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Selective recovery of zinc from spent pickling baths by the combination of membrane-based solvent extraction and electrowinning technologies

Jordi Carrillo-Abad [a], Montserrat Garcia-Gabaldon [a,*], Isabel Ortiz-Gandara [b], Eugenio Bringas [b], Ane Miren Urtiaga [b], Inmaculada Ortiz [b], Valentin Perez-Herranz [a]

[a] Departamento de Ingeniería Química y Nuclear, Universidad Politécnica de Valencia, P.O. Box 22012, E-46023 Valencia, Spain
[b] Departamento de Ingenierías Química y Biomolecular, Universidad de Cantabria, 39005 Santander, Spain

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ABSTRACT

This work deals with the analysis of an integrated zinc recovery process by means of electrowinning of the stripping solutions coming from the treatment of spent pickling baths (SPB) by a membrane-based solvent extraction (MBSX) process able of increasing the initial Zn/Fe molar ratio. Several stripping solutions containing different concentrations of zinc and iron in acid media obtained previously by the treatment of SPB by MBSX, were subjected to electrowinning to assess the efficiency and selectivity of zinc electrodeposition over iron under different operation conditions.

At similar values of the zinc concentration in the stripping solution, the influence of the Zn/Fe molar ratio on the zinc electrodeposition process was negligible. On the other hand, although the variation of the initial concentration of zinc in the stripping solution neither affected the efficiency of zinc electrowinning, it increased the minimum value of zinc concentration in solution beyond which iron co-deposition started. Finally, the increase in the applied current, promoted the increase in zinc fractional conversion and in the zinc space–time yield, while the zinc current efficiency was reduced due to the stronger effect of secondary reactions.

Although the change in the stripping characteristics seems not to strongly affect the zinc electrodeposition process, the use of a pretreatment step based on MBSX technology improved the results in terms of zinc percentage recovered and the rest of figures of merit, in comparison with those obtained by the direct electrowinning of SPB.

1. Introduction

The hot dip galvanizing process, which consists on the dipping of steel pieces in molten zinc in order to protect them from corrosion [1], generates a succession of effluents among which it is worth to note the spent pickling baths (SPB) as the highest polluting effluent. The SPB, whose purpose is to clean the pieces surface from rust and impurities by its attack with HCl, contains high concentrations of $ZnCl_2$, $FeCl_2$ in HCl media [2] and, consequently, they have to be treated previous to their disposal. However, the traditional treatment process, which consists in the effluent neutralization and the precipitation of the iron and zinc as hydroxides, presents as disadvantages the high consumption of chemical products together with the generation of a hazardous sludge that has to be treated [3]. In addition, the decrease of natural reserves of non-ferrous metals makes zinc recovery an interesting alternative of treatment.

In our previous works [4–8], zinc recovery from SPB by means of an electrochemical membrane reactor, which avoids the redissolution of the zinc deposits by the attack of the chlorine generated in the anode, has been successfully applied in order to obtain metallic zinc that can be directly reintroduced into the galvanizing process. However, the anomalous codeposition among zinc and iron [9,10] avoids the possibility of recovering all the zinc present in the SPB without iron presence in the deposit.

On the other hand, different membrane-based solvent extraction (MBSX) process configurations namely Emulsion Pertraction Technology (EPT) and Non-Dispersive Solvent Extraction (NDSX), which differ in the way of contacting the fluid phases and the number of the membrane contactors involved, have proved to be efficient alternatives to perform the selective separation of zinc over iron in HCl media employing tributylphosphate (TBP) and water as extraction and stripping agents, respectively [11–14]. In a previous work [14], the effect of several process variables on the kinetics

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* Corresponding author.
E-mail address: mongarga@iqn.upv.es (M. Garcia-Gabaldon).

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and selectivity of zinc over iron separation was analysed in order to obtain a highly concentrated zinc solution with a negligible content of iron to allow for further recovery of zinc by electrowinning. It was concluded that the kinetics of extraction and stripping of zinc and iron were promoted by EPT configuration in comparison with NDSX configuration, and increasing the TBP concentration in the range between 20% (v/v) and 50% (v/v). Therefore, a suitable selection of the optimal operation conditions is required to maximize the molar ratio zinc/iron in the stripping solution.

In this sense, this work is the combination of electrowinning and membrane-based solvent extraction technologies in order to create a hybrid process to maximize both the yield and selectivity of zinc recovery from spent pickling baths. More specifically, this work analyses the efficiency and selectivity of zinc electrodeposition from stripping solutions containing different concentrations of zinc and iron which were previously obtained by the treatment of SPB by EPT under different operation conditions. In addition, other parameters such as the influence of the applied current in the electrowinning process are also evaluated.

