Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2019.24111

157 (2019) 110–117
July

Recovery of zinc from spent pickling solutions by liquid–liquid extraction using TBP

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Received 26 November 2018; Accepted 9 March 2019

ABSTRACT

In this paper, recovery of zinc from real spent pickling solutions by liquid–liquid extraction with tributyl phosphate (TBP) was studied. In particular, the effects of some parameters were investigated, such as the volume ratio between the organic phase and real spent pickling liquor (O/A) (1:2, 1:1, 2:1, 4:1), the stirring time (5–20–30 min) and the TBP concentration (10%–55%–100%), in order to determine the conditions leading to higher zinc extraction efficiency, as well as selectivity in relationships to other metals such as iron. After zinc extraction, TBP was successfully regenerated. Among several tested solutions, water allows zinc recovery higher than 90%, especially at 10% diluted TBP solution. In addition, a double stripping step with water led to a near complete regeneration of TBP. In the present work, a process flowsheet is also proposed, where TBP at 10% concentration is used for zinc extraction from a spent pickling solution and then regenerated in a double-step stripping stage with water.

Keywords: Spent pickling liquor; Zinc extraction; Tributyl phosphate (TBP); TBP regeneration

1. Introduction

The pickling process is a steel finishing operation that involves a surface-cleaning process, where an acidic solution is used to remove scale and rust from steel surfaces containing oxides, to ensure high quality cleaning of metal surface for further processing. Nowadays, hydrochloric acid is preferred to sulfuric acid because of better surface quality and more economical acid regeneration process [1]. Of note, pickling plant waste is one of the major environmental problems related to the steel industry [2]. Pickling solutions are considered spent when the acid concentration decreases by 75%–85% and the concentration of dissolved metals such as iron (Fe) and zinc (Zn) significantly increases. In fact, the liquor becomes progressively enriched in Fe ions, mainly ferrous ions (Fe^{2+}); when pickled goods are covered with zinc, or the latter is present as impurity, also an accumulation of Zn^{2+} during the pickling process can be observed, thus making the pickling liquor gradually ineffective [3,4]. This build-up of metal impurity is detrimental for metal finishing process. There are several methods for the treatment of waste pickling liquors aiming at environmental protection and cost savings. Membrane separation techniques, ion exchange techniques, pyrometallurgical techniques, precipitation/neutralization, evaporation, and crystallization have been extensively used for regeneration of spent pickling liquors and metal impurity removal. Nowadays, pyrohydrolysis techniques are widely applied in this field, providing

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very high acid recovery efficiencies (>99%) and acceptable recovery of Fe as Fe_2O_3 [2,5–7].

The European and Italian standards give the allowable content of metals in waste as 2 mg dm^{-3} for Zn, 10 mg dm^{-3} for Fe, and 1 g dm^{-3} for chloride ions (Cl^-). However, in the pyrohydrolysis process, Zn concentration in spent pickling liquors should be lower than 0.5 g L^{-1}. In fact, $ZnCl_2$ evaporates and glues to the walls of the installation at the high temperatures used in the process (800°C). Furthermore, Zn may contaminate the Fe_2O_3 product [1,4,5,8–11].

Ion exchange and solvent extraction have been widely used to remove and recover Zn from spent pickling solutions. Liquid–liquid extraction (LLE) is a well-established method with several advantages compared with other extraction techniques. In fact, LLE provides high selectivity and high flexibility, giving the opportunity to treat effluents with a wide concentration range of metal ions [2,11]. Zn can be efficiently extracted through this method and could be recovered as commercially valuable by-products, such as $ZnCl_2$, useful as fluxing agent in a galvanizing plant, or $ZnSO_4$, useful in electrowinning plants [3], or Zn oxalate [12].

Up to date, several investigations have been carried out with the aim to compare and select highly efficient extractants for Zn in spent liquor solutions. Many authors have reported promising results by using tributyl phosphate (TBP), considered very suitable for Zn extraction due to the high selectivity over Fe^{2+} and good phase separation [5,8,11,13]. In some cases, performances of TBP mixed with other organic solvents were also investigated [8,11,14]. The main drawbacks of TBP extraction are the large TBP volume required and the high water transfer to the organic phase. Furthermore, TBP extraction often results in the simultaneous extraction of Fe^{3+} [5,15]. In order to overcome this limitation, reductants are frequently used to reduce Fe^{3+} to Fe^{2+} before the extraction process [9,15,17].

Some authors reported interesting results about Zn extraction from real pickling liquors in the presence of other interfering ions, such as Fe(II). Among them, a few researchers used very high concentrations of iron (up to 200 g L^{-1} of Fe) in co-existence with zinc [13,17,19].

Once TBP is enriched with the extracted metals, regeneration of the solvent for reusing and valuable metals recovery should be considered. Many researchers investigated TBP stripping with water [9,11,16–19] and only in a few cases a comparison among different stripping agents was performed [8,17].

