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Inmaculada Ortiz[a]; Eugenio Bringas[a]; M. Fresnedo San Román[a]; A. Miren Urtiaga[a]
[a] Departamento Ingeniería Química y Química Inorgánica, ETSIIyT, Santander, Spain

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Selective Separation of Zinc and Iron from Spent Pickling Solutions by Membrane-Based Solvent Extraction: Process Viability

Inmaculada Ortiz,* Eugenio Bringas,
M. Fresnedo San Román, and A. Miren Urtiaga

Departamento Ingeniería Química y Química Inorgánica, ETSIIyT,
Avda. los Castros, Santander, Spain

ABSTRACT

This work reports the viability of the selective separation of zinc from spent pickling solutions by means of membrane-based solvent extraction to get a high concentrated zinc solution with a negligible content of iron and other metals that could be used in a electrolytic process to recover zinc in a metallic form. By working with waste effluents as feed solutions that contained these main components, Zn 78 g/L av., Fe 90 g/L av., and HCl 237 g/L av., Tributyl phosphate (TBP) and water were selected as the extractant and back-extraction agent that allowed maximum zinc separation and recovery. With the kinetic results obtained in a bench-scale set-up containing two hollow fiber (HF) modules the selectivity

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*Correspondence: Inmaculada Ortiz, Departamento Ingeniería Química y Química Inorgánica, ETSIIyT, Avda. los Castros s/n, 39005 Santander, Spain; Fax: 34-942-201591; E-mail: ortizi@unican.es.

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of zinc over iron recovery, $\alpha_{Zn/Fe}$, was calculated. The parameter $\alpha_{Zn/Fe}$ depended on the initial metallic concentration in the feed solutions and reached a maximum value of $\alpha_{Zn/Fe} = 146$ (g Zn/g Fe).

Key Words: Membrane solvent extraction; Zinc; Iron; Selectivity; TBP.

INTRODUCTION

Zinc layers commonly are used to protect steel goods from corrosion. The process of zinc deposition consists of the following steps: (i) degreasing with a hot alkaline solution; (ii) rinsing with water; (iii) pickling with HCl 20%; (iv) rinsing; and fluxing with zinc and ammonium chlorides and hot-dip coating with molten zinc at temperatures about 450°C. In the pickling step, hydrochloric acid is consumed during the process, but the concentration of chloride ions does not change. As a result, the spent pickling solution contains zinc(II) and iron, present mainly in the form of iron(II), which forms appropriate chlorocomplexes. Typical metallic concentrations lie in the range 20–120 g/L for zinc and 100–130 g/L for iron, whereas, the hydrochloric acid concentration lies in the range 1–6 mol/L.[1] Besides, the solution may contain other heavy metals (Pb, Ni, Cu, Mn, etc.) as impurities. Thus, the resulting effluent presents a strong hazardous character and the need for a cleaning process before discharge. The conventional process to treat the spent pickling solution, the Ruthner process, evaporates the hydrochloric acid and forms granules of iron oxide in a fluidized bed at temperatures above 600°C; however the presence of zinc(II) in amounts higher than 0.5 g/L disturbs the process.[2,3]

The development of a selective process, allowing the recovery of zinc under conditions that permit the manufacture of electrolytic grade metal, would reduce the effluent toxicity recovering at the same time, the component of higher added value. Dispersion-free solvent extraction by using microporous hollow-fiber (HF) contactors has received considerable attention and has been proved to be very effective in the removal of solutes from aqueous solutions.[4–8] Membrane-based nondispersive extraction is characterized by the stabilization of the organic–aqueous interface at a porous material, avoiding the dispersion of the organic phase into the aqueous phase or vice versa and, thus, eliminating emulsion formation and phase entrainment. Additional advantages of nondispersive solvent extraction have been widely mentioned in the literature.[5–8]

Zinc removal from multicomponent aqueous solutions had been analyzed previously by using this technology.[9–11] With regard to the separation of the metal from solutions containing hydrochloric acid, Cierpiszewski et al.[3] reported the study of the behavior of different extractants in the separation between zinc and iron concluding that solvating extractants led to better extraction results than the other analyzed compounds. Jha et al.[1] reported a review of the extraction agents for similar applications; they concluded that the selection of the optimum extractant would depend on the metal concentration, solution acidity, and other constituents present in the aqueous phase. Kirschling et al.[2] studied the viability of the recovery of zinc from model HCl solutions (Zn 11–50 g/L and HCl 1.8 M) by using tributyl phosphate (TBP) and CYANEX 923 both in a conventional extraction set-up, as well as in a NSDX process; in the work, water was used as a back-extraction (BEX) agent. Other applications with using TBP as an extraction agent are mentioned in the literature.[12–15]

