

## **Selective Recovery of Zn(II) From Multimetal Acidic Chloride Solution with Hydrophobic Pyridine Derivatives**

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The main goal of this work was the application of derivatives of 1-(3-pyridyl)undecan-1-one as the selective extractants of zinc(II) ion from strong acidic chloride solutions containing also iron(II), iron(III) or lead(II). The effect of different variables influencing the extraction of zinc(II) ion such as the concentration of hydrochloric acid and chloride ion was investigated. The study also covered the selective stripping process. Laboratory-scale experiments were also performed and the obtained results indicated that the studied extractants were efficient and highly selective for zinc(II) and they can be proposed for the zinc ion removal from real spent pickling solution.

### **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, Pb, Fe, etc. The concentration of some metals in these wastes is relatively high thus making their recovery an interesting issue [1-3].

Solvent extraction is one of the most important techniques for the separation and recovery of metals in the industry. The undoubted advantage is the low power consumption and the ability to re-use extractants. This method is attractive from economic and environmental point of view. In recent years, a lot of novel compounds capable to coordinate the metal and to transfer the resulting complex to the hydrophobic organic solution have been proposed. These properties of the organic compounds are desirable both in analytical techniques and in metals extraction processes [4].

Derivatives of 1-(3-pyridyl)undecan-1-one are the most interesting group of non-commercial extracting agents. The pyridine ketoximes can form complexes with various metals ion, for example: zinc, copper, lead, iron, in the acidic solution. These compounds can form complexes with metals according to ion-pair and solvating mechanisms [5,6].

The aim of this work was to investigate the extraction properties of the pyridine derivatives towards Zn(II). The most important stage was to determine the effect of the different parameters on the selective Zn(II) removal from multimetal acidic chloride solutions.

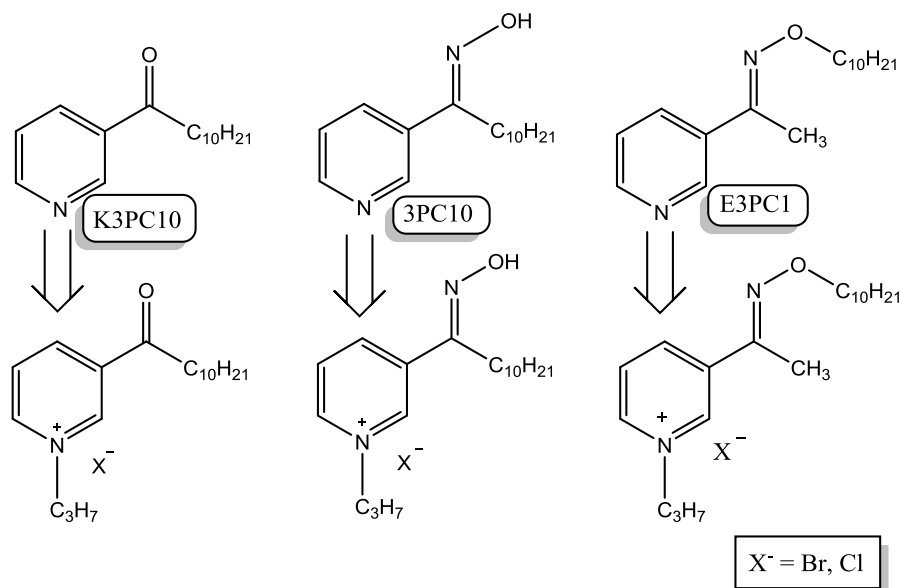


Figure 1. Structure of studied reagents.