In this work, a systematic investigation of liquid–liquid extraction of Zn from pickling waste acid solution by TBP was studied to guarantee a zinc low charged inlet stream in a pyrohydrolysis plant, which was studied in details in a previous work [7]. In particular, several experiments were carried out in order to determine the optimal operative conditions for the extraction of Zn by TBP in terms of volume ratio between the organic phase and real spent pickling liquor, of stirring time and of concentration of TBP, in the view of integrating this process with the previously mentioned pyrohydrolysis one. A complementary study was also performed to assess the effect of some parameters, such as the nature of the stripping agent, the volume ratio between TBP and stripping agent and the stirring time, on the TBP stripping process.

2. Experimental

2.1. Samples and chemicals

Spent pickling liquor samples were collected from a steel pickling bath of a hot-dip galvanizing industry in Sicily (Fig. 1). Pickling is preceded by a degreasing step where oils are removed from steel items by using surfactants.

Analytical grade chemicals were used, if not specified otherwise. TBP (used as extractant), nitric acid 70%, hydrofluoric acid 48%, and hydrogen peroxide 30% used in the acidic digestion (ACS purity grade reagent) were purchased from Sigma-Aldrich (Saint Louis, MO, USA). HCl 37% was purchased from Carlo Erba Reagents (Cornaredo, MI, Italy). Iron(II) chloride and zinc chloride used for artificial solutions (which were analyzed for comparison purposes) were obtained from Sigma-Aldrich. TBP was used pure and in solution with kerosene (Carlo Erba Reagents) at 10% and 55%. Milli-Q deionized water was used in the stripping step.

2.2. Physico-chemical characterization of spent pickling solution

The pH was measured using a digital VWR SB20 pH meter (VWR International, Radnor, PA, USA). Free acidity was evaluated by acid-base titration using sodium hydroxide as the titrant and methyl orange as indicator. Total organic carbon (TOC) was assessed using a TOC-V CSH instrument (Shimadzu, Kyoto, Japan).

The spent pickling liquor samples were diluted with 2% HNO_3 (V/V) 10 and 100 fold for trace and major elements determination, respectively. Metal concentrations were measured using a 7500A inductively coupled plasma mass spectrometer (ICP-MS; Agilent Technologies, Tokyo, Japan) fitted with an ASX-510 autosampler (CETAC, Omaha, NE, USA) and a peristaltic pump. Quantification analysis was performed using the external standard method and the internal standard correction. Yttrium (^{89}Y, 50 ng mL^{-1}) was used as internal standard.

2.3. TBP extraction stage

Spent pickling aqueous solution (A) and TBP (O) were kept in contact by stirring with a magnetic stirring bar in a beaker, using 3 mL of each phase, at different times (5, 20, and 30 min). Then, the solution was allowed to settle down for phase separation (few minutes). Experiments were performed

Fig. 1. Representative spent pickling liquor bath.

using 1:2, 1:1, and 2:1 O/A volume ratios. In some cases, also O/A 4:1 was investigated. TBP was used pure and diluted in kerosene at different concentrations (10%–55%–100%).

For comparison purposes, an artificial solution with 78 g L^{-1} HCl, 29 g L^{-1} Zn, and 153 g L^{-1} Fe was prepared. Metals were extracted keeping the solution in contact with TBP, pure and at 10% (diluted in kerosene), for 20 min. Experiments were performed using 1:1 and 2:1 O/A volume ratios. All experiments were carried out at room temperature.

In order to assess the extraction yield and selectivity, the organic and aqueous phases were analyzed for Fe and Zn by ICP-MS. Each detection was repeated three times with an error less or equal to 1%. Acidic digestion of the organic phase (250 μL) was performed using a microwave CEM Discover Digestor (CEM Corporation, Matthews, NC, USA) and 35 mL PTFE digestion vessel. Samples were diluted with 2 mL of ultrapure water (water purified with Milli-Q Direct Purification System), 4 mL of nitric acid, 2 mL of H_2O_2, and 1 mL of HF. The digestion was performed following the operative conditions shown in Table 1.

Therefore, the volume was made up to 50 mL with ultrapure water. Samples were diluted 100 fold with 2% HNO_3 (V/V) before analysis. The aqueous phase was diluted 100 fold with 2% HNO_3 and analysed. ICP-MS analysis was performed as described above.

2.4. TBP stripping stage

In the stripping step, TBP Zn-enriched (phase O) and the stripping agent (phase S) were manually kept in contact for different duration times of stirring (10 and 20 min) and at different O/S ratio (1:2, 1:4) with different aqueous solution H_2O, HCl 0.5 M, EDTA 0.5 M, and a solution of EDTA 0.5 M, buffered at pH 7 with CH_3COONH_4.