This work is aimed at the development of a selective process based on the use of membrane-assisted solvent extraction technologies to the recovery of the metallic zinc contained in acidic spent pickling solutions with high iron(II) concentration. After having checked the viability of the process in a laboratory HF set-up, an experimental planning was performed to analyze the influence of the initial metallic concentration on the separation selectivity.

EXPERIMENTAL SET-UP

Materials and Methods

Spent pickling solutions from surface treatment processes were used in the experiments. Physicochemical characteristics are shown in Table 1.

The organic compounds di(2,4,4-trimethylpentyl) phosphinic acid (CYANEX 272, CYTEC, Ontario, Canada), di(2-ethylhexyl) phosphoric acid (D2EHPA, Merck, Schuchardt, Germany) and TBP (Merck, Schuchardt, Germany) were tested as selective extractants for zinc. In the stripping process, water and a solution of sulphuric acid 1 M were used.

For the simultaneous extraction (EX) and BEX process, two HF modules were used, flowing the organic phase from the EX module to the BEX one. In the first module, the solute was transferred from the aqueous feed to the organic phase, and, in the second module, the solute was transported to the BEX phase. When the organic phase leaves the BEX module, it flows to the homogeneization tank of the organic phase and then it flows again to the extraction step. HF modules were purchased from Hoechst Celanese (Hoechst Celanese Corporation, North Carolina, USA); the modules used in the experiments have an effective mass-transfer area of 1.4 m^2 and an effective mass-transfer length of 150 mm. These contactors contained 10,200 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.

Table 1. Composition of the aqueous feed phase.

Property	Value	
Color	Green	
pH	$\sim$0	
Composition	mg/L	mol/L
Zn	80,000	1.22
Fe^{2+}	83,667	1.50
Fe^{3+}	8,333	0.15
Mn	386.3	6.98E−3
Pb	137.7	6.65E−4
Al	60.6	2.25E−3
Cr	52.0	1.00E−3
Ni	45.8	7.80E−3
Cd	20.6	1.83E−4
Cu	8.10	1.27E−4
Co	1.60	2.71E−4
HCl	237,000	6.5

Aqueous phases flowed through the inner side of the microporous HF membranes whose pores were filled with the organic extractant, and the organic extractant flowed concurrently in the shell side on both HF modules. Figure 1 depicts the experimental set-up comprising two modules, three tanks, and accessories.[16–19]

A pH meter was used to measure pH values in the stripping phase during the experiments.

Pumping of the feed phase was achieved by using diaphragm pumps ETRON3 (Alldos, Pfinztal, Germany) capable of flows up to 1250 mL/min. Pumping of the organic phase was achieved by means of a gear pump A 7144-07 (Micropump, Vancouver, Canada) capable of flows up to 4000 mL/min.

Finally, in the case of the BEX phase, a peristaltic pump 313 (Watson Marlow, Wilmington, USA) capable of flows up to 1000 mL/min was used.

Three flow meters were used to monitor the flow rates of the feed, stripping, and organic phases. They were situated at the outlet of the HF modules. The flow meters were equipped with back-pressure control valves to maintain the appropriate differential pressure control of the aqueous–organic interface in both modules.

The initial volume of the feed solutions in the stirred tanks was equal to 1 L. Separation experiments were carried out for 1 hr at room temperature (~20°C).

