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Selective extraction of zinc(II) over iron(II) from spent hydrochloric acid pickling effluents by liquid–liquid extraction

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Abstract

The selective removal of zinc(II) over iron(II) by liquid–liquid extraction from spent hydrochloric acid pickling effluents produced by the zinc hot-dip galvanizing industry was studied at room temperature. Two distinct effluents were investigated: effluent 1 containing 70.2 g/L of Zn, 92.2 g/L of Fe and pH 0.6, and effluent 2 containing 33.9 g/L of Zn, 203.9 g/L of Fe and 2 M HCl. The following extractants were compared: TBP (tri-n-butyl phosphate), Cyanex 272 [bis(2,4,4-trimethylpentyl)phosphinic acid], Cyanex 301 [bis(2,4,4-trimethylpentyl) dithiophosphinic acid] and Cyanex 302 [bis(2,4,4-trimethylpentyl) monothiophosphinic acid]. The best separation results were obtained for extractants TBP and Cyanex 301. Around 92.5% of zinc and 11.2% of iron were extracted from effluent 1 in one single contact using 100% (v/v) of TBP. With Cyanex 301, around 80–95% of zinc and less than 10% of iron were extracted from effluent 2 at pH 0.3–1.0. For Cyanex 272, the highest extraction yield for zinc (70% of zinc with 20% of iron extraction) was found at pH 2.4. Cyanex 302 presented low metal extraction levels (below 10%) and slow phase disengagement characteristics. Reactions for the extraction of zinc with TBP and Cyanex 301 from hydrochloric acid solution were proposed.
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1. Introduction

Metal plating has been identified as an environmentally risky industrial sector concerning the potential hazardous nature of its waste streams since they often contain reasonable amounts of acids and heavy metals such as Zn, Fe, Cr, Ni, etc. The concentration of some metals in these wastes is relatively high thus making their recovery an interesting issue as environmental and economical reasons are also subjacent.

A combination of several deposition and finishing operations are normally involved in metal-plating processing. In the case of zinc-plating or zinc hot-dip galvanizing process, a layer of zinc is deposited by immersing steel goods in molten zinc at tem-

peratures around 450–460 °C to provide corrosion protection or decoration. High-quality zinc layers require appropriate pre-treatment of the surface to be coated (washing, degreasing, rust removal and fluxing steps), so several types of effluents can be generated by the mixture of the various washing waters and the saturated solutions which are substituted regularly. These solutions are normally hydrochloric acid media and may also contain oils, processing additives and metals at high concentrations. In the pickling effluents from the zinc-plating processing, zinc and iron (mainly Fe^{2+}) dissolved in hydrochloric acid media form appropriate metal-chlorocomplexes that might be recovered.

The treatment of effluents produced by the metal-plating industry is normally carried out by precipitation using hydroxides (soda, lime or a mixture of both) as precipitating agents [1,2]. This treatment process might involve several steps such as: (1) reduction of Cr^{6+} to Cr^{3+} in acidic solution (pH between 2 and 3) by adding iron chloride ($FeCl_2$), sodium sulfide (Na_2S) or sodium bisulphite ($NaHSO_3$), (2) oxidation of Fe^{2+} to Fe^{3+} with

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H_2O_2, (3) precipitation of metals by pH neutralization (around 7.0–8.5) by adding hydroxides, (4) solids coagulation and flocculation, and (5) filtration of the suspension to separate the water (treated effluent that can be discharged into sewage or reused) from the sludge which is normally classified as hazardous material. The current level of utilization of sludge as secondary raw material is unsatisfactory; inertization methods are commonly proposed to incorporate the sludge into inorganic pigments [3] and ceramic or cement-based materials [4]. In fact, precipitation is an efficient method to produce a treated aqueous solution from spent pickling effluents but unfortunately both acid and metal content confined to the sludge are not reprocessed. In addition, the amount of precipitating agents required for treatment and the cost for the safe disposal of sludge produced are normally high, so there is an increasing interest in developing new treatment processes which allow the reduction of the quantity of wastes and also the recovery of valuable products to be recycled or reused in other applications. Some alternative methods have been found in the literature to treat pickling effluents such as membrane distillation [5], selective precipitation [6], anion exchange and membrane electrowinning [2], and microbial oxidation followed by liquid–liquid extraction and solvothermal synthesis of ferrites [7].

In this paper, the liquid–liquid extraction operation is proposed as an alternative method to conventional precipitation treatment in order to separate zinc and iron from pickling effluents produced by the hot-dip galvanizing industry. Liquid–liquid extraction is a well-established method used in hydrometallurgical processing of several metals such as Zn, Cu, Ni, Co, rare earths, Fe, Cr, purification of wet process phosphoric acid, reprocessing nuclear fuels, etc. It is basically a three-step separation method. In the *extraction step*, the metal-bearing aqueous feed solution (effluent) is contacted with an organic (or solvent) solution that contains an extractant agent dissolved in a diluent (normally commercial kerosene). The metal of interest reacts with the extractant and it is transferred from the aqueous to the organic phase. The liquid phases are then separated and the aqueous phase is submitted for the recovery of other metals, recycled or discharged, while the organic phase now loaded on metal of interest goes to the next step. If selectivity in the extraction step is low, the loaded organic phase goes to the *scrubbing step* to remove other metals or impurities co-extracted using a suitable aqueous solution that may be recycled to a stage upstream of the liquid–liquid circuit. Finally, in the *stripping step*, the metal in the loaded solvent is stripped out from the organic phase to some suitable aqueous solution resulting in a fairly concentrated solution on the metal of interest (as a metal salt form), which goes to further processing for metal or metal oxide production (electrolysis, evaporation, crystallization, etc.). Actually, the liquid–liquid extraction is a simple operation requiring only a shift in the equilibrium between extraction and stripping processes [8], so the selectivity of the extractant and its metal loading capacity for the metal of interest represent decisive parameters to be defined in a separation process based on the liquid–liquid extraction. Nowadays, there is a large number of available extractants for metal extraction showing selectivity characteristics coupled with advances in

engineering and increasing demands for higher purity products and more environmentally friendly processing routes. In this paper, the separation of zinc over iron(II) from spent hydrochloric acid pickling liquors using neutral and acidic commercial extractants is highlighted in order to identify suitable reagents to treat such type of effluent.

Neutral (or solvating) extractants extract metals from the aqueous phase in the form of neutral ion-pairs by replacement of the hydration sheath of the ion-pairs by solvent molecules. By far TBP (tri-*n*-butyl phosphate) is the best well known and most widely used of the family of neutral organophosphorus reagents for the separation of several metal ions such as U, Zn, Fe, rare earths, etc. The extraction of metals by TBP from various acidic media appears to involve two molecules of TBP which solvates the neutral metal-containing ion-pair by donation through the double-bonded oxygen atom [8]. TBP is a very effective reagent for zinc extraction and stripping from pickling solutions, however its main drawback is the transfer of high amounts of water to the organic phase [9]. Moreover, only a concentrated reagent solution (80–100%, v/v) can achieve high extraction efficiency [10] and it is an effective reagent to separate zinc(II) from iron(II) but not from iron(III), so a previous step to reduce Fe(III) to Fe(II) is necessary [10,11]. On the other hand, stripping of zinc from the loaded organic solutions with TBP is carried out with water or slightly acid solutions.