After stripping, 250 μL of aqueous phase was digested under previous conditions. After decomposition, the volume of the solution was made up to 50 mL with nanopure water, and the sample was aspirated into the plasma.

3. Results and discussion

3.1. Chemical characterization of spent pickling solutions

Table 2 shows the results of the chemical characterization of the spent pickling solution. The pH of the solution and the free acidity were <1 and 78 ± 3 g L^{-1}, respectively.

These results suggest that the solution can be considered spent since the reduction in acid concentration is in the range of 75%–85% of the initial values, as reported in the literature [1,3,4]. Of note, Zn and Fe concentrations were above the acceptance limits of 2 mg dm^{-3} for Zn and 10 mg dm^{-3} for Fe [5]. Due to the very strong acidic conditions, Fe is considered present as Fe(II) for the most part. Furthermore, TOC levels are significant; indeed, several organic species were identified by GC-MS analysis, attributable to oils and surfactants accumulated in the degreasing tank (detailed analyses are not reported here for sake of brevity).

Table 1
Operative conditions of microwave-assisted digestion

Stage	1	2
Temperature (°C)	140	200
Ramp time (min)	03:00	05:00
Hold time (min)	05:00	05:00
Pressure (bar)	400	400
Power (W)	100	200

Table 2
Chemical analysis of the feed solutions

Chemical property	Mean (SD)
Free acidity (g L^{-1})	78 (3)
pH	0.9 (0.1)
TOC (mg L^{-1})	747 (23)
Mg	122.4 (1.2)
K	354 (9)
V	10.0 (0.1)
Cr	139 (1)
Co	15.3 (0.2)
Ni	167 (2)
Cu	17.7 (0.4)
As	0.58 (0.04)
Ba	3.16 (0.04)
Na	476 (29)
Al	254 (3)
Ca	2,796 (123)
Mn	1,425 (20)
Fe	153,000 (5263)
Zn	29,000 (43)

Note: Element concentrations are in mg L^{-1}. Data are mean values ($n = 3$). SD: standard deviation.

3.2. Zn extraction with TBP

The extraction of the aqueous Zn with TBP involves the following reactions [20]:

$$2H^{+}_{(aq)} + ZnCl^{2-}_{4(aq)} + 2TBP \qquad \overline{H_2ZnCl_4{\cdot}2TBP} \tag{1}$$

where the species reported as product of the reaction is the organic complex of Zn salts. This reaction occurs when the HCl concentration was higher than 2.7 mol L^{-1}.

The increasing of the aqueous phase acidity and chloride concentration further shifts the reaction toward the products. Under lower HCl concentrations, other reactions become important, such as:

$$H^{+}_{(aq)} + ZnCl^{-}_{3(aq)} + 3TBP \qquad \overline{HZnCl_3{\cdot}3TBP} \tag{2}$$

$$ZnCl_{2(aq)} + 2TBP \qquad \overline{ZnCl_2{\cdot}2TBP} \tag{3}$$

Reaction in Eq. (2) mainly occurs at HCl concentrations between 0.8 and 2.7 mol L^{-1}, while reaction in Eq. (3) occurs at HCl concentrations below 0.8 mol L^{-1}.

3.2.1. Effect of the O/A ratio

The yield of Zn extraction process strongly depends on the ratio between organic and aqueous solution.

Fig. 2 shows the extracting efficiency *E* (derived from Eq. (4)) as a function of the O/A. as follows:

$$E = \frac{V_0 \times [\mathrm{Zn}]_0}{\left(V_{A,\mathrm{in}} \times [\mathrm{Zn}]_{A,\mathrm{in}}\right)} \times 100 \quad (4)$$

where *V* is the volume of the liquid phase, [Zn] is the Zn concentration expressed in molarity, and subscripts 0 and *A* indicate the organic and the aqueous feed phases, respectively.

Very high extracting efficiencies, up to 85%, are obtained using pure TBP, thus resulting to be suitable for Zn recovery from real spent acid pickling solutions. As expected, the highest extraction yield was observed at the highest performed O/A ratio, 2:1. Similar trends were found in the literature when real pickling liquors are treated with TBP [16,19]. The extraction yield is not significantly reduced if a 1:1 O/A ratio is used (from 85.6% to 81.8%), thus the latter extraction condition might be preferred since less TBP is required.

Equilibrium isotherm was evaluated for Zn extraction with pure TBP for a stirring time of 20 min (Fig. 3). The McCabe–Thiele method was used to evaluate the number of stages required at the higher O/A ratio of 2:1. As observable, a very high efficiency can be obtained using a two-stage extraction process.