## 2. Experimental

### 2.1 Reagents

- 1-(3-pyridyl)undecane-1-one (**K3PC10**),
- 1-propyl-3-undecanoylpyridinium bromide(**K3PC10-Br**),
- 1-propyl-3-undecanoylpyridinium chloride (**K3PC10-Cl**),
- 1-(3-pyridyl)undecan-1-one oxime (**3PC10**),
- 3-[1-(hydroxyimine)undecyl]-1-propylpyridinium bromide (**3PC10-Br**),
- 3-[1-(hydroxyimine)undecyl]-1-propylpyridinium chloride (**3PC10-Cl**),
- *N*-decyloxy-1-(3-pyridyl)ethanimine (**E3PC1**),
- 3-[1-(*N*-decyloxyimine)ethyl]-1-propylpyridinium bromide (**E3PC1-Br**) and
- 3-[1-(*N*-decyloxyimine)ethyl]-1-propylpyridinium chloride (**E3PC1-Cl**) were synthesized according to procedure described in previous papers [5-10].

All reagents used in this study were of reagent grade. Toluene (POCH, Poland) and decan-1-ol (Merck, Germany) were used as components of the organic phase. Sodium chloride (Chempur, Poland), sodium nitrate(V) (Sigma-Aldrich, Germany), hydrochloric acid (38%) (POCH, Poland), nitric acid (70%) (POCH, Poland), zinc(II) chloride (anhydrous) (Sigma-Aldrich, Germany), iron(III) chloride (hexahydrate), iron(II) chloride (anhydrous) (Sigma-Aldrich, Germany), copper(II) chloride (hexahydrate) (Sigma-Aldrich, Germany) and lead(II) nitrate (Sigma-Aldrich, Germany) were used to compose the aqueous phase.

### 2.2 Extraction studies

Extraction studies of individual metal were carried out in a test tube using an organic to aqueous volume ratio (O/W) equal to 1. Both phases were shaken for 30 minutes at room temperature (21 -

23 °C) using a Bio-mix BWR04. Aqueous feed solutions were prepared by dissolving the appropriate amounts of the chloride or nitrate salts of zinc(II), sodium and lithium in ultrapure water. The research was carried out at a constant chloride ion concentration (4 mol/L) and various hydrochloric acid concentrations (from 0 to 4 mol/L), or at a constant mineral acid concentration (HCl or HNO<sub>3</sub>, 0.5 mol/L) and various chloride ion concentrations (from 0 to 4 mol/L). The ionic strength of the aqueous solutions was constant  $I = 4$  mol/L. The selectivity test was performed using the aqueous feed solution containing 1 g/L of Zn(II), Fe(II), Fe(III) and Pb(II) (1.91 g/L) ions and 1 or 4 mol/L HCl. Cumulative concentration of chloride ion was equal 4 mol/L. An organic phase used in the extraction studies contained synthesised compound and toluene with 10% (v/v) addition of decan-1-ol. The concentration of the extractant was 0.1 mol/L. A loaded organic solution containing 0.1 mol/L of the extractant was employed for stripping tests in which the organic phase was shaken with: water, 0.05, 0.1 and 0.5% of HCl, 5% Na<sub>2</sub>SO<sub>4</sub> and 30% HNO<sub>3</sub>, 1% oxalic acid, 1% sodium oxalate or their mixtures at phase ratio O/W equal to 1. The metal concentration was determined by the atomic absorption spectrometry using Z8200 (Hitachi) apparatus.

### 2.3 Calculations

Metal ion concentration in the organic phase  $[M]_{org}$  were determined from the difference of the metal ion concentration in the aqueous phases before  $[M]_{aq,0}$  and after the extraction  $[M]_{aq}$ . Distribution ratio (D), percentage extractions (%E) and separation factor of Zn towards Fe and Pb ions ( $\beta_{Zn/M}$ ) were calculated from equations:

$$D = \frac{[M]_{org,eq}}{[M]_{aq,eq}} \quad (1)$$

$$\%E = \frac{[M]_{aq,0} - [M]_{aq,eq}}{[M]_{o,aq}} \times 100\% \quad (2)$$

$$\beta_{Zn/M} = \frac{D_{Zn}}{D_M} \quad (3)$$

where  $[M]_{aq,0}$  is the initial metal concentration,  $[M]_{aq,eq}$  and  $[M]_{org,eq}$  are the metal ion concentration after the extraction in the aqueous and organic phases, respectively.  $D_M$  are Fe or Pb distribution ratio.