In the MeS process, TBP is used as extractant agent for the selective removal of zinc(II) over iron(II) from spent hydrochloric acid pickling liquors [12]. In order to avoid co-extraction of iron, iron(III) is reduced to iron(II). Zinc is stripped out from the loaded organic solution with water or diluted HCl solution. The resulting strip solution is evaporated, either after addition of H_2SO_4 resulting in a diluted HCl condensate (used as strip solution) and a $ZnSO_4$ precipitate, or directly without any addition giving a diluted HCl condensate and concentrated $ZnCl_2$ mother liquor. The $ZnCl_2$ solution can possibly be treated in a pyrolysis plant or, more probably, used for the production of flocculating chemicals as those used in sewage water treatment.

Acidic (or liquid-cation exchange) extractants undergo an exchange of an acidic hydrogen ion on the extractant molecule for the metal cation to form the metal salt of the reagent in the organic phase thus releasing protons to the aqueous phase. Much research work has been concentrated on the study of zinc extraction with D2EHPA [di-(2-ethylhexyl)phosphoric acid], which selectively extracts zinc from other bivalent transition metals such as Cu, Co, Ni and others [13,14]. Recently, the reactive system $ZnSO_4$/D2EHPA was adopted by the European Federation of Chemical Engineering as the standard system for research studies in equipment when mass transfer and reaction rates must be accounted [15]. In recent years, phosphinic acid extractants like Cyanex 272 [bis(2,4,4-trimethylpentyl)phosphinic acid] were commercialized (mainly to separate Co from Ni) and, even more recently, monothio and dithio analogues to Cyanex 272 have been made available for industrial applications, e.g., Cyanex 302 [bis(2,4,4-trimethylpentyl) monothiophosphinic acid] and Cyanex 301 [bis(2,4,4-trimethylpentyl) dithiophosphinic acid], respectively. Thiophosphinic acids were originally developed for the selective recovery of zinc at a low pH from

effluent streams containing calcium, in order to avoid recycling the calcium which forms gypsum precipitates when sulfate ions are also present. If one compares the extractive behavior of D2EHPA and Cyanex 272, it can be pointed out that Cyanex 272 generally needs higher pH values than D2EHPA to extract the same metal ions because phosphinic acids derivatives are weaker acids than phosphoric ones [16]. On the other hand, the substitution of oxygen by sulfur atoms in the molecular structure of the organophosphorus extractants results in stronger acid reagents for soft Lewis acid metal ions such as Ag^+, Ni^{2+}, Zn^{2+}, Cu^+, Au^+ and platinum group metals, in accordance with the hard–soft acid–base principle as donor atoms of common bases have electronegativities increasing in the following order: $S < Br < N < Cl < O < F$ [17]. Therefore, according to their acidity characteristics, Cyanex 301 > Cyanex 302 > Cyanex 272, so the pH of extraction decreases with increasing sulfur substitution in the phosphinic acid.

The general reaction for the extraction of a metal cation M^{x+} by an organophosphorus acid extractant RH is given by

$$M^{x+} + n(RH)_m \rightleftarrows MR_x(RH)_{nm-x} + xH^+ \tag{1}$$
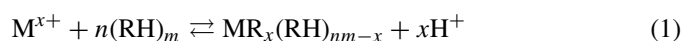
where m represents the degree of association of the extractant. For the extraction of zinc sulfate with D2EHPA, $n = 1.5$ and m depends on the diluent ($m = 1$ for aromatic diluents and $m = 2$ for aliphatic ones [18]). In addition, the molecular structure of the zinc-complex species formed in the organic phase depends on the metal loading level in this phase: ZnR_2RH at low loading conditions [15,19,20], and ZnR_2 [15] or $(ZnR_2)_4$ [20] at high loading conditions. In the case of Cyanex 272, $n = m = 2$ for bivalent cations such as Zn, Co, Cu and Mn in sulfate media giving $MR_2(RH)_2$ species [17,21,22] although the complex $ZnR_2(RH)$ has also been proposed [23].

Several organo-metal complexes have been proposed for the extraction with Cyanex 301 and Cyanex 302, so it seems that there is no agreement on this regard thus evidencing that the extraction mechanism of these reagents is rather complex and it still needs to be investigated in detail. The use of the slope analysis method for these reactive systems is difficult due to the extremely low pH at which metal extraction occurs, so the stoichiometry and geometry of such complexes are therefore inferred from the interpretation of other experimental evidence [17]. For the extraction of Cu^{2+} ions from the sulfate media using thio-substitutes extractants (Cyanex 301 and Cyanex 302), FAB-MS (fast-atom bombardment excitation source) analysis suggested a 1:1 stoichiometric ratio between the metal and ligands, supporting the evidence that Cu^{2+} ions are reduced to Cu^+ with the accompanying oxidation of the organic ligands to disulfide species [17]. Data also provided evidence for the formation of multinuclear oligomeric complexes in which the ligands bridge between metal centers. On the other hand, the extraction of zinc from chloride media by Cyanex 302 was also affected by the active component of Cyanex 301 [24], which is present in commercial Cyanex 302 as a minor component around 2% [22]. Several organo-metal complexes were proposed by graphical and numerical analysis of data using the computer program LETAGROP-DISTR. It has been found that $ZnR_2(RH)_2$ is dom-

inant at low concentrations of Cyanex 302, but the contribution of mixed species from Zn-Cyanex 301 and Zn-Cyanex 302 are significant at higher concentrations of Cyanex 302.

Although metal extraction reaction with Cyanex 302 and Cyanex 301 is still unknown, these reagents might be adequate for metal separation from very acid solutions as those produced by the galvanic industry. In addition, no industrial process using Cyanex 272, Cyanex 301 or Cyanex 302 to recover zinc from spent pickling liquors has been found in the literature. Therefore, in this work, several effluent streams containing predominantly zinc, iron and small quantities of chromium dissolved in acidic hydrochloric solutions were collected from the zinc-plating industry and the extractants TBP, Cyanex 272, Cyanex 302 and Cyanex 301 were chosen as active reagents to separate zinc from iron in an attempt to purify these solutions for future recycling of metals allowing the final recovery of zinc under the form of zinc chloride.

2. Experimental

2.1. Reagents

The neutral extractant TBP was supplied by Merck, while the acidic extractants Cyanex 272, Cyanex 302 and Cyanex 301 were supplied by Cytec Industries. All reagents were used without previous purification. Some physico-chemical properties of these extractants and additional information are given in Table 1. The diluent was commercial aliphatic kerosene, trade name of Exxsol D-80, supplied by Exxon. No modifier agent has been used in the solvent phase composition. All other chemicals were of reagent grade quality. In the liquid–liquid extraction tests, the aqueous phase consisted of an industrial effluent produced by the zinc hot-dip galvanizing industry as depicted in Section 2.2.

