



Zinc recovery and waste sludge minimization from chromium passivation baths

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ABSTRACT

This work reports the feasibility of applying emulsion pertraction technology (EPT) aiming at zinc recovery and waste minimization in the zinc electroplating processes that include Cr (III) passivation. The assessment consists of firstly the lifetime extension of the passivation baths by selective removal of the tramp ions zinc and iron, and secondly, the recovery of zinc for further reuse. Spent passivation baths from a local industry were tested, being the major metallic content: Cr^{3+} 9000 mg L^{-1} , Zn^{2+} 12,000 mg L^{-1} , Fe^{3+} 100 mg L^{-1} . Working in a Liqui-Cel hollow fiber membrane contactor and using the extractant bis(2,4,4-trimethylpentyl) phosphinic acid, reduction of zinc and iron concentrations below 60 mg L^{-1} and 2 mg L^{-1} , respectively were obtained, while trivalent chromium, the active metal that generates the passivation layer, was retained in the baths. Zinc was selectively transferred to an acidic stripping phase that in the experimental time reached a concentration of 157,000 mg L^{-1} . Zinc recovery by electrowinning from the acidic stripping phase without any pretreatment of the electrolyte solution provided a purity of 98.5%, matching the lower commercial zinc grade. As a result of the extension of the life time of the passivation bath, significant environmental advantages are derived such as minimization of the volume of hazardous wastes and savings in the consumption of raw materials.

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1. Introduction

Zinc electroplating followed by chromium passivation are surface finishing techniques commonly employed to enhance corrosion protection and decorative features of metallic pieces [1,2]. New trivalent chromium conversion coatings have been successfully implemented in plating industry to substitute the currently banned hexavalent chromium passivating processes [3]. However, these Cr (III)-based passivation baths become shortly contaminated by zinc and iron impurities. Then, the exhausted bath should be discarded and further managed as a hazardous waste and a new bath should be formulated.

The most common action to reduce the hazardous features of metal finishing liquid wastes is a conventional end-of-pipe physicochemical treatment [4], consisting on neutralization and metal precipitation that results in a metallic sludge classified as hazardous waste. The final destination of the sludge produced during the physicochemical treatment is usually landfill disposal, after an appropriate stabilization phase. However, the discharge of these wastes is highly undesirable since, on the one hand, they contain high amounts of heavy metals and are potentially eco-toxic residues [5] and, on the other hand, it involves an important loss of

chemicals and valuable metals together with the additional cost of treatment and disposal.

An alternative solution to end-of-pipe treatments is the development of processes aiming at material recovery and waste minimization [6–8]. One of the strategies for waste minimization in electroplating industry is the regeneration of baths or bath life extension. Best Available Technologies (BATs) for the removal of tramp ions (i.e. Zn^{2+} and Fe^{3+}) from chromic acid solutions have been reported [9]: ion-exchange, electrolysis, membrane electro-dialysis. In those cases, the Cr (VI) predominant species is the chromate anion, CrO_4^{2-} , that is not competing with the separation of iron and zinc cations. However, in the new hexavalent chromium-free passivating baths, chromium appears as a trivalent cation, making more difficult the appointed objective. New ion exchange chelating resins have been recently reported for the selective iron and zinc separation from Cr (III) passivation baths; however a high consumption of hydrochloric acid was needed for resin regeneration, due to the difficulty associated to iron stripping [10,11]. Emulsion Pertraction, also known as EPT, has been found an efficient process that enables successful recovery of metallic components from complex feed mixtures [12–14]. Moreover in a previous work [15], the regeneration of spent Cr (III) passivation baths by the selective zinc and iron membrane-based liquid–liquid extraction from complex solutions in nitric acid media was reported. Cyanex 272 (0.6 mol L^{-1}) was used as commercial extractant, while both hydrochloric acid and sulphuric acid were tested as stripping agents. However the conditions that allowed

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obtaining a purified and highly concentrated zinc sulphate solution were not identified in that work, neither the electrowinning of metallic zinc was checked.

The composition of this zinc sulphate solution is similar to the purified acidic zinc solutions coming from hydrometallurgical processes aiming at the recovery of zinc from zinc-containing wastes or secondary resources where sulphuric acid was used as leaching agent [16]. The recovery of zinc from these leach solutions can be carried out by several alternatives as i.e. vaporization and crystallization (obtaining pure zinc sulphate), precipitation as basic zinc carbonate, zinc metal by electrowinning, etc. The most common zinc applications employ refined zinc metal of commercial grade with a purity ranging between 98.5 and 99.995% for primary zinc [17] (i.e. galvanizing and zinc-based alloys) [18]. Electrolytic recovery of zinc is one of the oldest and most employed industrial processes. Nowadays, the sulphate electrolysis has become one of the most widely applied methods for zinc metal deposition over chloride media electrowinning [19]. It is well known that certain metallic impurities have negative effects on zinc electrodeposition (i.e. iron, cadmium, lead, copper, nickel, cobalt [20,21], etc.). Nevertheless, the effect of chromium presence onto zinc electrodeposition has not been evaluated so far.