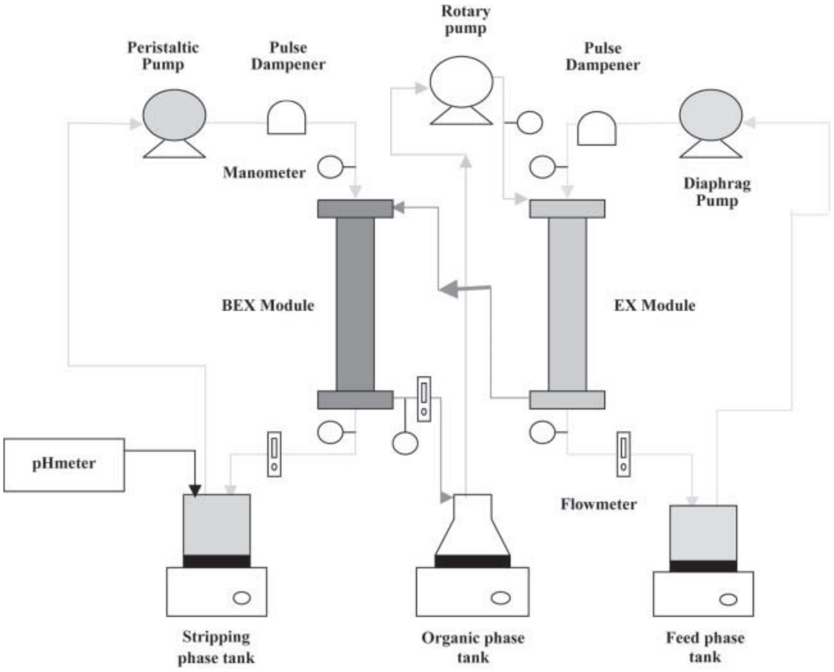

Figure 1. Experimental set-up.

Analytical Techniques

The metallic content of the feed solution was analyzed in a Perkin Elmer Plasma Emission Spectrometer ICP 400 (Perkin Elmer, Connecticut, USA). The iron(II) concentration was determined in a spectrophotometer SPECTROQUANT NOVA 400 (Merck, Darmstadt, Germany); the total zinc and iron content of the samples was analyzed by using an atomic absorption spectrophotometer, Perkin Elmer 3110 (Perkin Elmer, Connecticut, USA).

RESULTS AND DISCUSSION

Initially, some experiments were performed to select the optimum extractant for the separation of zinc from iron, which also is present in high concentration in the feed solution. These experiments were carried out with different extraction and BEX agents in a rotatory equipment. The results of these experiments expressed as extraction yield are shown in Table 2.

Table 2. Extraction yield of Zn(II) and Fe(II) by using different extractants.

	Extraction and back-extraction phase		Extraction phase	
	E: CYANEX 272 (60%) M: TBP (10%) D: Kerosene (30%) S: H_2SO_4 1 M	E: TBP (100%) S: Water	E: D2EHPA (60%) M: TBP (10%) D: Kerosene (30 %)	E: D2EHPA (60%) D: Kerosene (40%)
V_f/V_o	1/3	1/4	1/1	1/1
V_s/V_o	1/1	4/1	—	—
Feed pH	$\sim 0^a$	$\sim 0^a$	1^b	1.5^b
%Zn EX	42	*94.2*	31.7	41.5
%Zn BEX	100	*100*	—	—
%Fe EX	~ 0	~ 0	4.33	49.8
%Fe BEX	~ 0	~ 0	—	—

Note: E, Extraction agent; M, modifier; D, diluent; S, back-extraction agent, V_f, feed phase volume; V_o, organic phase volume; V_s, stripping phase volume; contact time, 1 hr.

[a] Feed phase conditions: [Zn] = 80 g/L; [Fe] = 92 g/L.

[b] Adjusted pH with NaOH 10 M.

Table 2 shows that by using TBP as extractant and water as BEX agents high yields were obtained, both in the extraction and BEX of zinc, whereas, the extraction of iron was almost negligible; therefore, the following experiments, performed in HF contactors, used an organic phase containing 100% TBP. The stripping of the organic zinc took place in a second HF contactor with service water as the BEX phase.

Once the viability of the separation of zinc from the acidic multicomponent feed solution was checked, several experiments were carried out to analyze the influence of the initial metal concentration on the separation kinetics and selectivity. Experimental conditions are shown in Table 3. Each run was carried out working with an initial clean organic phase and by using water as the BEX phase. Experiments were duplicated so that the results presented here are the mean values of the metal concentration, zinc and iron, obtained in both experiments. Figures 2–5 show the kinetic results of Experiments I–III of both metals, Fe and Zn, in the extraction and stripping phase. The presence of other metals such as Mn, Pb, Cr, etc., in the BEX solution is negligible, as it was demonstrated in previous experiments.