2.2. Characterization of effluents and definition of the aqueous phase to be treated

In a preliminary investigation, around 150 metal-plating companies were visited in order to get a representative picture of this industrial sector in the state of Minas Gerais, Brazil. It has been verified that the effluents produced by these companies could be classified into two main types: (1) concentrated hydrochloric acid solutions containing high amounts of zinc and iron, and other metals in smaller concentrations like chromium, aluminum, etc., and (2) concentrated solutions con-

Table 1
Physico-chemical parameters and characteristics of extractants used in this study

	TBP	Cyanex 272	Cyanex 302	Cyanex 301
Molar mass (g/mol)	266	290	306	322
Density at 24 °C (kg/m^3)	973	910	930	950
Viscosity at 25 °C (mPa s)	3.4	142	195	78
Aqueous solubility (mg/L)	400	16	3	7
pK_a in water	Not reported	6.37	5.63	2.61
Purity (%)	98	87	85	77

taining nitric and fluoridric acids with high concentrations of iron, nickel and chromium. The first type of effluent which is typical from the zinc hot-dip galvanizing industry was chosen for the present study. Therefore, in order to develop a method to separate zinc and iron from a hydrochloric acid solution by liquid–liquid extraction, samples of effluents produced by a given zinc-plating company were collected from three different baths along the industrial plant aiming to identify the critical effluent to be treated. For this attempt, samples were collected from the baths of pickling (tanks 1 and 2), washing and passivation with chromium. The solutions were filtered for the removal of oils and then chemically characterized with respect to the metals concentration of the metals zinc, iron and chromium by atomic absorption spectroscopy (GBC 932 plus model).

The acidity of effluents was not assessed by titration method with NaOH due to the high metal concentration in these solutions. In fact, the formation of colored metal precipitates as long as the pH of solutions was raised made the visualization of end-point quite difficult. Alternatively, the acidity was estimated by diluting samples of effluent with water (100 times dilution) and reading its pH using a digital pH-meter (Digimed).

2.3. Liquid–liquid extraction experiments

Metal equilibrium distributions between the organic and the aqueous phases were obtained by contacting a given volume ratio of the two liquids in a 1 L glass reactor which was immersed in a bath at controlled temperature. All experiments were carried out at temperature of $25 \pm 1\,^\circ$C and liquids were mechanically stirred at 420 rpm using a glass impeller marine type.

In the experiments with TBP, the effluent was contacted with the organic solutions for 20 min. This time was found sufficient to reach equilibrium as verified in preliminary tests. The following variables were investigated for the extraction step: initial concentration of extractant (25–100% (v/v) of TBP) and the organic/aqueous ratio of phases (0.5–3.0). Stripping of the metal loaded organic solutions was investigated using water as the stripping agent at changing aqueous/organic ratio of phases (1–4).

The experiments with Cyanex 272, Cyanex 301 and Cyanex 302 were carried out in two steps. Firstly, the concentration of extractant was kept constant at 1.5 mol/L and the pH (or acidity) of the effluent was varied from 2 M to 0.003 M (pH 2.5) by adding NH$_4$OH very slowly to avoid precipitation of metal hydroxides. Tests were carried out by contacting 250 mL of both phases. Samples of 5 mL of the aqueous phase were withdrawn and the same volume of NH$_4$OH was added to keep the aqueous/organic volumetric ratio constant. These tests were done aiming to identify the most suitable extractant and acidity level in order to extract zinc preferentially over iron from the effluent. So, in the second part of experiments, the extractant that showed the best results was investigated and the acidity level of effluent was adjusted according to the previous tests; in these tests, the effluent was contacted with organic solutions at distinct initial concentrations of extractant (0.5–1.5 mol/L). Finally, the equilibrium isotherm for zinc extraction was assessed using the

Table 2
Composition of effluents generated by a given zinc-plating industry

Effluent	Pickling		Washing	Passivation
	Tank 1	Tank 2		
Zinc (g/L)	70.20	33.90	0.71	0.33
Total iron (g/L)	92.20	203.91	7.28	0.02
Fe(II) (g/L)	90.00	222.40	n.d.	n.d.
Fe(III) (g/L)	2.20	8.51	n.d.	n.d.
Chromium (g/L)	n.d.	0.04	0.01	0.97
Acidity (M)	0.25	2.00	n.d.	n.d.

n.d., not determined.

method of successive contacts. The stripping step was investigated varying the concentration of the stripping agent (1–5 mol/L of HCl) at constant aqueous/organic ratio of unity. In addition, the loaded organic solution was also stripped out by four successive contacts using 5 M HCl solution. In all tests, equilibrium was attained within 5 min, although a contact time of 10 min was typically allowed for each contact to assure equilibrium was reached.

3. Results

3.1. Characterization of effluent streams produced by the zinc-plating processing

Table 2 shows the composition of different effluent streams generated by a zinc-metal-plating industry. These streams were produced in the steps of pickling, washing and passivation with chromium. All effluents are hydrochloric acid solutions. The concentrations of zinc, iron and chromium exceeded the maximum concentration allowed by COPASA NT 187/2 [25] for the discharge of non-domestic effluents in the public sewage collection system of Minas Gerais state, Brazil, so these streams are considered to be hazardous materials. According to this norm, the concentration of zinc, iron and chromium must be below 5 mg/L, 15 mg/L and 10 mg/L, respectively, pH between 6 and 10, and temperature below 40 °C. Therefore, all wastewaters analyzed require previous treatment to reduce their metal content in order to fulfill the local environmental legislation.

Excepting for the effluent generated in the passivation step where the concentration of chromium was found to be relatively high (around 1 g/L), it can be seen that zinc and iron are the predominant metal species in the wastewaters, mainly those from the pickling tanks where both metals are highly concentrated. In the pickling solutions, the concentration of iron was found to be higher than that found for zinc and, in addition, iron(II) was found to predominate over iron(III), so liquid–liquid operation appears as a feasible separation method to extract zinc selectively over iron(II) from pickling effluents because a lower consumption of extractant agent would be required. In addition, due to high acidity of the effluents (mainly from tank 2), it seems to be advantageous to remove zinc at very acidic conditions, in order to minimize costs with alkalis to raise the pH

of the aqueous solutions. It is interesting to observe also that acidity and the concentrations of zinc and iron in the pickling solutions analyzed differ significantly, so both pickling liquors (tanks 1 and 2) were selected for liquid–liquid studies. In order to treat the effluent from tank 1 (hereafter named effluent 1), TBP was selected as extractant agent due to its lower metal concentration, lower Fe/Zn ratio (around 1.3) and lower acidity (pH ≈ 0.6) while acidic extractants Cyanex 272, Cyanex 302 and Cyanex 301 were chosen to treat the effluent from tank 2 (named effluent 2) due to their higher concentration of metals, higher Fe/Zn ratio (around 6.0) and higher acidity as well. In this study, no reduction of iron(III) to iron(II) was done in the effluents 1 and 2 prior to the liquid–liquid experiments due to the predominance of iron(II) as shown in Table 2.