### 3. Results and Discussion

The effect of variable concentration of HCl in the aqueous phase containing constant chloride ion concentration (4 mol/L) on the zinc(II) extraction with the studied extractants are presented in Figure 2. It was worth noting that the extraction of Zn(II) increases progressively with the increasing HCl concentration. The extraction of zinc(II) from the acidic chloride solutions also strongly depends on the structure of the studied reagents and the greatest results are observed for E3PC1, E3PC1-Cl and E3PC1-Br.

Other metals are also extracted with noticeable yield, all obtained derivatives are excellent extracting reagents for copper(II), as well as they are suitable for the recovery of lead(II) and iron(III) from strongly acidic solutions. For the alkylpyridylketone and its quaternary salts (K3PC10, K3PC10-Br and K3PC10-Cl) the results of the copper(II) recovery do not depend on the acidity but

depend strongly on the concentration of chloride ion. However, on using 3PC10 and E3PC1 and their quaternary salts, the extraction of Cu(II) strongly depends on acidity of the aqueous phase [11]. The novel reagents have also been studied as the Pb(II) extractants from chloride and chloride/nitrate solutions [8,10]. In this case, also the best ligands were the compounds containing ether group (E3PC1, E3PC1-Br and E3PC1-Cl) which extract Pb(II) in approximately 90%. Furthermore, the ether derivatives have no ability to extract iron(II) but can extract iron(III) from the acidic solutions (%E = 20-60% and depends on the extractant structure).

The stripping efficiency depends on type of metals, extractants and stripping agents, and ranges from 87 to 100% for zinc and copper, 60-98% for iron and 55-57% for lead(II) in double stripping process.