The evolution of Zn concentration in the feed solution is shown in Fig. 2. It can be noted that the extraction yield ranges between 50% and 70%. On the

Table 3. Experimental conditions.

	Exp. I	Exp. II	Exp. III
Aqueous feed phase			
Conc. initial Zn (g/L)	78	38.4	19.2
Conc. initial Fe (g/L)	94	46.9	22.1
pH	~0	0.11	0.50
Volume (L)	1	1	1
Dilution (%)	0	50	75
Flow rate (mL/min)	636	571	561
Organic phase			
TBP 100%			
Volume (L)	1	1	1
Flow rate (mL/min)	582	526	540
Stripping phase			
Water			
pH	7.4	7.3	7.3
Volume (L)	1	1	1
Flow rate (mL/min)	434	519	546

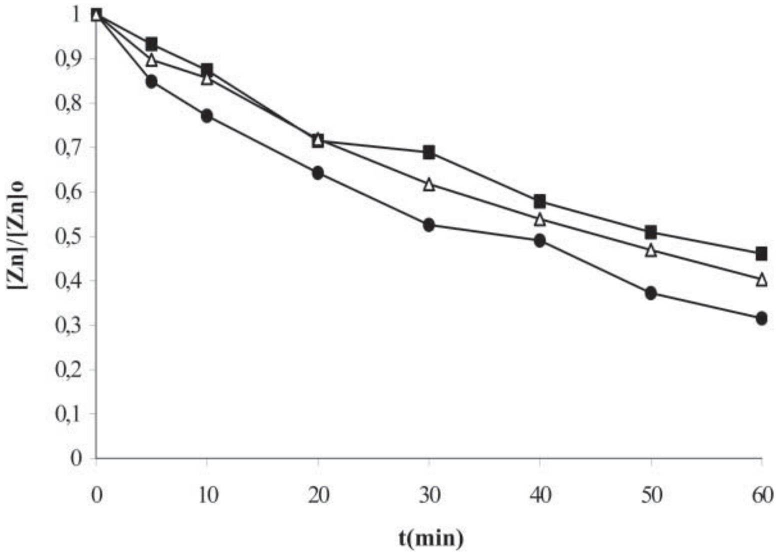

Figure 2. Evolution of the feed Zn dimensionless concentration with time. *Key:* ●, Experiment I. ■, Experiment II. Δ, Experiment III.

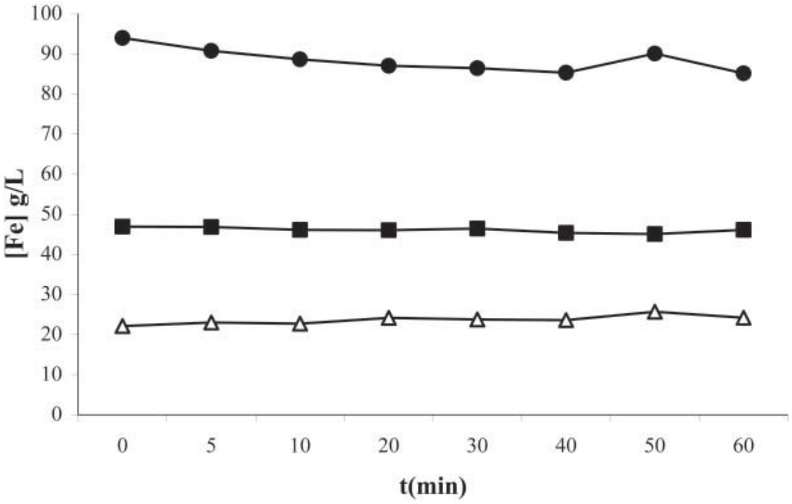

Figure 3. Evolution of the feed Fe concentration with time. *Key:* ●, Experiment I; ■, Experiment II; Δ, Experiment III.