Fig. 1 shows the Eh–pH diagrams of zinc(II) and iron(II) species in hydrochloric acid media in order to preview the predominant metallic species which are possibly stable in the effluents 1 and 2. Eh–pH diagrams are useful tools to understanding problems of dissolution, leaching and selective precipitation. In the present work, such diagrams were done using the program HSC Chemistry (version 4.0) and metal, protons and chloride concentrations (as well as the ionic strength) assumed in the calculations were based on values shown in Table 2. The following

assumptions were done: (1) all iron present in the effluent was considered to be iron(II), (2) the concentration of chromium was considered negligible, and (3) protons and chloride concentrations were estimated from the acidity value shown in Table 2 assuming total dissociation of HCl. Dotted lines shown in Fig. 1 indicate the stability area of water, so the stability region of species which are theoretically soluble in the effluent can be outlined. Based on such assumptions, it can be verified from Fig. 1 that iron(II) exists exclusively as $FeCl^+$ while zinc occurs as neutral $ZnCl_2$ in both effluents. According to Regel et al. [26] and Cierpiszewski et al. [27] who used the program Medusa to roughly estimate the distribution of various chlorocomplexes in spent HCl pickling liquors, iron(II) may also exists as Fe^{2+} additionally to $FeCl^+$ while zinc exists almost completely in the anionic forms as $ZnCl_4^{2-}$ and $ZnCl_3^-$. Both analysis are theoretical and dependent on the species considered to exist in the aqueous system (and their respective concentrations as well), and also the stability constants used in the calculations. For the operational conditions assumed in the Eh–pH diagrams (see Fig. 1), the presence of Fe^{2+} may occur only if oxidant conditions prevail. Alternatively, Fe^{2+} may also exist at lower chloride concentrations. With regard to anionic zinc chloride complexes, these may appear in the Eh–pH diagrams if higher concentrations of chloride are assumed.
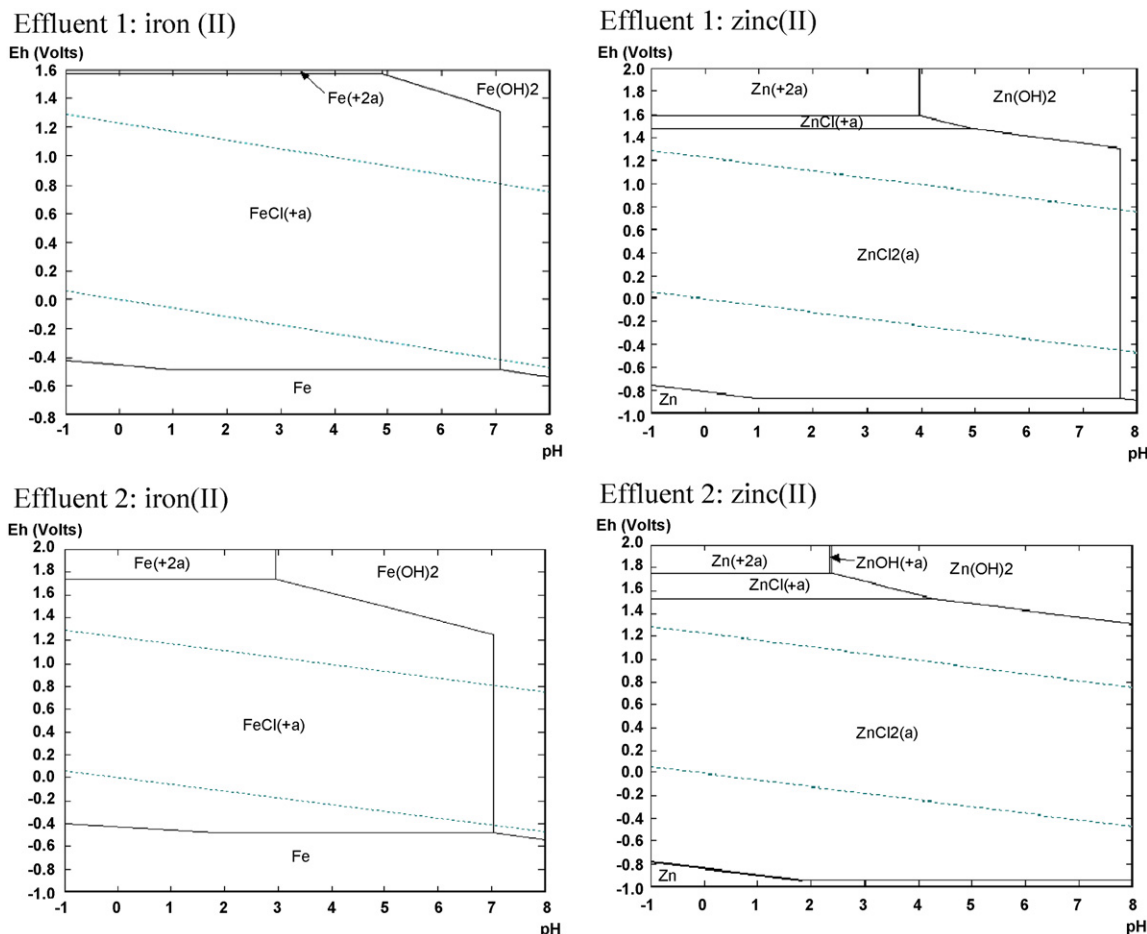

Fig. 1. Eh–pH diagrams for zinc(II) and iron(II) speciation in hydrochloric acid media for effluents 1 and 2.
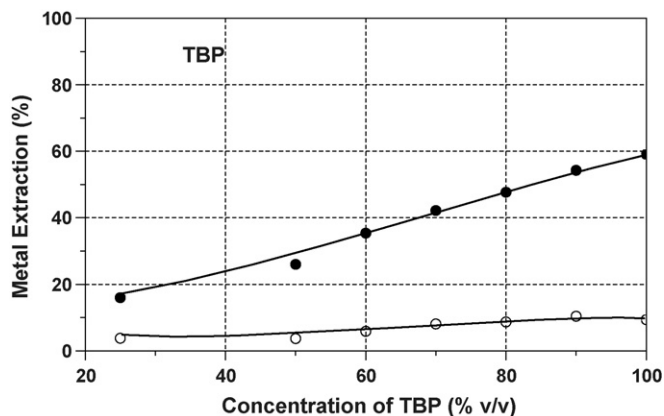
Fig. 2. Extraction of zinc and iron from effluent 1 at changing concentrations of TBP (A/O ratio = 1 and $T = 25\,^\circ$C): ($\bigcirc$) Fe and ($\bullet$) Zn.

Fig. 3. Extraction of zinc and iron from the effluent 1 with 50% (v/v) of TBP and 100% (v/v) of TBP at changing O/A volumetric ratio of phases ($T = 25\,^\circ$C): ($\bigcirc$) Fe-TBP 50%, ($\bullet$) Zn-TBP 50%, ($\triangle$) Fe-TBP 100%, and ($\blacktriangle$) Zn-TBP 100%.

3.2. Selective extraction of zinc over iron(II) by liquid–liquid extraction with TBP

Fig. 2 shows the extraction of zinc and iron from effluent 1 at changing concentrations of TBP. It has been observed that both metal extractions increase with the increase of TBP concentration in the organic phase; however the extraction yield for zinc is more pronounced than that verified for iron. Zinc was preferentially extracted over iron and higher extraction efficiency for zinc was obtained when concentrated TBP solutions were used [9–11]. For the conditions shown in the Fig. 2, the Zn/Fe selectivity factor (defined as the ratio between the distribution ratio of both metals) increased from 4.9 to 14.0 when the concentration of TBP was raised from 25% to 100% (v/v), respectively. According to these results, if an organic solution containing 100% (v/v) of TBP is used to treat effluent 1, the concentration of zinc would be reduced from 70.2 g/L to 2.7 g/L in one single contact, while the iron concentration would change from 92.2 g/L to 85.3 g/L, so an effective operation to separate zinc from iron should be carried out in staged equipment such as mixer-settlers or pulsed columns. In addition, either a previous step to reduce iron(III) to iron(II) or a scrubbing stage are required to improve the zinc/iron separation efficiency. With regard to water transfer to the organic phase, the volume of the aqueous phase reduced from 2.5% to 8.0% in one single contact when the concentration of TBP was increased from 25–50% to 90–100% (v/v).

