from polluted groundwaters. In both cases, after proving the process viability, the influence of the operation variables on the process efficiency has been analysed.

5. Acknowledgements

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6. References

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