The present work aims at the experimental assessment of a material recovery and waste minimization strategy, chasing a “zero discharge” goal, in the surface finishing industry. The novelty of this work consists in the study of the implementation of an EPT process into the usual batch operation mode in the electroplating industry aiming at, on one hand, extending the lifetime of the passivating bath, and therefore avoiding the corresponding physicochemical treatment before discard and the formation of the hazardous metallic sludge, and on the other hand identifying the operating conditions allowing the appropriate acidic stripping composition to recover high purity metallic zinc. The following procedure was followed: (i) in a first step, the emulsion pertraction technology was applied for the removal of zinc and iron from the spent passivation bath. The extraction and back-extraction results were evaluated. The possibility of bath regeneration was analysed; (ii) secondly, the amount of waste that could be prevented by applying the EPT technique was determined by studying the physicochemical waste treatment. Thus the amount of press-filter metallic sludge that would be generated by applying this conventional technique was evaluated and (iii) finally, the recovery of metallic zinc from the stripping solution obtained after extractant regeneration was assessed. Electrowinning experiments of the zinc sulphate solution were carried out for this purpose.

2. Materials and methods

2.1. Exhausted passivating bath regeneration: emulsion pertraction technology

The spent passivation bath used as feed solution was provided by a local plating industry. The bath is formulated by the commercial supplier using chromium (III) nitrate salt. The characterization of the samples used in this work is given in Table 1. It should be noticed that the range of iron concentrations is low, because this metal was continuously removed in the industrial plant by means of an integrated ion-exchange process [10,11]. The concentrations of Cr, Zn and Fe were determined by atomic absorption spectrophotometry (Perkin Elmer 3110 AAS), after adequate dilution. W was analysed by inductively coupled plasma emission, while the anionic species were quantified by ion chromatography (Dionex DX-120).

The experimental set-up used in the emulsion pertraction experiments is shown in Fig. 1. A polypropylene hollow fiber membrane module (2.5 × 8 Extra-Flow Liqui-Cel X-50) enables the

Table 1
Chemical characteristics of the spent passivation bath.

Compounds	Feed concentration (mg L ⁻¹)	Stripping concentration (mg L ⁻¹)
Cr ³⁺	9750	170
Zn ²⁺	12,880	157,000
Fe ^{total}	101.6	11
W ⁶⁺	304.6	5100
SO ₄ ²⁻	2268	≈384,000
Cl ⁻	2886	
NO ₃ ⁻	62,456	
F ⁻	797	
pH	≈2.1	≈1.9

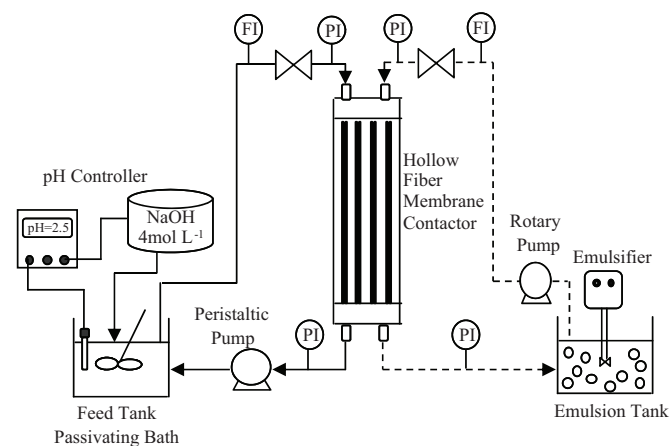


Fig. 1. Experimental emulsion pertraction set-up.

non-dispersive contact between the aqueous passivating bath and the organic extractant phase. Both streams, the feed passivation bath and the emulsion formed by the extractant and the stripping phases, were run in batch mode. The EPT tests were carried out in 4 consecutive cycles. In each cycle, 1 L of fresh feed phase was used while the emulsion phase was reused, and the experimental cycle proceeded during 6 h. Then, the feed reservoir was emptied and replenished with new passivation bath. A solution (0.8 L, 0.6 mol L⁻¹) of bis(2,4,4-trimethylpentyl) phosphinic acid in kerosene, is used as selective extractant, and 0.2 L of sulphuric acid (4 mol L⁻¹) as stripping phase. The emulsion formed by the organic extractant and the aqueous stripping phase was created by applying vigorous stirring and was stable in the emulsion tank during the operation time. When samples of the emulsion were taken and settled by gravity for further analysis some minutes were required to complete phase separation. Therefore, the emulsion was considered stable during its residence time inside the membrane module and addition of surfactant was not required. Table 2 shows the

Table 2
Membrane module characteristics and values of the operational variables in the EPT test.