The extraction of zinc and iron from effluent 1 with organic solutions containing 50% and 100% (v/v) of TBP at changing organic/aqueous volumetric ratio of phases is shown in Fig. 3. It can be observed that the efficiency of the Zn/Fe separation increases at higher TBP/aqueous solution volumetric ratio. For 50% (v/v) of TBP, the Zn/Fe selectivity factor increased from 4.4 to 16.0 as the O/A volumetric ratio was changed from 0.5 to 3.0; for 100% (v/v) of TBP, it increased from 9.1 to 98.0.

In order to evaluate the stripping process, effluent 1 was firstly contacted with 100% (v/v) of TBP at O/A = 2.5 thus resulting in a loaded organic phase containing 62.0 g/L of zinc and 4.0 g/L of iron. The loaded solvent was contacted with water at changing A/O volumetric ratio of phases. The stripping of zinc increased
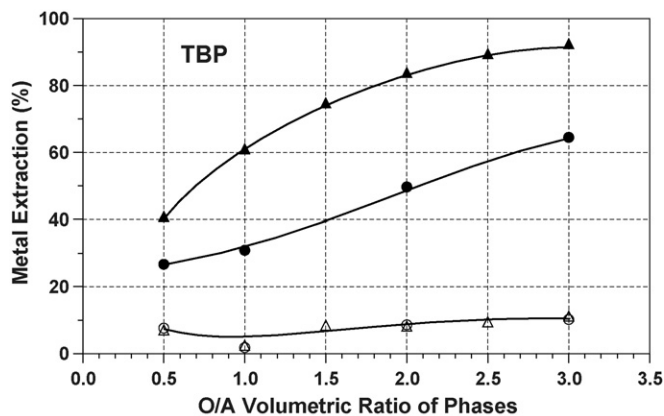
from 26.3% to 34.7% as the A/O ratio was raised from 1 to 4, respectively, so it must be carried out in stages in the continuous experiments. In the case of iron, no effective influence on the yield was verified with the A/O changing. Around 51% of iron was stripped out from the solvent phase. As stripping was found to be a non-selective operation for zinc, these results emphasize the importance of a previous step of iron reduction in order to minimize the presence of iron in the loaded organic phase with TBP. Despite the amount of iron(III) was found to be relatively small as compared to iron(II), some oxidation may occur with time and even during the extraction tests as the solutions are strongly stirred in contact with atmospheric air.

The liquid–liquid equilibrium associated with neutral extractants involves the solvation of the neutral metal complex by the molecules of extractant to form the organic soluble species. According to Fig. 1, zinc exists predominantly as $ZnCl_2$ in effluent 1 so the chlorocomplexes of zinc are extracted by TBP according to the following equation:

$$ZnCl_2 + 2S \rightleftarrows ZnCl_2 \cdot 2S \quad \text{with} \quad \log(K_{eq}) \approx -0.9638 \quad (2)$$
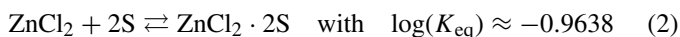
where S represents the molecule of extractant and K_{eq} is the apparent equilibrium constant of Eq. (2). This reaction was obtained by the slope analysis method (log–log plot between the zinc distribution coefficient, D, and the concentration of TBP in the organic phase, C_S, in M shown in Fig. 4) on the experimental data shown in Fig. 2 assuming low co-extraction of iron and an excess of extractant in the organic phase, i.e., $C_S = C_S^0$ where superscript 0 represents the initial condition. As verified in Fig. 4, the fit was quite satisfactory ($R^2 = 0.9967$). According to Morris and Short [28], Eq. (2) is dominant for concentrations of HCl and Cl$^-$ below 0.8 M and 1.0 M, respectively.

3.3. Selective extraction of zinc over iron(II) by liquid–liquid extraction with Cyanex 272, Cyanex 301 and Cyanex 302

The percentage of extraction of the metals zinc, iron and chromium from the effluent 2 at changing pH (or acidity) with extractants Cyanex 272, Cyanex 302 and Cyanex 301 is shown
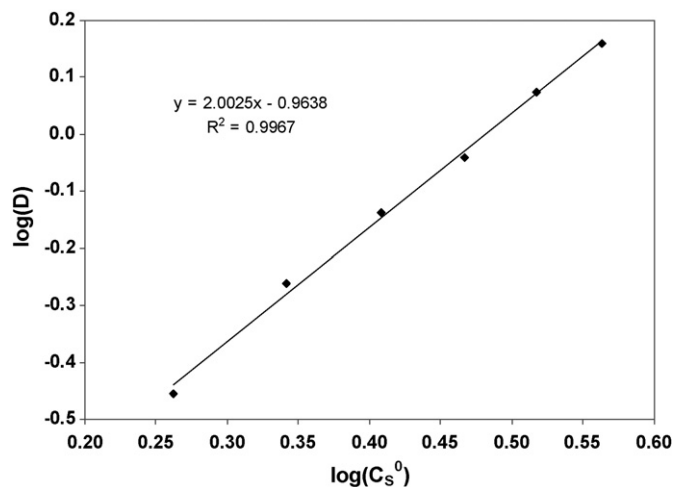
Fig. 4. Effect of TBP concentration on the extraction of zinc from the effluent 1 (A/O ratio = 1 and $T = 25\,^{\circ}$C).

in Fig. 5. As a general trend, it can be observed that metal extraction increased with pH, e.g., with the decrease in the concentration of protons (or acidity) of the aqueous phase. Such behavior is typical of cationic acidic extractants, so the extraction mechanism of these metals with the extractants Cyanex 272 and Cyanex 301 might be described by Eq. (1). With regard to Cyanex 302, an unsatisfactory result has been obtained for the extraction of metals. As shown in Fig. 5, metals were practically not extracted with Cyanex 302 possibly due to the formation of a dense and viscous intermediate organic phase during experiments named third phase. This phenomenon may occur due to low solubility characteristics of the organic metal-complex formed in this phase. To avoid the third phase formation, modifier agents such as long-chain alcohols are usually added to the composition of the solvent phase. As shown in Table 1, reagent Cyanex 302 is relatively more viscous than the remaining extractants considered in this study, so it can possibly affect metal extraction as well. In addition, the behavior of metal extraction with Cyanex 302 is quite complex and may involve other effects such as redox reaction between metal and ligands of the extractant, interference of the active component of Cyanex 301 present in the commercial Cyanex 302 [17,24], and even any other effect like tautomerism, for example, which is related to an exchange between the oxygen and sulfur atoms at the monothio-phosphorus molecular structure of Cyanex 302, as pointed by Tait [29] in the extraction of cobalt and nickel.