3.2.2. Effect of the stirring time

The effect of the stirring time on Zn extraction from real spent pickling liquors was studied at different O/A volume ratios (1:1, 2:1, 4:1) and at different TBP concentrations (10%, 55%, and 100%). In order to determine the optimal stirring time, extractions at 5, 20, and 30 min were performed. As shown in Fig. 4, equilibrium conditions are almost reached after 20 min. A very few authors reported, in the results section, the effect of the stirring time on the extraction of zinc(II) with TBP [16].

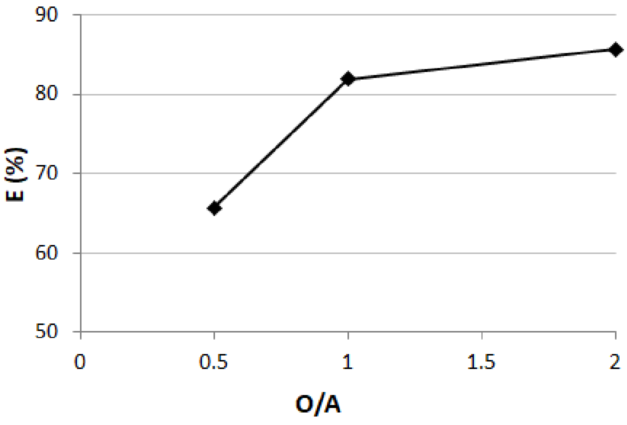

Fig. 2. Effect of the O/A volumetric ratio on the Zn extraction with TBP. $[\mathrm{Zn}]_{\mathrm{in}} = 29$ g L^{-1}. Extractions performed with 100% TBP (V/V) at room temperature with a stirring time of 20 min.

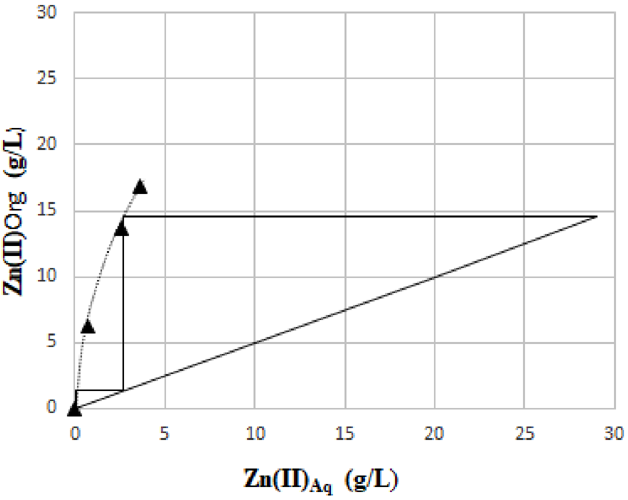

Fig. 3. Equilibrium isotherm for zinc extraction with pure TBP at O/A = 2:1.

Efficiency values higher than 80% were detected at each condition reported and the effect of the O/A ratio was confirmed since higher efficiency values are obtained at higher O/A ratios. In fact, the highest value of about 90% was obtained using an O/A ratio of 4:1 and with a 10% TBP solution.

3.2.3. Effect of TBP concentration

The role of TBP concentration on the extraction efficiency of zinc was studied at the selected stirring time of 20 min. Fig. 5a shows the results obtained at different O/A volume ratios (1:1, 2:1, 4:1) when the real spent pickling solution is used. As observed, the extraction efficiency is slightly higher at lower concentration of TBP in the organic phase (although it may be stated that the trend is practically steady). This result differs from what was reported from other authors [19], probably due to the significant presence of oils and surfactants in the real pickling solution that can affect the extraction process. In fact, extraction experiments with an artificial solution were performed in order to compare the results. As observed in Fig. 5b, where the extraction efficiency is reported vs. the TBP% for a solution prepared mimicking the HCl, Zn, and Fe concentrations of the real one, the trend is positive and higher efficiency values are obtained as the TBP concentration increases. However, since the aim of this work was to study the extraction process with TBP in the specific case of pickling solutions coming from a real plant, the effective conditions selected to obtain the highest Zn recovery concern a 10% TBP concentration, 20 min stirring time and 2:1 O/A ratio.

3.2.4. Selectivity of Zn extraction

In the industrial pickling solutions coming from hot-dip galvanizing plants, both Zn and Fe are usually present at very high concentration (80–160 g L^{-1} of Fe, 20–40 g L^{-1} of Zn). Fe is mainly in the reduced form (Fe^{2+}) because of the strong acidity of the pickling solutions, although Fe^{3+} becomes the prevalent Fe species as the waste oxidizes [13]. It was observed that TBP is a suitable extracting agent for Fe^{3+} while