Variable	Value
Membrane module characteristics	Membrane area, 1.4 m ² Fiber inner diameter, 240 μm Membrane thickness, 40 μm Porosity 40%
Operation mode	Recirculation
Flowrate _{feed} (inner side)	12 L h ⁻¹
Flowrate _{emulsion} (shell side)	12 L h ⁻¹
Volume _{feed}	1 L × 4 cycles
Volume _{emulsion}	1 L
Volume _{stripping}	0.2 L
Volume _{organic}	0.8 L
Transmembrane pressure _{feed/emulsion}	0.15 bar
Time	6 h × 4 cycles

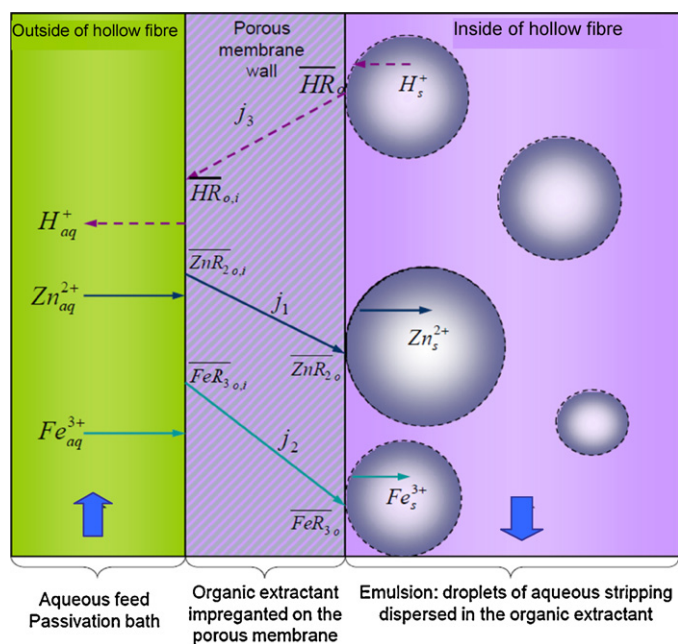
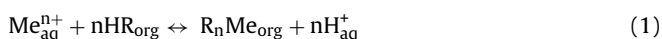


Fig. 2. Cross section of the membrane and fluxes of species.

values of the main operational variables used to carry out the EPT test. Further details about the experimental equipment and analytical procedures can be found in a previous work [15].

Metal transfer is performed at the aqueous–organic interface located at the porous membrane wall that provides a mass transfer area of 1.4 m². The regeneration of the organic phase and transference of the metals to the stripping acid are attained in the same membrane unit, by the back extraction reaction that takes place at the surface of the emulsion droplets. The chemical reactions involved are

- At the aqueous feed – organic interface, outer membrane side,



- At the organic phase – aqueous interface, droplet surface,

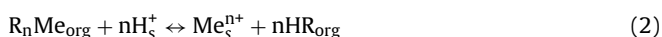


Fig. 2 shows a cross section of the membrane and the fluxes of species involved in the separation process. The extraction selectivity is highly dependant on the pH of the aqueous phase [22]; thus, at the operation pH of the passivating baths (1.8 < pH < 2.5) the extractant reacts preferentially with Fe (III) and Zn (II) while it would require pH > 3 for the extraction of chromium. As it can be observed in the stoichiometry of the extraction reaction, Eq. (1), the pH of the aqueous feed decreases while the EPT experiment proceeds due to the exchange of metallic cation by protons. In order to keep the feed pH at a value of 2.5 during the whole experiment, a pH controller dosed a 4 mol L⁻¹ sodium hydroxide (Panreac) solution.

2.2. Determination of the waste sludge generation: physicochemical waste treatment

Simulations of the primary treatment (flocculation/neutralization/precipitation) of spent passivation baths were performed at laboratory scale. A volume of 50 mL of the spent bath sample was taken. An inorganic flocculant, DKFLOC-1018 (Acideka, Spain), a synthetic material consisting on aluminium polychloride (18%), was added at a volumetric ratio of 40% (v/v), and the mixture was homogenized. The addition of flocculants

promotes aggregation of small metal hydroxide particles into larger flocs [23,24], enhancing the filtering behaviour. Then, sodium hydroxide, 40% (w/w) (RE, Panreac) was slowly added to the stirred solution until the pH was between 8.5 and 9.0, optimal range for the precipitation of a wide variety of metals present in wastewaters [24]. The obtained metallic sludge was filtered using a filter paper with a pore size of 30–40 μm. After removal of the major part of water by gravity, the remaining humidity of the cake was naturally evaporated for 24 h. This filtration procedure provides a dryness degree similar to that obtained by press-filtering at larger scale. After weighted, cakes were introduced into an oven at 105 °C for 24 h until constant weight in order to evaluate the humidity and the metallic content.

2.3. Zinc sulphate solution valorisation: zinc electrowinning

The sulphuric acid stripping agent loaded with metals obtained from the EPT test was further treated to evaluate the feasibility of zinc recovery by means of electrochemical deposition.

A conventional two-electrode, one-compartment electrochemical cell was employed. A 3 cm² stainless steel sheet was used as cathode and a Pt wire acted as anode. The power supply was a HQ Power PS 3020 (30 V/20 A). A volume of 50 mL of the stripping solution loaded with zinc and without any previous treatment was employed as electrolyte. The experiments were performed at room temperature. Working under stirring conditions, the formation of a sulphur deposit was observed. This effect was assigned to the reduction of sulphates by electrogenerated hydrogen. Therefore, it was decided to work without stirring. According to the voltammetry characterisation of the system the reduction voltage was in the range of 1–10 V.

