

Hydrometallurgical Recovery of Tin from Waste-Printed Circuit Boards[†]

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Abstract: This study presents a hydrometallurgical process for the leaching and recovery of tin from waste-printed circuit boards (wPCBs). The process aims to separate and recover tin from filter dust produced during the crushing of wPCBs in a recycling facility. The separation of the metallic and non-metallic fractions was carried out by gravimetric separation. The metallic fraction consisted mainly of Cu (23.8%), Fe (17.8%), Sn (12.7%), Pb (6.3%), and Zn (3.4%). During the leaching tests, the effects of (a) HCl concentration (2, 4, 6 M), (b) pulp density (0.1, 0.2, 0.3 g/mL), and (c) the addition of NaCl (no addition, 1 M, 3 M) were investigated. All tests were conducted at an ambient temperature without agitation. A leaching efficiency of 78.2% was obtained during leaching with 6 M HCl and 0.3 g/mL pulp density, while 94.8% of tin was leached under the same conditions with the addition of 3 M NaCl. Tin was recovered from the pregnant solution by addition of 2 M NaOH at pH = 3.0, with an efficiency of 97.4%. The precipitate, despite being amorphous, was easily filtered and it consisted of 64.7% Sn and less than 2% of impurities. The proposed process consists of a leaching stage with 6 M HCl, 3 M NaCl, 0.3 g/mL pulp density, and a contact time of 24 h, and a recovery stage by chemical precipitation at pH = 3.0. The total tin recovery of the suggested process was 92.3%.

Keywords: tin; recovery; hydrometallurgy; PCBs; leaching; chemical precipitation



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1. Introduction

The demand for raw materials in the electronics industry is increasing. Meanwhile, the available ores are reaching depletion, and the traditional mining industry struggles to cope with the demands [1,2].

The high electronics consumption leads to an increase in the waste from electrical and electronic equipment (WEEE). WEEE contain various raw materials that could possibly be recovered when managed properly. An important part of WEEE are the printed circuit boards (PCBs). PCBs account for the 4–7% of WEEE and are rich in base and precious metals, while they also contain plastic parts and ceramics. Due to their high metal content, waste PCBs are a valuable source of raw materials and need to be recycled [2–4].

The recycling of electronic scrap, industrially, is based mainly on physical and pyrometallurgical methods. Although pyrometallurgy provides high metal recoveries and is an established technology, the high energy demand and environmental restrictions make it unsustainable [4]. On the other hand, hydrometallurgical methods are not energy-intensive and do not produce gaseous emissions, thus they are considered more sustainable compared to the pyrometallurgical ones [4,5]. The main interest in PCBs recycling concerns precious metals and copper content; however, other metals, such as tin, are contained in high concentrations as well [5,6]. In 2022, the global tin market exceeded 395,000 tn, with half of this amount used by the electronics industry for PCB soldering. Tin content in waste PCBs can exceed 5%, while in natural ores it is less than 0.9%. Due to high demand, the tin

price has increased in the last decade. According to the London Metal Exchange, metal tin prices for 24k \$/tn, which is three times that of copper.

This study, part of the HYDROPCB project (Development of a hydrometallurgical process for metal recovery from printed circuit boards in pilot scheme: A zero waste process) presents the results obtained in an effort to selectively recover tin from filter dust, produced during the crushing of PCBs in a hammer mill at a local recycling facility.

2. Materials and Methods

In the present research, a dust sample was provided by a local recycling facility.

2.1. Solid Characterization

The determination of the metal content in the dust and the solid products was performed via flame atomic absorption spectrometry (AAS) after digestion at 100 °C and dissolution. The content of the non-metallic fraction was estimated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The leach solutions were analyzed by flame AAS, and the solids were characterized by X-ray diffraction analysis (XRD) and scanning electron microscopy (SEM). The separation of the metallic from the non-metallic fraction was carried out on a shaking table.

2.2. Leaching of Tin

The metallic fraction was leached in HCl solution at room temperature and without agitation. The effect of the main process factors on tin recovery was investigated. The factors studied were the S/L ratio (0.1, 0.2, and 0.3 g/mL), the leaching agent concentration (2, 4, and 6 M), and the addition or omission of NaCl (1 M and 3 M). The contact time was 24 h.