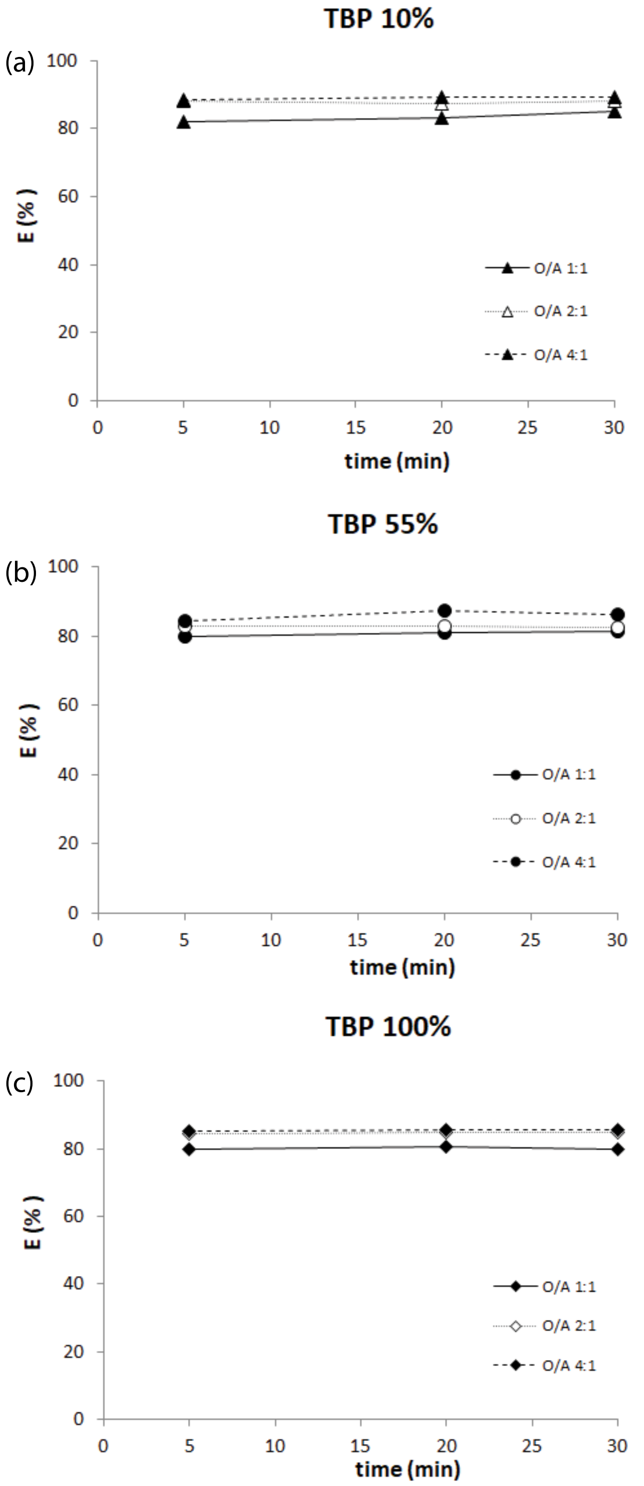

Fig. 4. Effect of the stirring time on Zn extraction with TBP. $[Zn]_{in} = 29$ g L^{-1}. O/A: 1:1, 2:1 and 4:1 at 10% (a), 55% (b) and 100% (c) of TBP. Extractions performed at room temperature.

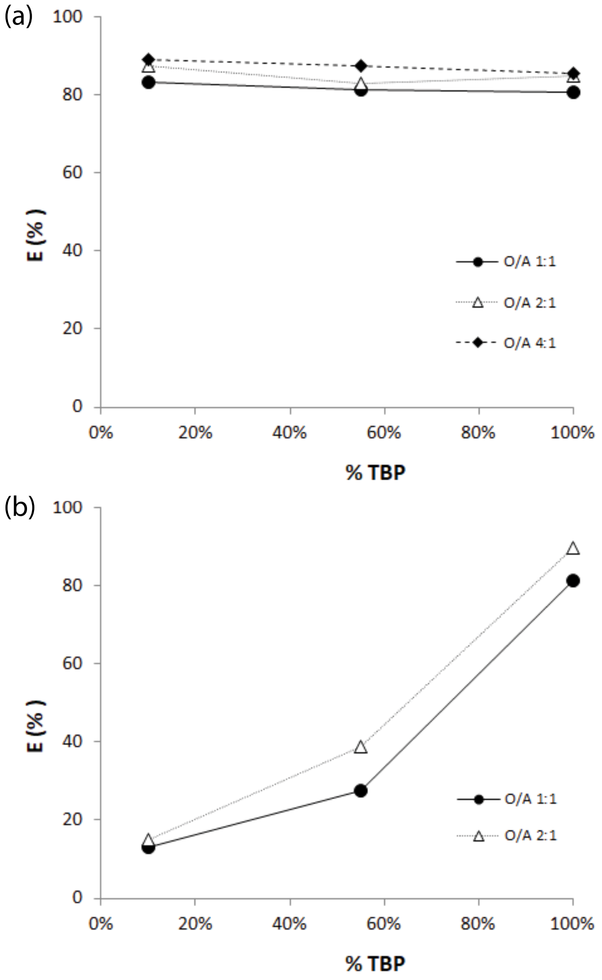

Fig. 5. Effect of the TBP concentration on the Zn extraction with TBP using the real spent pickling solution (a) and an artificial solution (b) with $[Zn]_{in} = 29$ g L^{-1}, $[Fe]_{in} = 153$ g L^{-1} and $[HCl]_{in} = 78$ g L^{-1}. Stirring time: 20 min. Extractions performed at room temperature.