A mass of the electrodeposited metallic film was separated from the cathode, dissolved in nitric acid and then rinsed with water in a volumetric flask. The content of zinc and metallic impurities were quantified by ICP (ICPE-9000, Shimadzu) coupled with a CCD (charge-coupled device) detector.

3. Results and discussion

3.1. Regeneration of the exhausted passivation bath: EPT experimental results

As previously explained, the EPT tests were carried out in 4 consecutive cycles, each one with a length of 6 h. The evolution with time of the concentration of the three metallic species, zinc, iron and chromium in the feed phase is represented in Fig. 3, while Fig. 4 collects the concentrations of the metals in the stripping phase. It is observed that chromium extraction was very low, as expected, because at the feed pH of 2.5, chromium extraction by bis(2,4,4-trimethylpentyl) phosphinic acid is not favoured [15,25]. The chromium concentration decrease observed was mainly a dilution effect caused by the addition of sodium hydroxide solution to the feed tank, necessary for the maintenance of constant pH, otherwise, the pH would decrease due to the exchange reaction between metal cations and protons, as explained before. Nevertheless, the influence of pH onto chromium extraction was evaluated in a previous work [26], resulting that the loss of chromium mass at a pH of 2.5 was maintained below 3%. After 4 consecutive cycles, iron is almost completely removed from the feed phase reaching a final concentration in the range of 0.8–2.0 mg L⁻¹ (97–99% iron removal). The final concentration of iron is due to the presence of small quantities of Fe (II) that is not readily extracted at the operation pH. Zinc is also removed from the feed phase down to values between 3 and 58 mg L⁻¹ (99.99–99.49% zinc removal) during cycles 1–3. However, in the fourth cycle the kinetics of zinc removal decreases,

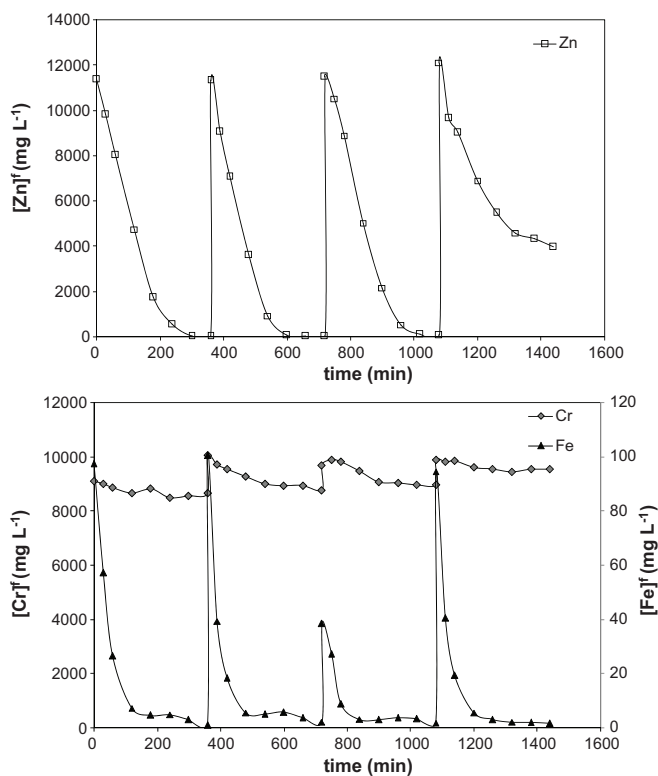


Fig. 3. Evolution with time of zinc, iron and chromium feed tank concentrations during the 4 cycles.

probably due to the exhaustion of the stripping agent, as it will be explained later on. These results show that the regeneration of the passivation bath can be achieved, needing only addition of a small volume of the concentrated commercial bath in order to adjust the chromium content.

With regard to the stripping results, data in Fig. 4 shows that the low chromium amount that was extracted from the feed phase, is completely back-extracted into the stripping agent, providing a final chromium concentration in the stripping phase of 170 mg L^{-1} . The zinc concentration in the stripping phase increases continuously until a practically constant concentration of 160 g L^{-1} is achieved. The final plateau for zinc concentration matches with the zinc extraction limitation observed in the feed phase (Fig. 3) during cycle 4th. Both phenomena can be explained by the exhaustion of protons in the stripping solution. As the experiment progressed, the

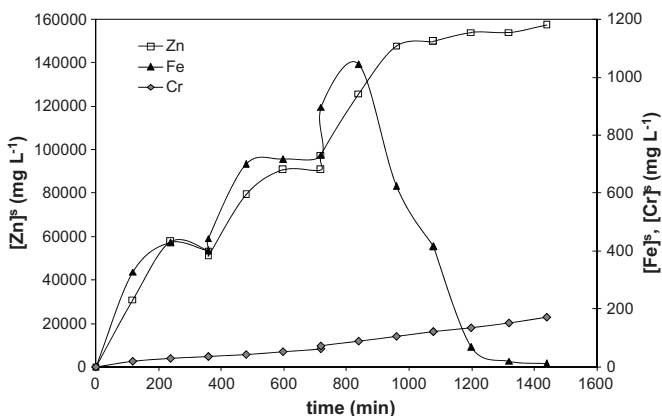


Fig. 4. Evolution with time of zinc, iron and chromium in the acid stripping during the 4 cycles.

available concentration of protons in the stripping phase decreased. The final pH of the stripping phase reached a value of 1.9. Thus, the extraction driving force is reduced progressively and so the extraction kinetics. Under these conditions, zinc back-extraction into the sulphuric acid phase is not allowed and the zinc extracted from the feed phase is accumulated in the organic extractant phase.