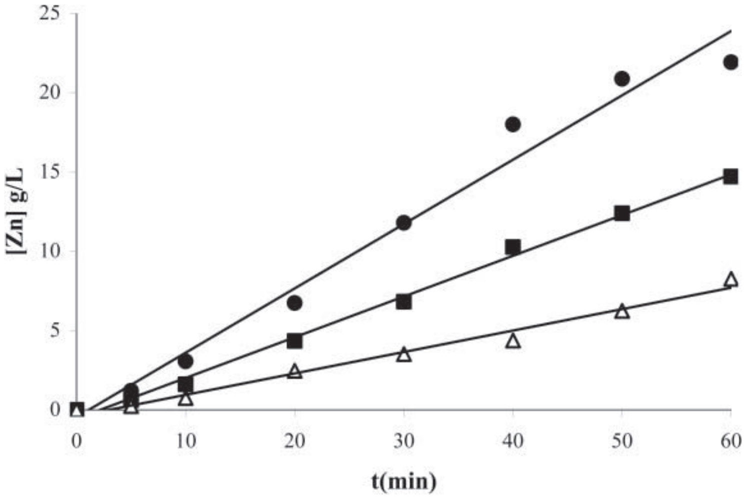

Figure 4. Evolution of Zn concentration with time in the stripping phase. *Key:* ●, Experiment I; ■, Experiment II; Δ, Experiment III.

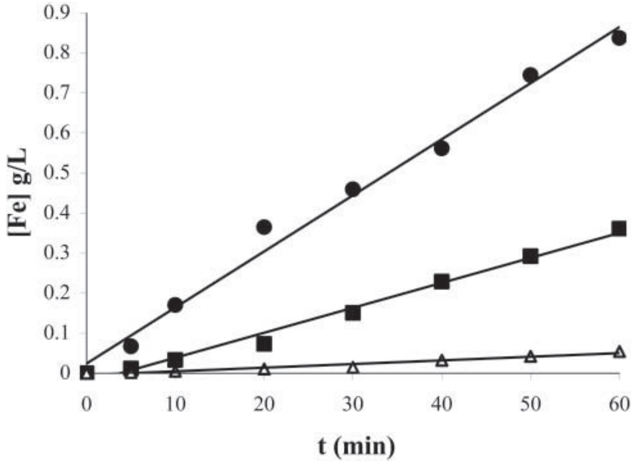

Figure 5. Evolution of Fe concentration with time in the stripping phase. *Key:* ●, Experiment I; ■, Experiment II; Δ, Experiment III.

other hand, the change in the concentration of Fe in the aqueous feed phase was almost negligible, as shown in Fig. 3.

The evolution of the concentration of Zn and Fe with time in the BEX phase is shown in Figs. 4 and 5, respectively. The concentration level was higher in the experiments that were performed with more concentrated feed solutions. In the case of Fe, although the concentration change during the extraction step was negligible, an increase in the concentration in the stripping could be appreciated, as shown in Fig. 5.

The initial pH in the BEX solution was neutral (pH of water is close to 7.0) and decreased when the metal concentration increases, indicating a simultaneous transport of hydrochloric acid. Figure 6 shows the evolution of pH with time in the BEX phase.

Separation Selectivity

The analysis of the selectivity of the separation process of zinc from iron contained in the multicomponent acidic mixtures has been performed from the kinetic results of the stripping solution. In the batch separation process, the zinc selectivity has been defined as the ratio of the permeate flux of Zn in the BEX module to the permeate flux of Fe in the same

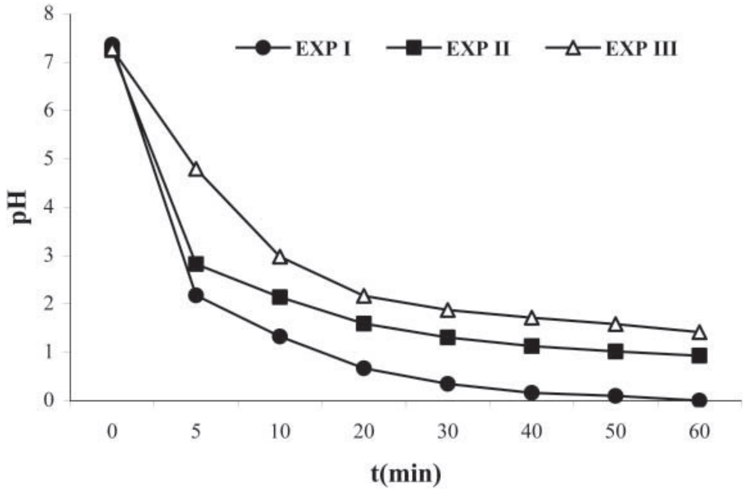

Figure 6. pH evolution with time in the stripping phase. *Key:* ●, Experiment I; ■, Experiment II; Δ, Experiment III.