Contrary to Cyanex 302, the extractants Cyanex 272 and Cyanex 301 have shown to be selective reagents for zinc in detriment of iron present in the hydrochloric acid solution, so the latter two reagents could be used to separate zinc and iron from the pickling effluent. However, from the economical point of view, a much better result has been found for Cyanex 301 because it is selective to zinc even at very acidic conditions (see pK_a values in Table 1). Consequently, a lower consumption of hydroxides will be required to further treat the effluent. For the sake of comparison, the best result with Cyanex 272 was found at pH 2.4 (extraction level around 70% for zinc and 20% for both iron and chromium) while the same extraction level for
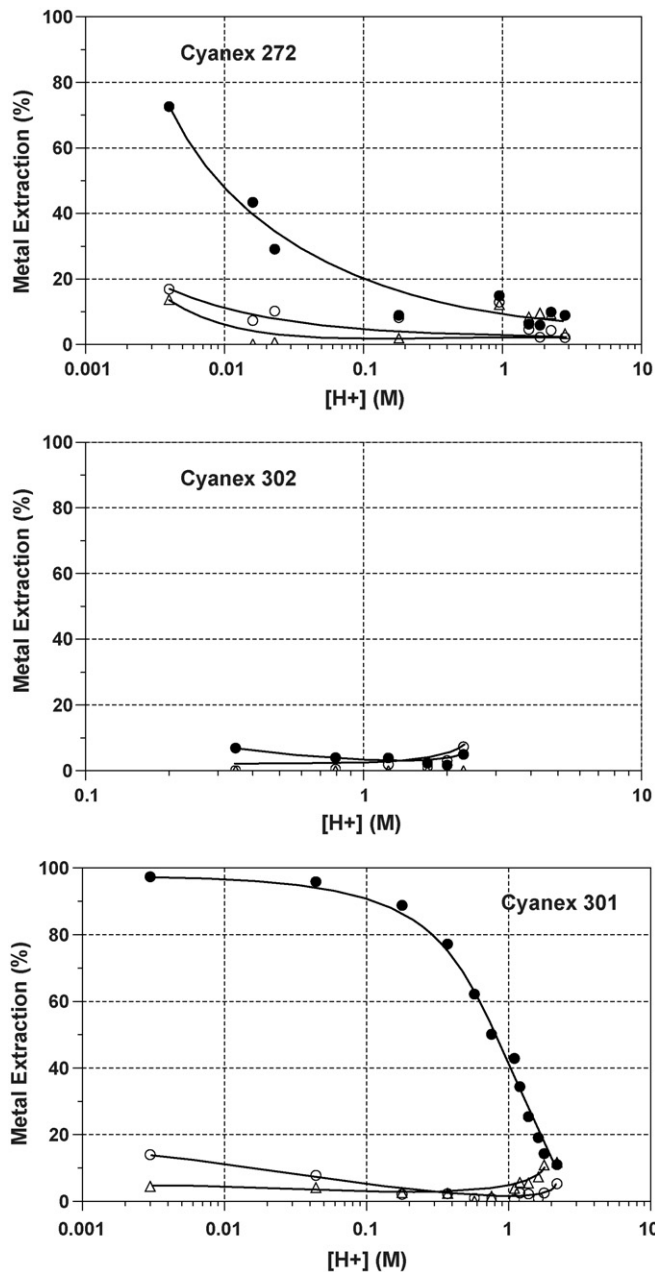

Fig. 5. Extraction of zinc, iron and chromium from the effluent 2 with Cyanex 272, Cyanex 302 and Cyanex 301 as a function of equilibrium pH (or acidity) of the aqueous phase ([extractant]^0 = 1.5 mol/L, A/O ratio = 1, and $T = 25\,^{\circ}$C): (○) Fe, (●) Zn, and (△) Cr.

zinc with Cyanex 301 was obtained at pH ≈ 0.4 with extractions below 5% for both iron and chromium.

Fig. 6 depicts the effect of the pH (or acidity) of the aqueous phase on the selectivity of zinc against iron when effluent 2 is contacted with Cyanex 301 as reagent. For the operational conditions investigated in this study, a maximum in the selectivity Zn/Fe (around 350) was found at pH ≈ 0.75. At higher pH values (or lower acidities), the increase in the extraction of iron reduces the selectivity factor, thus evidencing that Cyanex 301 is a promising reagent to separate zinc and iron from hydrochloric acid media at very acidic conditions, so it can be used to treat effluent streams generated by metal-plating industries.
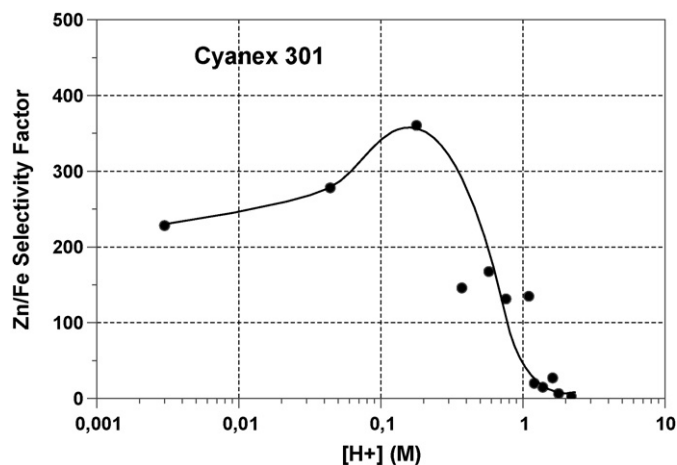
Fig. 6. Zn/Fe selectivity factor with Cyanex 301 as a function of the pH (or acidity) of the aqueous phase (effluent 2, [Cyanex 301]^0 = 1.5 mol/L, A/O ratio = 1, and T = 25 °C).

The extraction of zinc and iron from effluent 2 at changing initial concentrations of Cyanex 301 as extractant is shown in Fig. 7. Experiments were carried out at pH 0.75 and A/O ratio of unity. As expected, a higher percentage of extraction of zinc and iron were obtained when the concentration of Cyanex 301 was raised. The same behavior was observed for the Zn/Fe selectivity factor which increased almost linearly with the initial concentration of extractant, from 25 to 360 as the concentration of Cyanex was raised from 0.4 M to 1.5 M, respectively. The extraction of iron was found to be very small (below 10% and average of 2.6%).