However, iron back-extraction shows a different behaviour. It is observed that iron concentration in the stripping solution increases up to a maximum of 1000 mg L^{-1} , and then abruptly drops down to 11 mg L^{-1} , showing that iron is extracted again by the organic extractant phase from the stripping solution. Iron stripping requires more acidic conditions than zinc stripping, and when the acidic stripping phase becomes exhausted and its pH turns into a value higher than 1.0, the back-extraction equilibrium in the sulphate media favours iron accumulation into the organic extractant [22,27]. This phenomenon allows the selective back-extraction of zinc over iron in the stripping phase by controlling its pH, giving a highly concentrated zinc sulphate solution that contains very low concentrations of iron and chromium.

After having obtained a stripping solution enriched in zinc, by allowing the uploading of iron in the extractant from the stripping, the organic phase can be easily regenerated by a new contact with fresh sulphuric acid solution of high concentration. The resultant iron sulphate solution could be precipitated as jarosite ($\text{MFe}_3(\text{OH})_6(\text{SO}_4)_2$), where M is an alkali species (usually sodium or ammonium), after complete oxidation of Fe (II) to Fe(III) [28]. Jarosite is a common mineral waste that appears in hydrometallurgical processes for zinc electrolytic deposition. Anyway, recent studies have covered successfully the possible jarosite reuse as a new environmentally friendly construction material [29–31].

A parallel experiment working under similar conditions was made confirming the reproducibility of the process (experimental curves not shown). Comparable behaviour for metals removal in the feed passivation bath was found and the metals concentrations reached in the stripping after 24 h experiment phase were $159,200 \text{ mg L}^{-1}$ for zinc, 78 mg L^{-1} for iron and 116 mg L^{-1} for chromium.

3.2. Waste sludge minimisation and zinc recovery by electrodeposition

The amount of waste generation that could be prevented by applying the EPT technique was evaluated, after analysis of the conventional neutralization-precipitation treatment applied to the spent passivation bath. In the present study, with the amount of flocculant employed, 0.25 L of NaOH solution (40%, w/w) per liter of spent passivation bath were required to reach a pH of 8.6. Similar values of sodium hydroxide consumption in the physicochemical treatment of wastewaters have been reported [24]. The solids content in the metallic sludge after filtering was in the range of 29 wt.%, similar to the values obtained in a filter press [4]. Thus, it was concluded that the wet filter cake obtained in the laboratory is representative of the amount of cake that would be generated in a waste management facility and therefore the information obtained was used for further calculations.

Assuming that physicochemical treatment at industrial scale is carried out using similar levels of flocculant and sodium hydroxide the amount of filter cake generated would be approximately 1240 kg/m^3 of spent passivating bath, with a water content of 71%. This filter cake should be managed further on by solidification techniques and landfill disposal of the stabilized waste. Taking into account the experimental results shown in Section 3.1, this waste production could be prevented by implementing the emulsion pertraction technology to regenerate the spent passivating bath. Additionally, the loss of valuable metals, expressed in terms of element, is easily quantified: 13 kg of zinc and 10 kg of chromium

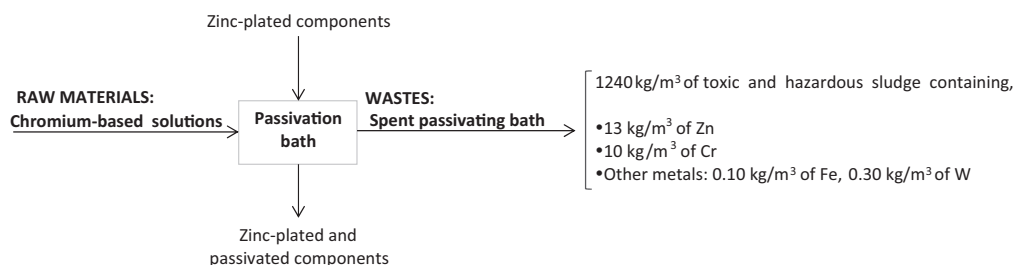


Fig. 5. Waste generation in the physicochemical treatment of spent passivating baths.

are lost per each cubic meter of spent passivating bath. These data are summarized in Fig. 5.