it does not lead to significant extraction rates when only Fe^{2+} is present [4,8,11,17–19].

Data shown in Table 2 indicate that the spent pickling solutions contain Fe (including Fe^{2+} and Fe^{3+}) concentration one order of magnitude larger than Zn, giving a warning on possible interactions of Fe ions with the Zn extraction process. Therefore, the selectivity of the Zn extraction over the total Fe was evaluated under the conditions investigated. For sake of brevity, results for Zn and Fe extractions at the selected stirring time of 20 min are reported in Fig. 6.

As observed, besides Zn, also Fe is extracted with TBP, as part of iron was probably oxidized. In fact, as reported by El Dessouky et al. [17], selectivity of zinc(II) extraction in the presence of Fe (not selectively present as Fe^{2+}, but as a mixture of Fe^{3+} and Fe^{2+}) is difficult to realize.

However, the selectivity increases as the TBP concentration decreases and it is slightly improved by increasing the extraction volume ratio. In fact, a very high Zn over Fe extraction selectivity of 73.5% is obtained at O/A = 4:1 and 10% TBP.

3.3. TBP regeneration by stripping

As known, TBP used to extract Zn can be, in turn, recovered by stripping, using some stripping agents such as water

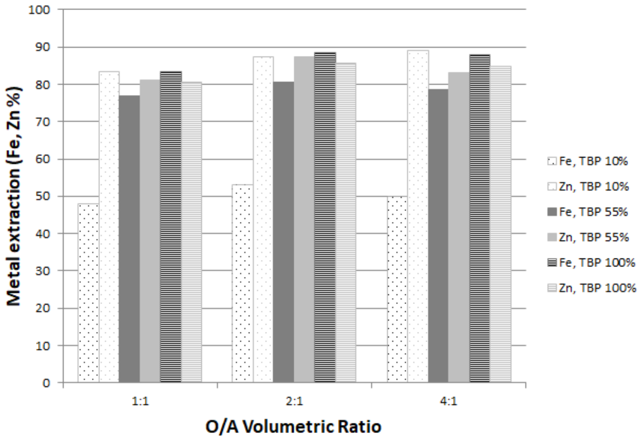

Fig. 6. Effect of the O/A ratio on the selectivity of Zn over Fe extraction with TBP. $[Zn]_{in}$ = 29 g L^{-1}, $[Fe]_{in}$ = 153 g L^{-1}. Stirring time: 20 min. TBP: 10%, 55%, and 100%. Extractions performed at room temperature.

or aqueous solutions. With this aim, several experiments were carried out in order to select the most suitable stripping agent and operative conditions in terms of stirring time and organic/solvent (O/S) volume ratio.

Metals extraction from the organic phase was carried out using a 1:4 O/S ratio with a stirring time of 30 min. Several stripping aqueous solvents were tested: pure water, dilute HCl (0.5 M), EDTA solution (0.5 M) and an EDTA solution (0.5 M) buffered at pH 7.

As shown in Fig. 7, where the effect of the stripping agent nature on the Fe and Zn stripping efficiencies is reported, an effective Zn stripping from TBP is obtained with water, HCl and buffered EDTA solution at both pure and 10% TBP concentration.

However, with the aim to extract also Fe from TBP, water was chosen as the most suitable stripping agent. Furthermore, a more efficient removal of metals is obtained when 10% diluted TBP solution is used. In fact, very high Fe and Zn stripping efficiencies were detected with water, of about 100% for Fe and 90% for Zn.

Aiming at studying the possible separation of Fe and Zn streams after stripping from TBP, a set of experiments using water in a double step was performed (using O/S = 1:4 and stirring time = 30 min).

As reported in Fig. 8, the histograms show an extraction efficiency of about 90% of iron and more than 30% of zinc in the first step, in the case of 10% TBP (Fig. 8b). Of the remaining Zn and Fe amounts, about 90% was stripped in the second step, thus providing a near complete regeneration of TBP, especially with concern to iron. Thus, the extraction process in two steps provides a very high purity of the regenerated TBP and generates two separated streams, each enriched with one of the two metals. In fact, iron is preferentially extracted over zinc in the first extraction step, whereas zinc is quite fully extracted in the second one. This can be very useful in the case of reuse of these streams in a separated way. Therefore, at the end of the liquid–liquid extraction process, a metal “free” TBP stream is obtained, ready to be used for a subsequent Zn extraction from spent pickling solutions.