module:

$$\alpha_{\mathrm{Zn/Fe}} = \frac{J_{\mathrm{ZnR}}}{J_{\mathrm{FeR}}} \tag{1}$$

where the permeate flux of the metallic species that is transferred from the organic to the BEX solution is calculated by the following equation:

$$J_{\mathrm{M}} = +\frac{V}{A}\left(\frac{d[M]}{dt}\right) \tag{2}$$

M is the concentration of the metallic species in the BEX phase.

Under the experimental conditions used in this work, the evolution of the concentration of Zn and Fe in the BEX tank, Figs. 4 and 5, showed a linear trend with time, Eq. (3):

$$M = at + b \tag{3}$$

The values of the regression coefficient (r) and the slope "a" of Eq. (3) are shown in Table 4.

The mass transport flux has been obtained from combination of Eqs. (2) and (3) as:

$$J_{\mathrm{M}} = +\frac{V}{A}a \tag{4}$$

With the values of the parameters shown in Table 5, the selectivity of the separation of Zn over Fe, $\alpha_{\mathrm{Zn/Fe}}$ has been calculated by using Eqs. (1) and (4). The results are shown in Table 5. This table reports the values of the separation selectivity, $\alpha_{\mathrm{Zn/Fe}}$, in each experiment, indicating that diluted solutions ($[\mathrm{Zn}]_o \leq 40\,\mathrm{g/L}$) led to higher values of the separation selectivity, $\alpha_{\mathrm{Zn/Fe}} = 125\,\mathrm{mol\ Zn/mol\ Fe}$, whereas, with concentrated feed solutions ($[\mathrm{Zn}]_o \geq 40\,\mathrm{g/L}$), the selectivity decreases to an almost asymptotic value around 30 mol Zn/mol Fe.

Table 4. Parameters of the fitting of experimental results to Eq. (3).

Exp.	Metal	$[M]$ (g/L)	r	Slope "a"	0.0.
I	Zn	78.0	0.990	0.406	-0.448
I	Fe	94.0	0.995	0.014	0.0239
II	Zn	38.4	0.997	0.259	-0.681
II	Fe	46.9	0.992	6.30×10^{-3}	-0.0281
III	Zn	19.2	0.993	0.135	-0.401
III	Fe	22.1	0.978	9.23×10^{-4}	-5.22×10^{-3}

Table 5. Permeate flux and selectivity factor values.

	Exp. I		Exp. II		Exp. III	
	Zn	Fe	Zn	Fe	Zn	Fe
Initial conc. (g/L)	78	94	38.4	46.9	19.2	22.1
J (g/m^2 min)	0.29	0.01	0.185	4.50×10^{-3}	0.096	6.59×10^{-4}
J (mol/m^2 min)	4.44×10^{-3}	1.79×10^{-4}	2.83×10^{-3}	8.06×10^{-5}	1.47×10^{-3}	1.18×10^{-5}
$\alpha_{Zn/Fe}$ (g/g)	29		41		146	
$\alpha_{Zn/Fe}$ (mol/mol)	25		35		125	

CONCLUSIONS

This work reports the viability of using NSDX for the recovery of zinc from spent acidic pickling solutions that contain high concentrations of iron(II). After the selection of TBP as an extraction agent and water as a BEX agent, an experimental study was carried out to analyze the influence of the initial metallic concentration in the feed solution on the separation efficiency. In a separation process constituted of two coupled steps, extraction of the metals to the organic and BEX from the organic phase, the separation selectivity, $\alpha_{Zn/Fe}$, defined as the ratio of the values of the BEX flux of both metals, was calculated. In the range of initial concentrations Zn 20–80 g/L, Fe 25–90 g/L, $\alpha_{Zn/Fe}$ changed from a maximum value of 125 mol Zn/mol Fe that was obtained with the lower concentration feed solutions to an almost asymptotic value of 30 mol Zn/mol Fe.

This work reports the viability of a technological alternative for the valorization of the zinc contained in a hazardous waste.

Further work will deal with the development of a kinetic model that could be used for the prediction of the selectivity of the separation process.

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