The slope analysis method was used to roughly estimate the extraction reaction of zinc with Cyanex 301. For this attempt, it was assumed that the iron extraction is not significant and also that there is an excess of Cyanex 301 in the organic solutions. Such assumptions are rather questionable because data were collected from effluent 2, so a rigorous study using synthetic solutions are more adequate to assess the reaction of zinc with Cyanex 301 at hydrochloric acid solutions. Fig. 8(a) and (b) shows the plots of log(D) for the extraction of zinc with Cyanex
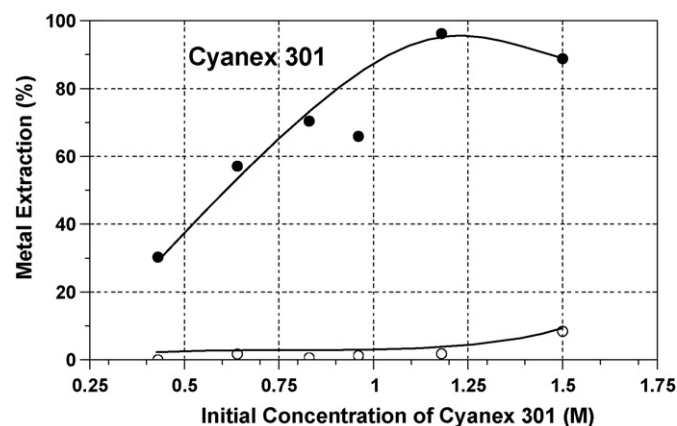

Fig. 7. Effect of the concentration of Cyanex 301 on the extraction of zinc and iron from the effluent 2 (pH 0.75, A/O ratio = 1, and T = 25 °C): (○) Fe and (●) Zn.
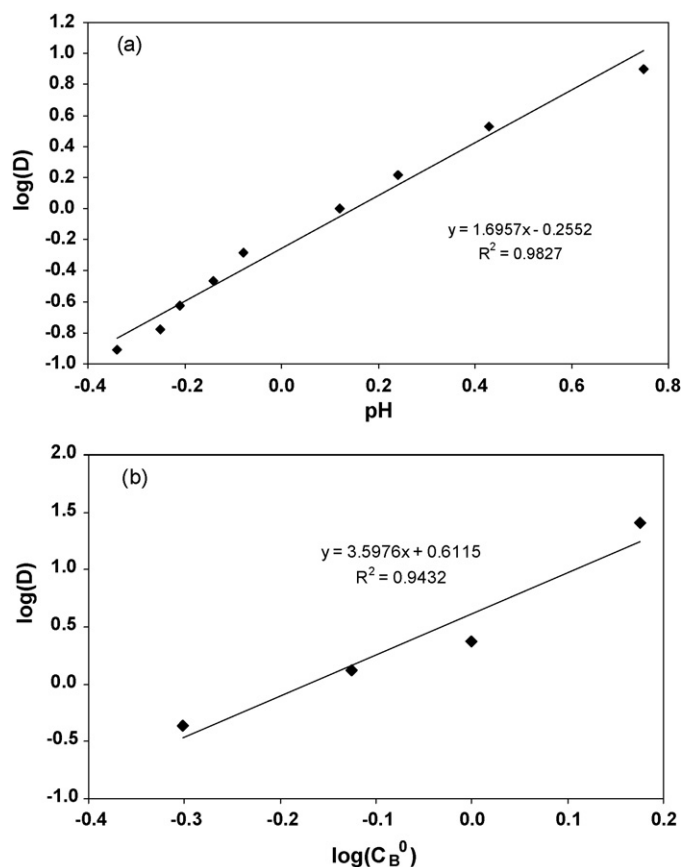

Fig. 8. Effect of (a) pH and (b) initial concentration of Cyanex 301 on the extraction of zinc from the effluent 2.

301 from effluent 2 with the changing of the equilibrium pH and the initial concentration of extractant, respectively. According to these figures, two atoms of hydrogen and four molecules of Cyanex 301 may participate on the extraction of zinc. Therefore, the following reaction can possibly occur for the extraction of zinc from pickling effluents with Cyanex 301:

$$ZnCl_2 + 4(RH) \rightleftharpoons ZnCl_2 \cdot R_2(RH)_2 + 2H^+$$
$$\rightleftharpoons ZnR_2(RH)_2 + 2H^+ + 2Cl^- \qquad (3)$$
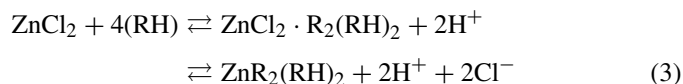
producing HCl and assuming Cyanex 301 is monomeric [29]. As previously mentioned, Eq. (3) is a rough estimate of the liquid–liquid equilibrium of zinc chloride with Cyanex 301 and it must be used only as an indicative basis of the extraction mechanism.

The isotherm for the extraction of zinc from effluent 2 using Cyanex 301 as extractant agent is shown in Fig. 9. The shape of this curve is typical for extraction systems that require a minimum number of theoretical extraction stages by the method of McCabe-Thiele [8], so the extraction of zinc from pickling effluents with Cyanex 301 could be carried out using a few number of contact stages.

Finally, metal stripping from a loaded organic phase was investigated. The results are shown in Table 3. Zinc and iron are both easily stripped out from the solvent using HCl as stripping agent. The stripping efficiency increases with acidity of the aqueous phase. Practically all zinc and iron were stripped
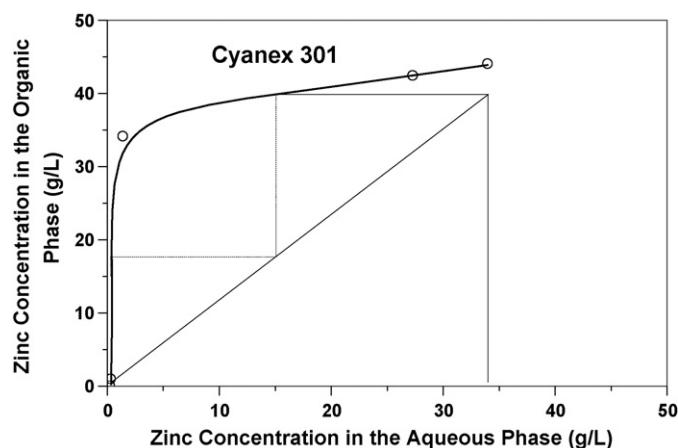
Fig. 9. Isotherm of zinc extraction from the effluent 2 with Cyanex 301 (pH 0.75, [Cyanex 301]^0 = 1.5 M, A/O ratio = 1, and T = 25 °C).

Table 3
Metal stripping with HCl solutions at changing concentrations (A/O ratio = 1, T = 25 °C)

HCl concentration (M)	Stripping of Zn (%)	Stripping of Fe (%)
1	47.4	59.0
2	64.7	67.0
3	78.6	76.0
5 (contact 1)	94.5	36.0
5 (contact 2)	3.6	24.0
5 (contact 3)	0.7	21.0
5 (contact 4)	1.1	18.0

by four contacts at 5 M HCl. Stripping was shown to be a non-selective process, so the presence of iron in the loaded solvent must be minimized to improve separation efficiency. The inclusion of a previous step before liquid–liquid extraction to reduce iron valence in the pickling liquor is strongly recommended.

4. Conclusions

The treatment of spent hydrochloric acid pickling effluents aiming to recover metal values by liquid–liquid extraction was investigated in this paper using neutral (TBP) and acidic (Cyanex 272, Cyanex 301 and Cyanex 302) commercial extractants. Iron was practically found as iron(II) in the effluent and metallic chlorocomplexes $ZnCl_2$ and $FeCl^+$ were theoretically identified using Eh–pH diagrams. TBP and Cyanex 301 have shown to be selective extractants for zinc over iron(II) at very acid conditions (pH below 1). However, iron(III) can be extracted by both reagents, so a previous reduction step is strongly recommended because stripping step was found to be a non-selective process. The main drawback of TBP to treat such effluent seems to be the volume of reagent required to separate zinc from iron(II) efficiently. The transfer of water to the solvent phase should be considered on the equipment dimensioning. In the case of Cyanex 301, the main drawback is related to its chemical stability that may represent a serious problem. According to Flett [30], dithiophosphinic acids are not stable mainly at the pres-

ence of iron(III), so this species must be eliminated from the aqueous phase before the extraction step to avoid degradation of the Cyanex 301 by this metal.