Next, recovery of the zinc contained in the stripping solution obtained in the EPT treatment of the passivating bath was evaluated. The final chemical composition of the stripping solution is presented in Table 1. The high zinc concentration, $157,000 \text{ mg L}^{-1}$, and the low content of iron and chromium seem favourable for zinc recovery and purification by electrowinning techniques. A typical composition of electrolyte solutions used in the literature for zinc recovery is $50\text{--}90 \text{ g (Zn}^{2+}) \text{ L}^{-1}$ and $120\text{--}200 \text{ g (H}_2\text{SO}_4) \text{ L}^{-1}$ [32]; however, the purification of zinc sulphate solutions by solvent extraction and the employment of insoluble dimensionally stable anodes have been reported to make it possible working outside the conventional composition range [33]. Barakat et al. [19] employed an electrolyte solution for zinc electrowinning containing $153,300 \text{ mg L}^{-1} \text{ Zn}^{2+}$, 14 mg L^{-1} total Fe and approximately 35 g L^{-1} free acid concentration, quite similar to the present electrolyte composition. It was found that the electro-recovery of zinc proceeded with acceptable current efficiency down to a zinc concentration in the electrolyte of 50 g L^{-1} . Lower zinc concentrations required sharp increases of energy consumption.

In this work, several attempts at different current voltages and experimental times were carried out. Fig. 6 shows the appearance of the zinc layer electrodeposited at 7.5 V (at a current density of 70 mA cm^{-2}) during 30 min. The experiment was halted when a sufficient coat of zinc was deposited, but the final zinc concentration in the electrolyte was still high enough for not limiting the current efficiency. It can be observed that the appearance of the zinc deposited on the cathode was metallic grey and rough. The quality of the deposit was considered adequate taking into account that the electrolyte was used as received from the EPT stripping solution without addition of any enhancers for the improvement of the deposit morphology.

The chemical analysis of the zinc deposit is shown in Table 3. The content of zinc was approximately 98.5%. This purity grade matches



Fig. 6. Appearance of electrodeposited zinc (at 70 mA cm^{-2} during 30 min) from the EPT stripping acid solution.

the prime western grade zinc quality obtained during pyrometallurgical processes [28,34], however, the main impurity found in this type of commercial grade zinc is lead, which is not present in the electrodeposited sample. This is a very promising result, considering that no preliminary cleaning of the stripping solution had been made. Some of the main applications of zinc with a 98.5% purity grade are i.e. hot-dip galvanizing, production of brasses and bronzes, pigments for the formulation of paint coatings, in primary batteries or as sacrifice anode [28,34]. No traces of chromium were found in the analysed sample of the zinc deposit, indicating the lack of influence of the chromium presence on the quality of electrodeposited zinc under the experimental conditions considered in the present work. The content of iron and copper in the deposit accomplished the maximum limits for the special high grade quality (99.995%) according to the European Standard for Primary Zinc [17]. Also a very low sulphur percentage was determined. The main impurity found in the zinc deposit was tungsten. The presence of this metal was unexpected, since it is not a common component of passivation baths. Then it was checked the tungsten concentration in the stripping solution determining a value of 5100 mg L^{-1} . Further analysis of the presence of this element in the passivation baths and its separation selectivity by the EPT process is under way. Nevertheless, both sulphur and tungsten impurities could be removed by applying a subsequent refining method consisting on a fractional distillation, a common practice after pyrometallurgical processes when higher zinc purity is required [34,35].

From the results presented, it can be concluded that zinc recovery from the stripping solution of the emulsion pertraction process by electrowinning can be attained, with acceptable deposit purity; the feed acidic solution had a zinc concentration higher than 157 g L^{-1} and a pH around 1.9 and the electrowinning process was carried out for 30 min at 7.5 V and with current density of 70 mA cm^{-2} .

3.3. Economic study

A novelty in the present work is the assessment of the implementation of EPT into the process line of a surface finishing industry mimicking the industry operation conditions in batch cycles. The extension of the lifetime of the passivating bath by removing the tramp ions (Zn and Fe) was sought, in order to reduce on one hand

Table 3
Chemical composition of electrodeposited zinc (at 70 mA cm^{-2} during 30 min) from the EPT stripping acid solution.

Element	Concentration (wt.%)
Fe	0.00054
Cr	–
Cu	0.00064
S	0.02
W	1.5
Total impurities	1.52
% Zinc balance	98.48

Table 4
Economic evaluation of the integration of EPT into the process line of a surface finishing industry.

Concept	Amount ^a
(1) Expected saving materials/costs	
•New formulation of passivating bath	Passivating tank volume in the industry
•Chemicals for the physicochemical treatment	
Flocculant	~400 L/m ³
Sodium Hydroxide (40%, w/w)	~250 L/m ³
•Waste disposal in landfill	~1240 kg/m ³
(2) Recovery of materials and/or by-products	
•Chromium in solution in the passivating bath	~10 kg/m ³
•Zinc in acidic stripping solution ^{b,c}	~160 g L ⁻¹
(3) Most important investment costs	
•EPT membrane module	Membrane area requirements depend on the plant production

^a Data referred to m³ of spent passivating bath.

^b Value referred to the stripping volume.

^c The solution composition would accomplished the requirements to be electrodeposited without further pretreatment.

the consumption of the commercial passivating bath reducing the times that has to be freshly formulated, and on the other hand the consumption of reagents for the treatment of the spent passivating bath and the generation of a new hazardous solid waste.

Another novelty herein presented consists in the evaluation of the closing loop strategy (i.e. “zero discharge” goal) that would require not only attaining the appropriate quality of the regenerated passivating bath, but also the recovery of the valuable compounds contained in the stripping phase after EPT that would be otherwise discarded as a waste.