2.3. Chemical Precipitation of Tin

The pregnant leach solution produced under conditions of a 0.3 g/mL S/L ratio, 6 M HCl, and 3 M NaCl was diluted in water by 1.2 times and the solution was used to study the chemical precipitation of tin. The factor investigated was pH value. At the optimum pH, the resulting precipitate was analyzed by WD-XRF.

3. Results

3.1. Solid Characterization

The chemical composition of the PCB dust and the metallic fraction after the physical separation in the shaking table are presented in Table 1. The non-metallic fraction percentage in the initial dust was 30% *w/w*.

Table 1. Chemical composition of the dust before and after metal fraction separation.

Metal	Initial Dust (% wt.)	Metallic Fraction after Separation (%wt.)
Sn	5.01	12.74
Cu	5.19	23.86
Fe	8.17	17.84
Zn	1.90	3.36
Ni	0.76	1.48
Pb	1.53	6.28
Al	3.18	3.29

3.2. Leaching of Tin

The effect of the leaching agent's concentration and pulp density on tin recovery is given in Figure 1.

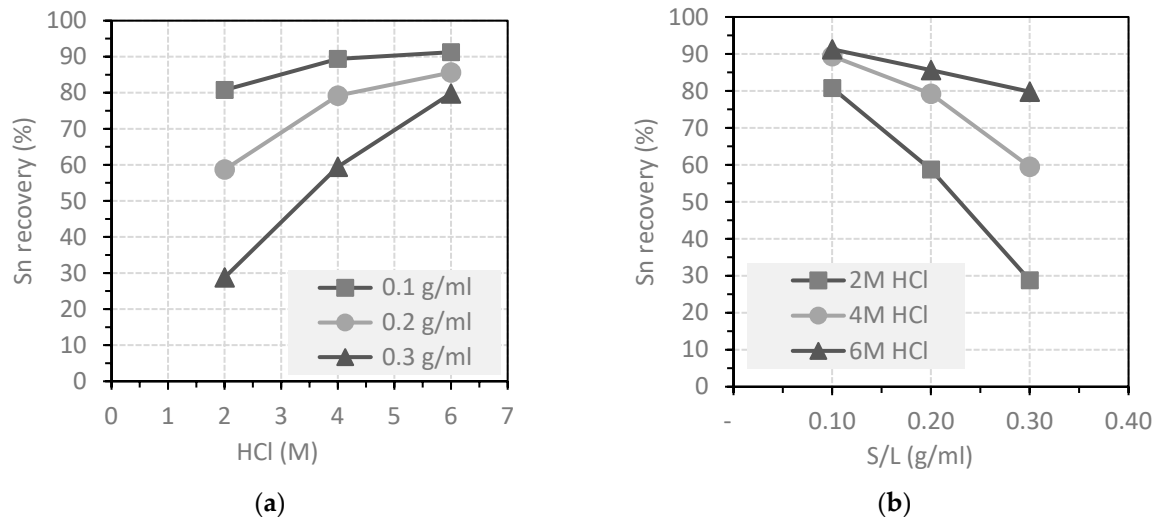


Figure 1. (a) Effect of HCl concentration on tin recovery; (b) Effect of pulp density on tin recovery.

The highest tin recovery was obtained by leaching in 6 M HCl solution. Tin salts form soluble and highly stable complexes in the presence of chloride ions. Thus, an increase in HCl concentration leads to higher tin recovery. Furthermore, the effect of the chloride ion concentration in the leachate was investigated by the addition of NaCl. The results are presented in Figure 2.

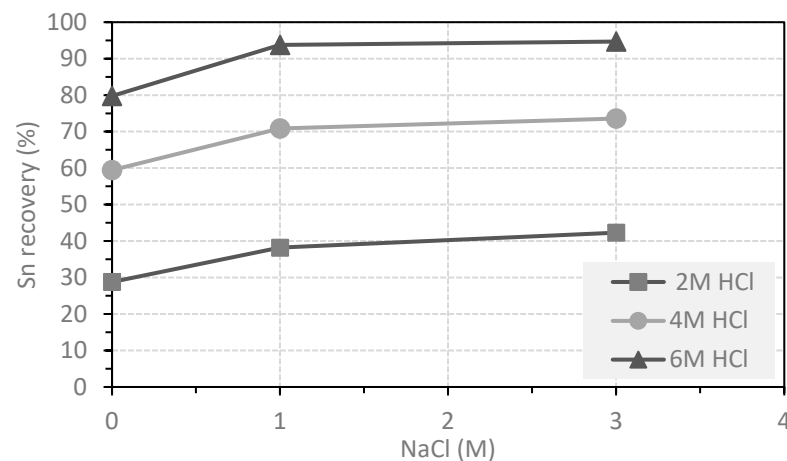


Figure 2. Effect of NaCl concentration on tin recovery for S/L = 0.3 g/mL.