References

[1] K. Schugerl, T. Burmaster, M. Gudorf, Selective extractive recovery of metals from heavy-metal-hydroxy sludges of a pickling plant and galvanic processing, in: D. Shallcross, R. Paimin, L. Prvcic (Eds.), Proceedings of the International Solvent Extraction Conference, vol. 2, Melbourne, Australia, 1996, pp. 1549–1552.

[2] G. Csicsovszki, T. Kékesi, T.I. Török, Selective recovery of Zn and Fe from spent pickling solutions by the combination of anion exchange and membrane electrowinning techniques, Hydrometallurgy 77 (2005) 19–28.

[3] K.W. Milanez, C.T. Kniess, A.M. Bernadim, H.G. Riella, N.C. Kuhnen, Characterization of Fe-, Zn- and Cr-based inorganic pigments using galvanic solid waste, Ceramica 51 (2005) 107–110 (in Portuguese).

[4] J.M. Magalhães, J.E. Silva, F.P. Castro, J.A. Labrincha, Physical and chemical characterisation of metal finishing industrial wastes, J. Environ. Manage. 75 (2005) 157–166.

[5] M. Tomaszewska, M. Gryta, A.W. Morawski, Recovery of hydrochloric acid from metal pickling solutions by membrane distillation, Sep. Purif. Technol. 22–23 (2001) 591–600.

[6] J. Jandová, J. Maixner, T. Grygar, Reprocessing of zinc galvanic waste sludge by selective precipitation, Ceramics-Silikáty 46 (2002) 52–55.

[7] Y. Konishi, T. Nomura, K. Mizoe, A new synthesis route from spent sulfuric acid pickling solution to ferrite nanoparticles, Hydrometallurgy 74 (2004) 57–65.

[8] G.M. Ritcey, A.W. Ashbrook, Solvent Extraction—Principles and Applications to Process Metallurgy. Part I, Elsevier, 1984.

[9] A. Grzeszczyk, M. Regel-Rosocka, Extraction of zinc(II), iron(II) and iron(III) from chloride media with dibutylbutylphosphonate, Hydrometallurgy 86 (2007) 72–79.

[10] M. Rozenblat, M. Regel-Rosocka, J. Szymanowski, Extraction of zinc(II) and iron(III) from spent pickling solutions of high zinc(II) content, in: Proceedings of the Internatioanl Solvent Extraction Conference, Beijing, China, 2005, pp. 1328–1334.

[11] M. Regel-Rosocka, I. Miesiac, A.M. Sastre, J. Szymanowski, Screening of reagents for recovery of zinc(II) from hydrochloric acid spent pickling solutions, in: P.M. Cole, J.S. Preston, K.C. Sole, D.J. Robinson (Eds.), Proceedings of the Internatioanl Solvent Extraction Conference, Cape Town, South Africa, 2002, pp. 768–773.

[12] S.O.S. Andersson, H. Reinhardt, Recovery of metals from liquid effluents, in: T.C. Lo, M.H.I. Baird, C. Hanson (Eds.), Handbook of Solvent Extraction. Part IIIB, John Wiley & Sons, 1983, pp. 751–762.

[13] G. Owusu, Selective extractions of Zn and Cd from Zn–Cd–Co–Ni sulphate solution using di-2-ethylhexyl phosphoric acid extractant, Hydrometallurgy 47 (1998) 205–215.

[14] D.D. Pereira, S.D.F. Rocha, M.B. Mansur, Recovery of zinc sulphate from industrial effluents by liquid–liquid extraction using D2EHPA (di-2-ethylhexyl phosphoric acid), Sep. Purif. Technol. 53 (2007) 89–96.

[15] M.B. Mansur, M.J. Slater, E.C. Biscaia Jr., Equilibrium analysis of the reactive liquid–liquid test system ZnSO₄/D2EHPA/*n*-heptane, Hydromet-allurgy 63 (2002) 117–126.

[16] M. Cox, Solvent extraction in hydrometallurgy, in: J. Rydberg, C. Musikas, G.R. Chopin (Eds.), Principles and Practices of Solvent Extraction, Marcel Dekker Inc., New York, 1992, pp. 357–412.

[17] K. Sole, J.B. Hiskey, Solvent extraction of copper by Cyanex 272, Cyanex 302 and Cyanex 301, Hydrometallurgy 37 (1995) 129–147.

[18] Z. Kolarik, Critical evaluation of some equilibrium constants involving acidic organophosphorus extractants, Pure Appl. Chem. 54 (1982) 2593–2674.

[19] C.I. Sainz-Diaz, H. Klocker, R. Marr, H.-J. Bart, New approach in the modelling of the extraction equilibrium of zinc with bis-(2-ethylhexyl)phosphoric acid, Hydrometallurgy 42 (1996) 1–11.

[20] S. Kumar, G.L. Tulasi, Aggregation vs. breakup of the organic complex, Hydrometallurgy 78 (2005) 79–91.

[21] D.P. Mantuano, G. Dorella, R.C.A. Elias, M.B. Mansur, Analysis of a hydrometallurgical route to recover base metals from spent rechargeable batteries by liquid–liquid extraction with Cyanex 272, J. Power Sources 159 (2006) 1510–1518.

[22] K. Sole, J.B. Hiskey, Solvent extraction characteristics of thiosubstituted organophosphinic acid extractants, Hydrometallurgy 30 (1992) 345–365.

[23] A.M. Sastre, N. Miralles, E. Figuerola, Extraction of divalent metals with bis-(2,4,4-trimethylpentyl)-phosphinic acid, Solvent Extr. Ion Exch. 8 (1990) 597–614.

[24] R. Benito, B. Menoyo, M.P. Elizalde, Extraction equilibria of Zn(II) from chloride medium by Cyanex 302 in toluene, Hydrometallurgy 40 (1996) 51–63.

[25] Norma Técnica COPASA 187/2–Lançamento de efluentes líquidos não domésticos na rede pública coletora de esgotos, Minas Gerais, Brazil, 2002.

[26] M. Regel, A.M. Sastre, J. Szymanowski, Recovery of zinc(II) from HCl spent pickling solutions by solvent extraction, Environ. Sci. Technol. 35 (2001) 630–635.

[27] R. Cierpiszewski, I. Miesiac, M. Regel-Rosocka, A.M. Sastre, J. Szymanowski, Removal of zinc(II) from spent hydrochloric acid solutions from zinc hot galvanizing plants, Ind. Eng. Chem. Res. 41 (2002) 598–603.

[28] D.C.F. Moris, E.L. Short, Zinc chloride and zinc bromide complexes. Part II. Solvent-extraction studies with zinc-65 as tracer, J. Chem. Soc. 2 (1962) 2662–2671.

[29] B.K. Tait, Cobalt-nickel separation: the extraction of cobalt(II) and nickel(II) by Cyanex 301, Cyanex 302 and Cyanex 272, Hydrometallurgy 32 (1993) 365–372.

[30] D.S. Flett, Solvent extraction in hydrometallurgy: the role of organophosphorus extractants, J. Organomet. Chem. 690 (2005) 2426–2438.