The integration of EPT in an industrial process would lead to some savings in materials and chemicals but also to some investments or capital costs. The concepts susceptible of economic assessment have been summarized in Table 4. From this preliminary evaluation it can be said, that due to the reduction of the amount of chemicals consumed, hazardous solid waste for landfill disposal produced and metals recovered for further reuse, the EPT implementation in an electroplating process leads to designing a sustainable process.

4. Conclusions

This work reports the feasibility of applying Emulsion Pertraction Technology (EPT) with hollow fiber membrane contactors aiming at waste minimization and zinc recovery in zinc electroplating processes that include trivalent chromium passivation. The main benefits of the EPT process are first the extension of the life-time of the passivating baths by the selective removal of the tramp ions zinc and iron, and second, a concentrated zinc acidic solution can be obtained with an adequate composition to recover metallic zinc for further reuse. Iron and zinc can be selectively removed from the bath, while chromium, the active metal that generates the passivation layer is retained in the baths. The results presented in this work allow drawing the following conclusions:

- (i) The regeneration of the passivation bath and the extension of its useful life-time by implementing EPT are feasible. The use of a Liqui-Cel contactor, with a membrane area of 1.4 m², and bis(2,4,4-trimethylpentyl) phosphinic acid as selective extractant allowed a reduction of the zinc content of 1 L of passivating bath from the initial concentration of 12880 mg L⁻¹ down to values between 3 and 58 mg L⁻¹ (99.99–99.49% of Zn removal) in a period of time of 6 h. Under the same conditions iron was almost completely removed and its initial concentration of

101.6 mg L⁻¹ was decreased down to the range 0.8–2.0 mg L⁻¹ (97–99% iron removal) in a shorter period of time, showing that the EPT design will be usually limited by the zinc mass transfer rate. The selective transfer of zinc over iron into the acidic stripping phase could be obtained by working under the presented experimental conditions and after 24 h, resulting in the following concentrations: 157,000, 11 and 170 mg L⁻¹ of zinc, iron and chromium, respectively. The low iron concentration was achieved by the retention of this compound in the extractant phase caused by the pH increase due to the H⁺ consumption in the stripping agent.

- (ii) Zinc recovery from the acidic stripping stream was evaluated. Metallic zinc could be electrodeposited, providing an adequate purity of 98.48%, without any pretreatment of the electrolyte solution.
- (iii) As a result of the extension of the life of the passivation bath together with the preliminary evaluation of the savings in (1) the amount of chemicals (400 L flocculant, 250 L of sodium hydroxide (40%, w/w) and 10 kg of Cr³⁺ per m³ of spent passivating bath), (2) the reduction on the generation of hazardous waste disposal (1240 kg/m³ spent passivating bath) and (3) the amount of valuable metals recovered (160 g L⁻¹ of acidic stripping generated), it can be said that the implementation of an EPT unit in an electroplating process contributes to the design of sustainable processes.

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References

- [1] K. Graham, *Electroplating Engineering Handbook*, fourth ed., Springer, 1984.
- [2] M. Cartier, *Handbook of Surface Treatments and Coatings*, Wiley, 2003.
- [3] European Union Law, Directive 2000/53/EC of the European Parliament and of the Council of 18 September 2000 on End-of Life Vehicles, 2009, <http://eurlex.europa.eu/>, (accessed 30.09.09).
- [4] T.J. Weber, *Wastewater treatment, Met. Finish.* 105 (2007) 699–714.
- [5] J.M. Magalhães, J.E. Silva, F.P. Castro, J.A. Labrincha, Effect of experimental variables on the inertization of galvanic sludges in clay-based ceramics, *J. Hazard. Mater.* 106 (2004) 139–147.
- [6] L.D. Duke, Hazardous waste minimization: is it taking root in U.S. Industry?: waste minimization in metal finishing facilities of the San Francisco Bay Area, California, *Waste Manage.* 14 (1994) 49–59.
- [7] B.R. Babu, S.U. Bhanu, K.S. Meera, Waste minimization in electroplating industries: a review, *J. Environ. Sci. Health Part C: Environ. Carcinogen. Ecotoxicol. Rev.* 27 (2009) 155–177.
- [8] W.J. MacLay, F.P. Reinhard, Waste minimization and recovery technologies, *Met. Finish.* 105 (2007) 817–850.
- [9] European Commission, Reference document on Best Available Techniques for the surface treatment of metals and plastics, <http://eippcb.jrc.es>, (accessed 16.07.10).
- [10] I. Fernández-Olmo, A. Ortiz, A. Urriaga, I. Ortiz, Selective iron removal from spent passivation baths by ion exchange, *J. Chem. Technol. Biotechnol.* 83 (2008) 1616.
- [11] A. Ortiz, I. Fernández-Olmo, A. Urriaga, I. Ortiz, Modeling of iron removal from spent passivation baths by ion exchange in fixed-bed operation, *Ind. Eng. Chem. Res.* 48 (2009) 7448.
- [12] A.M. Urriaga, M.J. Abellán, J.A. Irabien, I. Ortiz, Membrane contactors for the recovery of metallic compounds pollutants. Modelling of copper recovery from WPO process, *J. Membr. Sci.* 257 (1–2) (2005) 161–170.
- [13] E. Ortiz, M.F. Bringas, A.M. San Román, Urriaga, Selective separation of zinc and iron from spent pickling solutions by membrane-based solvent extraction: process viability, *Separ. Sci. Technol.* 39 (2004) 2441–2455.
- [14] E. Bringas, M.F. San Román, I. Ortiz, Separation and recovery of anionic pollutants by the emulsion pertraction technology. Remediation of polluted groundwaters with Cr(VI), *Ind. Eng. Chem. Res.* 45 (2006) 4295–4303.
- [15] A. Urriaga, E. Bringas, R. Mediavilla, I. Ortiz, The role of membranes in the selective separation and recovery of zinc for the regeneration of Cr(III) passivation baths, *J. Membr. Sci.* 356 (2010) 88–95.