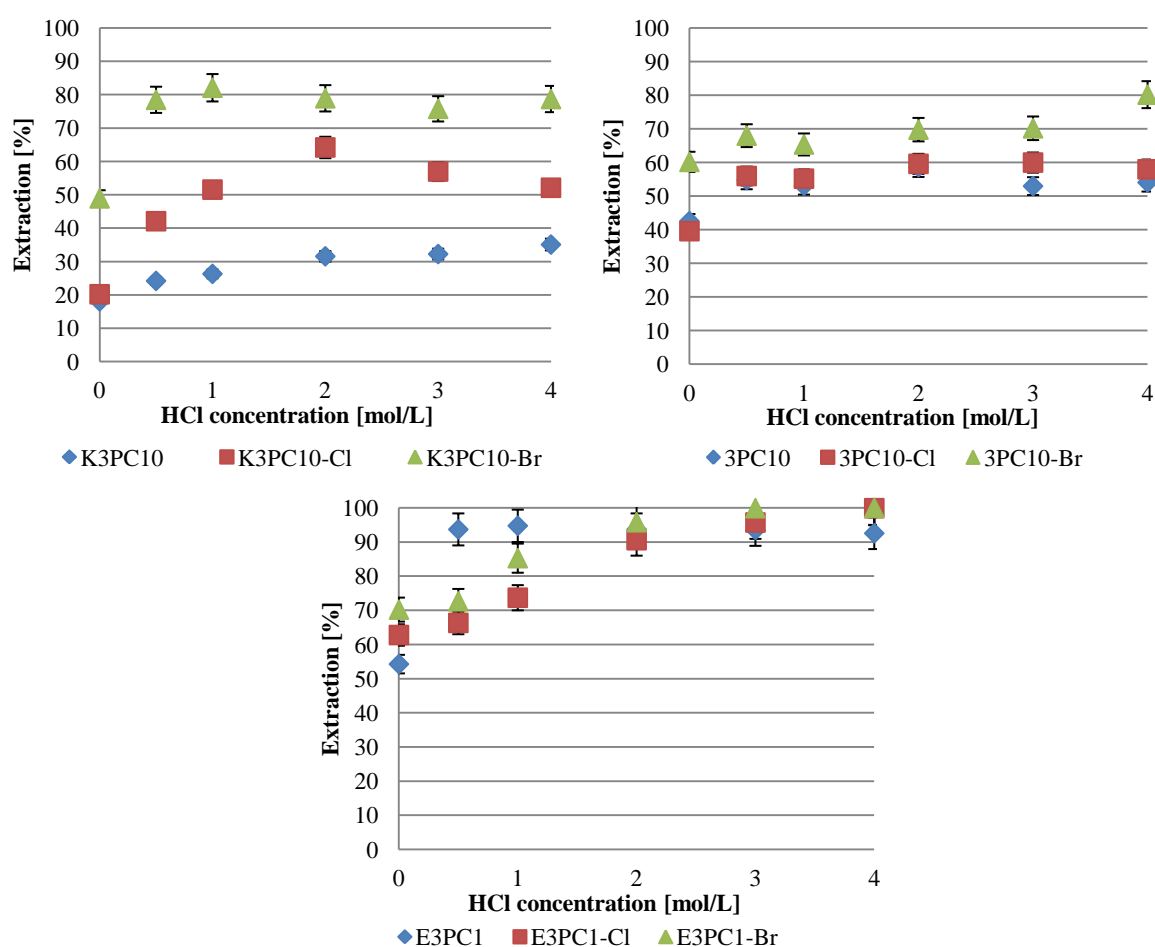


Figure 2. Influence of HCl concentration on zinc extraction

The selective recover of the metal ion from different sources is an important issue in the production of a high-pure metal. The effective recovery of metal ion is possible only if the process (extraction or stripping stage) is sufficiently selective [12,13]. The selectivity of the extraction from the multimetal aqueous solutions, which contain zinc(II), iron(II) and iron(III), were studied for the solutions containing 4 M  $\text{Cl}^-$  (NaCl/HCl). The obtained results indicate that the most selective

extractant of zinc(II) over iron are 3PC10 and E3PC1 (Table 1).

Table1. Extraction of zinc(II) from multimetal aqueous solutions with 3PC10, 3PC10-Br, E3PC1 and K3PC10-Br

Composition of aqueous solution	Extraction [%]											
	3PC10 [6]			3PC10-Br			E3PC1			K3PC10-Br		
	Zn	Fe(II)	Fe(III)	Zn	Fe(II)	Fe(III)	Zn	Fe(II)	Fe(III)	Zn	Fe(II)	Fe(III)
4M HCl	100	0	0	61.2	0	12.3	100	0	13.9	66.1	0	22.0
2M NaCl /2M HCl	100	0	0	54.8	0	0.9	100	0	29.8	83.1	0	46.5

In the case of lead(II) the selectivity studies of the extraction were performed using the synthetic aqueous solutions containing 1 g/L Zn(II), 1.91 g/L Pb(II), 1.1 g/L Fe(III) (or 1.1 g/L Fe(II)) and 4 mol/L HCl. This level of chloride ion concentration was chosen because at 4 mol/L HCl a maximum extraction of zinc(II) with hydrophobic pyridine derivatives was observed. The studied 3PC10-Cl salt can be used for a selective extraction of Zn(II) over Fe(II) and Fe(III) (extraction below 0.1%), whereas the co-extracted Pb(II) can be removed in the stripping process.

According to the experimental data, a flow sheet has been constructed (Figure 3), in which after the extraction iron(III) ion remained in the feed solutions, but the co-extracted Zn(II) can be first removed by washing with water (100% removal) and then Pb(II) can be stripped with the 1% solution of oxalic acid and sodium oxalate (10:1, w/w).