2. Materials and methods

2.1. Membrane-based solvent extraction experiments

The experiments were performed at laboratory scale using one mesoporous hollow fiber membrane contactor (HFMC, Liqui-Cel® Extra-Flow 2.5x8, Hoechst Celanese) containing 10,200 polypropylene fibers with an effective mass-transfer area of 1.4 m^2 and an effective mass-transfer length of 0.15 m. The fibers had a nominal porosity of 40%, an average pore size of 0.03 μm and an internal diameter of 240 μm with a wall thickness of 30 μm. Fig. 1 shows the experimental set-up used for the extraction and back-extraction of zinc from the aqueous systems using the Emulsion Pertraction Process configuration. In EPT configuration the extraction and back extraction of the target species were conducted in a single membrane module and the non-dispersive contact occurred between the feed SPB and the pseudo-emulsion prepared by dispersing the stripping solution into the organic phase. The difference in the transmembrane pressure between the aqueous phase and the emulsion phase was maintained constant at approximately 0.15 bars in order to avoid the dispersion of the organic fluid into the feed aqueous phases. The organic and the stripping phases can be easily separated by gravity settling. Further details of the experimental procedure are found elsewhere [15,16].

Table 1
Composition of real SPB.

Component	Concentration
$[H^+]$ (mol L^{-1})	1.10 ± 0.04
$[Zn^{2+}]$ (mol L^{-1})	1.87 ± 0.05
$[Fe]_{TOTAL}$ (g L^{-1})	1.70 ± 0.05
$[Fe^{2+}]$ (g L^{-1})	1.66 ± 0.04
$[Fe^{3+}]$ (g L^{-1})	0.04 ± 0.03
$[Cl^-]$ (g L^{-1})	8.48 ± 0.08

The feed solutions consist of 500 mL of SPB provided by a local industry and containing mainly zinc, iron, chloride and free acid (Table 1). The organic solution was formulated by dilution of the extractant TBP (97%, Sigma–Aldrich) in the aliphatic solvent Shellsol D70 (Kremer Pigmente). Tap water was utilised as stripping solution in all the experiments. The pseudo-emulsion was formulated by dispersing 200 mL of the stripping solution into 800 mL of the organic phase using a stirrer MRVS-08 (SBS).

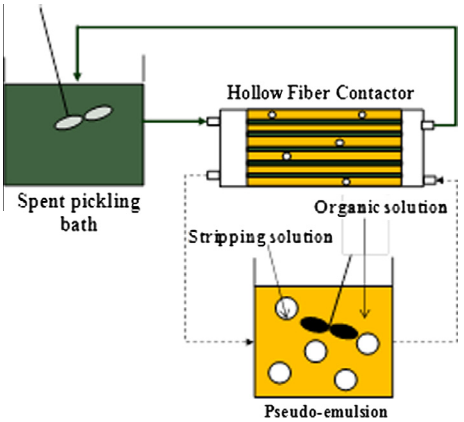

Fig. 1. EPT experimental setup.

Due to the dependence of zinc and iron extraction and back-extraction kinetics on the operation conditions [14] and with the aim of attaining stripping solutions with different concentrations of zinc and iron, EPT experiments were performed under different operation conditions namely the operation time in the range between 1 and 3 h and the concentration of the selective extractant TBP varying from 20% (v/v) and 50% (v/v). Table 2 summarizes the conditions of EPT and electrowinning (EW) experiments, and the pH and composition of the stripping solutions employed in electrolysis experiments.

Zinc and iron determination was performed by atomic absorption spectrophotometry (AAS). The determination of zinc was performed on a Perkin–Elmer model Analyst 100 atomic absorption spectrophotometer using a zinc hollow cathode lamp at 213.9 nm wavelength, 0.7 nm spectral bandwidth and an operating current of 5 mA. The iron concentration was performed using the same equipment with a Fe hollow lamp; the wavelength selected was 248.3 nm, the applied operating current was 5 mA and the spectral bandwidth was 0.2 nm [4–8].

2.2. Electrowinning experiments

The electrowinning (EW) experiments were performed in a membrane reactor. Although this reactor is well defined in our previous works [4–8], its schematic representation is shown in Fig. 2, which also includes the main reactions for both electrodes. The membrane reactor is filled, after the cell assembly, with an equal volume of 250 cm^3 of catholyte and anolyte in their respective compartments. A graphite cathode, titanium anode and Ag/AgCl reference electrode were employed in this reactor. Both cathode and anode were completely immersed in the solutions and

Table 2
Experimental conditions of EPT and EW experiments.

Exp.	Operation conditions			Stripping solution			
	EPT		EW	$[Zn^{+2}]$ (M)	$[Fe^{+2}]$ (M)	pH	$[Zn^{+2}]/[Fe^{+2}]$
	TBP (%v/v)	Operation time (h)	Applied current (A)				
1	20	1	−1.00	0.07	0.005	1.67	14.0
2		2		0.20	0.010	1.28	20.0
3		3		0.48	0.026	0.61	18.5
4	50			0.61	0.040	0.80	15.3
5[a]		1.5	−0.70	0.43	0.149	0.73	2.90
6[a]				0.45	0.085	0.79	5.30
7[a]				0.42	0.042	0.74	10.0
8				0.39	0.012	0.63	32.5
9			−1.00	0.40	0.019	0.89	21.1
10			−1.50	0.37	0.017	0.60	21.8

[a] Stripping solutions doped with $FeCl_2$ to modify the molar ratio zinc/iron.