- [16] M.K. Jha, V. Kumar, R.J. Singh, Review of hydrometallurgical recovery of zinc from industrial wastes, *Resour. Conserv. Recycl.* 33 (2001) 1–22.
- [17] European Standard EN 1179:2003. Zinc and Zinc Alloys: Primary Zinc, Technical Committee CEN/TC 209, 2003.
- [18] U.S. Geological Survey, A.C. Tolcin, Mineral Commodity Summaries: Zinc, January 2010, <http://minerals.usgs.gov/minerals/pubs/commodity/zinc/mcs-2010-zinc.pdf>, (accessed 18.07.10).
- [19] M.A. Barakat, M.H.H. Mahmoud, M. Shehata, Hydrometallurgical recovery of zinc from fine blend of galvanization processes, *Separ. Sci. Technol.* 41 (2006) 1757–1772.
- [20] D. Herrero, P.L. Arias, B. Güemez, V.L. Barrio, J.F. Cambra, J. Requies, Hydrometallurgical process development for the production of a zinc sulphate liquor suitable for electrowinning, *Miner. Eng.* 23 (2010) 511–517.
- [21] C. Bozhkov, M. Petrova, St. Rashkov, Nickel and cobalt synergism effect in zinc electrowinning from sulphate electrolytes, *J. Appl. Electrochem.* 22 (1992) 73–81.
- [22] Cytec Industries, Cyanex®272 extractant, 2010. <http://www.cytec.com>, (accessed 18.07.10).
- [23] V.K. La Mer, T.W. Healy, in: D. Doyle, J.B. Poole (Eds.), *Solid-Liquid Separation*, H.M.S.O., London, 1966.
- [24] European Commission, Reference Document on Best Available Techniques for the Waste Treatments Industries, 2010, <http://eippcb.jrc.es>, (accessed 16.07.10).
- [25] M.D. Lanagan, D.C. Ibana, The solvent extraction and stripping of chromium with Cyanex 272, *Miner. Eng.* 16 (2003) 237–245.
- [26] R. Mediavilla, I. Ortiz, A. Urriaga, Selective extraction of zinc and iron from passivating baths, *Desalination* 250 (2010) 1014–1015.
- [27] N. Miralles, A.M. Sastre, E. Figuerola, M. Martinez, Solvent extraction of iron (III) by bis (2,4,4-trimethylpentyl) phosphinic acid: experimental equilibrium study, *Hydrometallurgy* 31 (1992) 1–12.
- [28] F.E. Goodwin, *Zinc and Zinc Alloys*, Kirk-Othmer Encyclopedia of Chemical Technology, John Wiley & Sons, Inc., published on line 17th February 2006, <http://www.mrw.interscience.wiley.com/emrw/0471238961/home/>, (accessed 16.07.10).
- [29] V. Mymrin, A. Vazquez Vaamonde, Technical note: new construction materials from spanish jarosite processing wastes, *Miner. Eng.* 12 (1999) 1399–1402.
- [30] P. Asokan, M. Saxena, S.R. Asolekar, Hazardous jarosite use in developing non-hazardous product for engineering application, *J. Hazard. Mater.* B137 (2006) 1589–1599.
- [31] V.A. Mymrin, H.A. Ponte, P.R. Impinnisi, Potential application of acid jarosite wastes as the main component of construction materials, *Constr. Build. Mater.* 19 (2005) 141–146.
- [32] P.E. Tsarikidis, P. Oustadakis, A. Katsiapi, S. Agatzini-Leonardou, Hydrometallurgical process for zinc recovery from electric arc furnace dust (EAFD). Part II: downstream processing and zinc recovery by electrowinning, *J. Hazard. Mater.* 179 (2010) 8–14.
- [33] E. Guerra, M. Bestetti, Physicochemical properties of ZnSO₄-H₂SO₄-H₂O electrolytes of relevance to zinc electrowinning, *J. Chem. Eng. Data* 51 (2006) 1491–1497.
- [34] R.B. Gordon, T.E. Graedel, M. Bertram, K. Fuse, R. Lifset, H. Rechberger, S. Spatari, The characterization of technological zinc cycles, *Resour. Conserv. Recycl.* 39 (2003) 107–135.
- [35] F. Porter, *Zinc Handbook: Properties, Processing, and Use in Design*, CRC Press, New York, 1991, pp. 21–22.