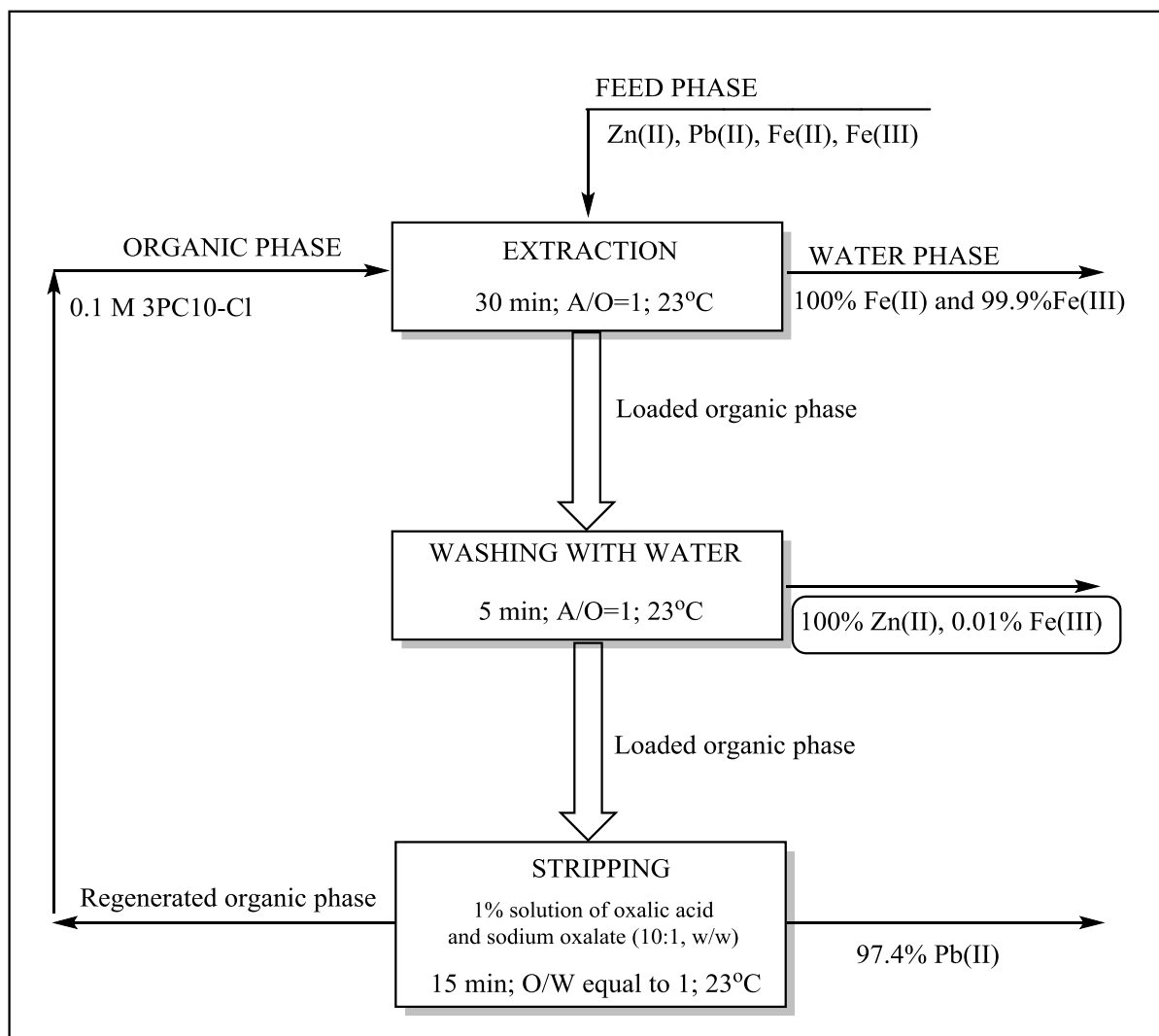


Figure 3. Flow-sheet for recovery of Zn(II) from Zn(II)-Pb(II)-Fe(II)-Fe(III) chloride solution using 3PC10-Cl

#### 4. Conclusion

The obtained results showed that, regardless on the extractant structure, the increase of the chloride concentration increased the extraction of Zn(II). However, at the studied conditions better extraction properties towards zinc(II) demonstrated E3PC1 and its quaternary salts. The extraction and stripping processes kinetic of Zn, Pb and Fe were fast. The stripping process was also proposed as a method enabling the separation of the Zn(II) from the solution containing both Zn-Pb-Fe. Moreover, regardless of the stripping phase composition, the regenerated organic phase can be used frequently without affecting the extraction ability.

#### Acknowledgement

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