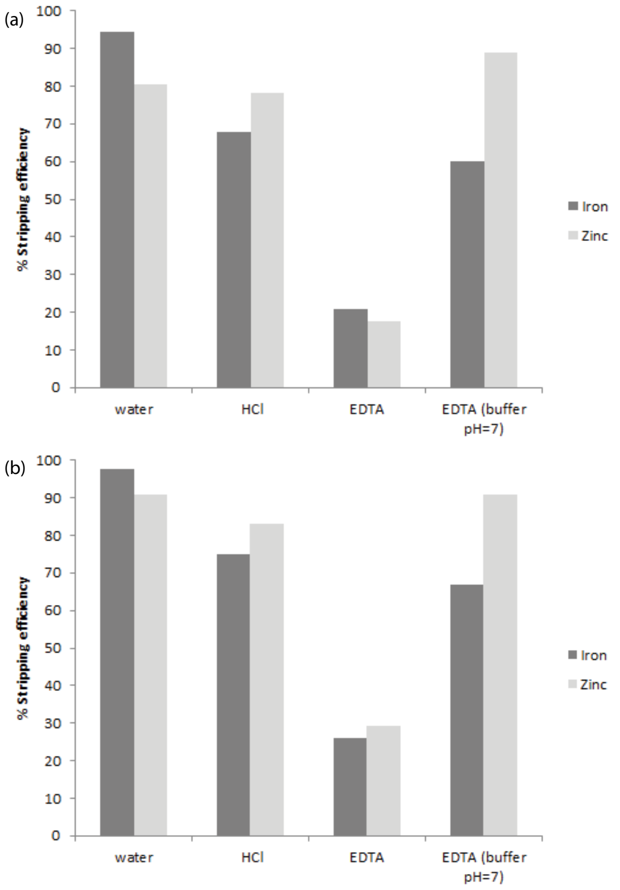

Fig. 7. Effect of the nature of the stripping agent on the stripping efficiency of Zn and Fe from TBP. Stirring time: 30 min; O/S ratio: 1:4 at TBP: 100% (a) and 10% (b). Extractions performed at room temperature.

4. Proposed flowsheet for recovery of zinc from spent pickling liquors

Several authors proposed some flowsheets for metals recovery from spent pickling liquors, generally based on studies about extraction equilibrium isotherms, followed by stripping for regeneration of the organic extractant in mixer–settler units [3,17–19].

Based on the experimental results obtained in this work, a process flowsheet is proposed in Fig. 9. It consists of a first step of zinc extraction from a spent pickling waste with TBP and a subsequent double stripping step with water, in order to regenerate the organic agent.

The spent pickling liquor containing zinc ions is contacted with a TBP solution in kerosene at 10% for 20 min, in a two-stage extraction at O/A volume ratio equal to 2:1. Zinc reacts with the extractant and it is transferred from the aqueous to the organic phase. The aqueous phase, depleted of zinc, can be sent to the pyrohydrolysis regeneration unit and the organic phase, now loaded with metals, flows to the following stripping step. Also some of the metal impurities are partially extracted, although their concentrations were found to be very low compared with those of the metals of higher interest.

In details, the stripping stage consists of two steps where the metals in the loaded organic phase are stripped out by using deionized water contacting for 30 min at an O/S volume ratio of 1:4. First, iron is selectively extracted over the zinc (about 90% of Fe vs. 30% of Zn) and the stream can be recycled to the pyrohydrolysis unit. In the second stage, more than 90% of Zn is extracted, thus generating a stream rich in zinc that can be recovered as $ZnCl_2$ solution, or as $ZnSO_4$, by adding sulfuric acid, as reported in Lum et al. [3], or as zinc oxalate or carbonate, adding oxalic acid or sodium carbonate, as reported in El Dessouky et al. [17].