Based on the experimental results and preliminary tests, the values of the factors for maximum tin recovery were determined as follows:

- 6 M HCl concentration in the leaching solution;
- 3 M NaCl concentration in the leaching solution;
- S/L ratio of 0.3 g/mL;
- Residence time of 24 h;
- Room temperature;
- No agitation.

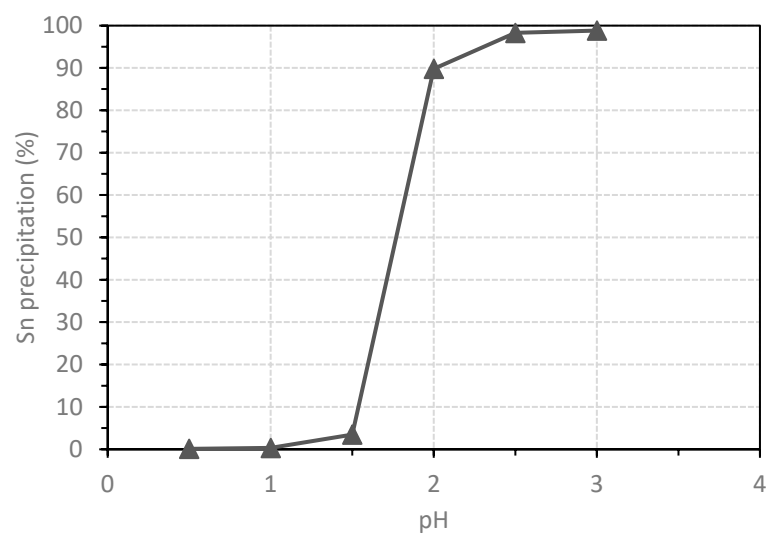
The choice of room temperature and the absence of agitation was justified to ensure low energy consumption. The chemical analysis of the pregnant leach solution produced with a 0.3 g/mL S/L ratio, 6 M HCl, and 3 M NaCl is shown in Table 2.

Table 2. Chemical analysis of the pregnant solution.

Metal	Concentration (g/L)
Sn	8.93
Cu	0.11
Fe	3.44
Zn	0.92
Ni	0.10

3.3. Chemical Precipitation of Tin

The effect of pH on tin precipitation from the pregnant solution was experimentally tested. The precipitation occurred by the addition of 5 M NaOH solution, 300 rpm agitation, and 4 h precipitation time. The results are presented in Figure 3.

**Figure 3.** Effect of pH on tin precipitation.

The hydrolysis of tin starts at pH = 1.5, and the precipitation is completed at equilibrium pH = 3.0. Table 3 shows the solution's chemical analysis before and after the tin precipitation at pH = 3.0.

Table 3. Chemical analysis of the solution before and after tin precipitation at pH = 3.0.

Metal	Concentration (g/L)	
	Before Precipitation	After Precipitation at pH = 3.0
Sn	7.44	0.09
Cu	0.09	0.05
Fe	2.87	2.53
Zn	0.77	0.63
Ni	0.08	0.08

The precipitate resulting at this pH was characterized by WD-XRF and the results are presented in Table 4. The precipitate was amorphous according to the results obtained by XRD.

Table 4. Chemical composition of the tin precipitate at pH = 3.0.

Metal	Precipitate (% wt.)
Sn	60.25
Cu	0.65
Fe	6.28
Zn	2.73
Ni	0.09

4. Conclusions

The results of the present study led to the following conclusions:
More than 80% of tin can be leached in 6 M HCl for a S/L ratio of 0.3 g/mL.

- The addition of NaCl in the leaching solution increases tin recovery to 95%.
- An increase in the S/L value reduces the tin dissolution efficiency.
- More than 95% of tin was precipitated from the pregnant solution at pH = 3.0.
- Tin content in the resulting precipitate exceeds 60% wt.
- Metal impurities in the precipitate did not exceed 10% wt.

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