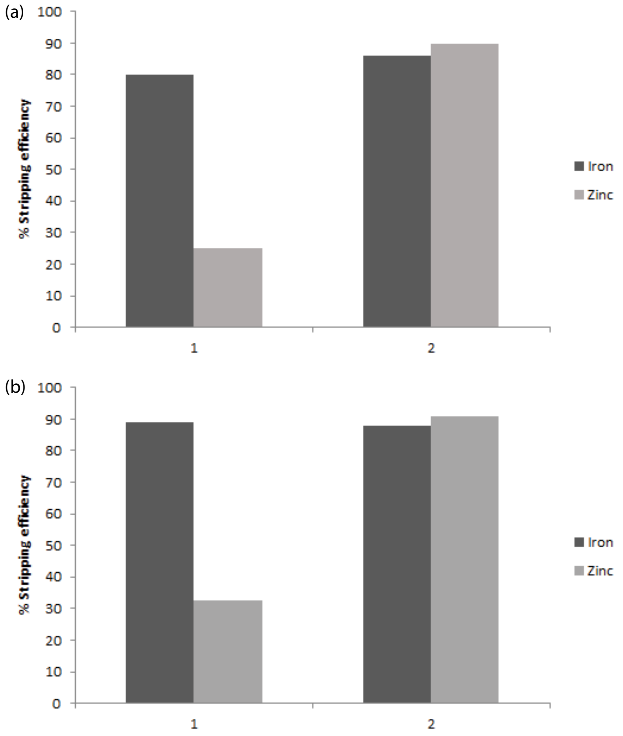

Fig. 8. Fe and Zn stripping efficiencies in the double step extraction with water. Stirring time: 30 min; O/S ratio: 1:4 at TBP: 100% (a) and 10% (b). Extractions were performed at room temperature.

5. Conclusions

Several liquid–liquid extractions were carried out in order to, first, extract metals from spent pickling solutions (real effluents from a pickling plant in Sicily, Zn concentration 29 g L^{-1}) by using TBP, and then, to regenerate the TBP by using a suitable stripping agent. Experimental results show that extraction with TBP can be successfully used for Zn recovery from spent pickling liquors. The identified optimal parameters investigated are the volume ratio of the organic-to-aqueous phase O/A at 2:1, the stirring time of 20 min and the TBP concentration of 10%, with a Zn extraction yield over 85%. Despite the presence of very high concentrations of Fe in the feed solution (153 g L^{-1}) and the possibility of Fe extraction by TBP, a very good selectivity of Zn extraction over iron was observed at 10% TBP concentration, in particular in the selected operative conditions (stirring time of 20 min and higher O/A ratios).

Several stripping agents were investigated to obtain effective stripping of both iron and zinc from TBP. Among them, water was selected to achieve a near complete TBP regeneration in two steps, obtaining a stream enriched in iron (in the first step) and a stream enriched in zinc (in the second step) from where zinc salts can be easily recovered by adding very common salts as sulfuric or oxalic acids.

Finally, a process flowsheet is proposed for recovery of zinc from spent pickling liquor by TBP before entering the pyrohydrolysis plant and for the subsequent regeneration of the organic solvent by water in two steps.

Acknowledgments

The authors acknowledge the financial support from Regione Sicilia under the European Programme "P.O. - F.E.S.R. Sicilia 2007/2013 – Linea di intervento 4.1.1.1bis - CUP G23F12000050004".

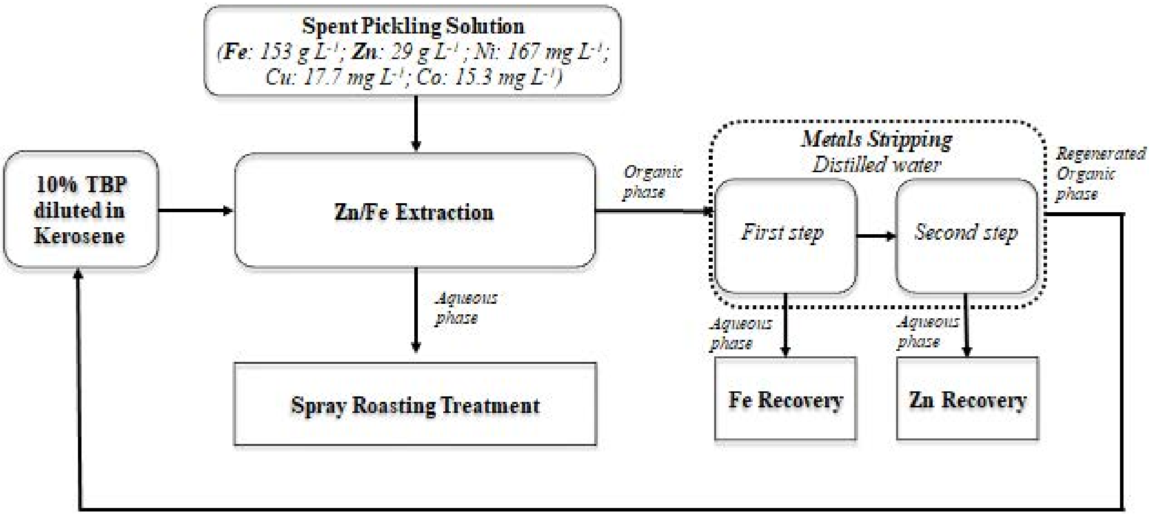

Fig. 9. Proposed flow sheet for removal of zinc from a spent pickling waste containing 153 g L^{-1} of iron and 29 g L^{-1} of zinc.

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