M. LISIŃSKA, B. GAJDA, M. SATERNUS, S. BROZOVÁ,
T. WOJTAL, M. RZELEWSKA-PIEKUT

ISSN 0543-5846
METABK 61(3-4) 609-612 (2022)
UDC – UDK 669.011:661.13.002.68:541.135:661.73:621.7:338.004.6=111

# THE EFFECT OF ORGANIC ACIDS AS LEACHING AGENTS FOR HYDROMETALLURGICAL RECOVERY OF METALS FROM PCBs

Received – Primljeno: 2021-12-02
Accepted – Prihvaćeno: 2022-03-10
Original Scientific Paper – Izvorni znanstveni rad

The hydrometallurgical treatment, compared to other recycling processes, is of great interest due to its higher efficiency and better economy. In hydrometallurgy, popular agents used in the leaching processes of e-waste include inorganic acids, ammonia, chlorides, thiourea, thiosulphates. Organic acids are also becoming more and more popular. The article presents an overview of possible paths of the metal recovery from e-waste with the use of various organic acids. The results of own research on the leaching of printed circuit boards with the use of organic acids including citric acid, oxalic acid, acetic acid, formic acid, malic acid, lactic acid are also presented.

*Key words:* hydrometallurgy, e-waste, leaching, organic acid, metals recovery

## INTRODUCTION

Continuous technological progress has been observed for a long time, resulting in a con-stantly growing number of e-waste. Discarded printed circuit boards (PCBs) that are part of most electronic devices, incl. mobile phones and computers contain many metals, in particular large amounts of copper [1]. Taking into account the growing demand for technological devices in industrialized and developing countries, the priority is the real need to recycle metals instead of extracting them from ores [2]. Therefore, new and effective ways of treating this waste and the re-use of recovered metals are increasingly being sought. The interest in the hydrometallurgical treatment of waste electronic equipment has increased in recent years due to its advantages [3]. Leaching electronic waste does not require the use of complicated and expensive devices. The main problem of hydrometallurgical processes is the high consumption of chemicals that require further management [4]. Therefore, in recent years, research into the recovery of valuable metals from waste has also focused on the use of more environmentally friendly leaching liquids, namely organic acids.

Organic acids are considered to be leaching media that do not pollute the environment; they are ecological and efficient, and can be used for the selective leaching of metals [5-6]. Organic acids are biodegradable and the waste generated in the leaching stage is easy to handle [6-7]. Although some organic acids are more expensive than inorganic acids, their use is still cost effective [8]. Organic acids are used to recover metals from electronic waste, but research in this area is in the initial phase of experiments and the number of publications is limited.

Possible mechanisms of metal dissolution are presented in works [9-10]. Organic acids dissolve metals by supplying protons and ligands. They can dissolve the metallic fractions of e-wastes by acidification and complexation. Organic acid dissociates to donate $H^+$ for proton-promoted dissolution process [9-10].

$$RCOOH + H_2O \rightleftharpoons RCOO^- + H_3O^+ \quad (1)$$

The reduction of protons generates hydrogen (Reaction 2) and oxidizes the metal (Reaction 3) [9-10]:

$$2H_3O^+ + 2e^- \rightarrow H_2 + 2H_2O \quad (2)$$

$$M \rightarrow M^{2+} + 2e^- \quad (3)$$

In a complexation mechanism, the ligands from organic acids, for example citrate (Cit) from citric acid, forms stable complexes with metals present in PCBs powder. The complexation reaction can increase the solubility of metals in solution [9-10]:

$$nRCOO^- + M + nH_3O^+ \rightarrow$$
$$(RCOO)_n M + nH_2O + \frac{n}{2} H_2 \quad (4)$$

where: M - metal; R - organic substituent group.

This article presents an overview of research on the recovery of metals from used printed circuit boards with the use of organic acids and own research.

M. Lisińska, M. Saternus, T. Wojtal: Silesian University of Technology, Faculty of Material Science, Katowice, Poland
B. Gajda: Czestochowa University of Technology, Czestochowa, Poland
S. Brožová: VSB - Technical University of Ostrava, Ostrava, Czech Republic
M. Rzelewska-Piekut: Poznan University of Technology, Institute of Chemical Technology and Engineering, Poznan, Poland
Corresponding author: magdalena.lisinska@polsl.pl.

## REVIEW OF RESEARCH USING ORGANIC ACIDS

The following organic acids were used to recovery metals from PCBs and other electronic waste: citric acid ($C_6H_8O_7$) [9-14], oxalic acid ($C_2H_2O_4$) [9, 12-13], gluconic acid ($C_6H_{12}O_7$) [13], malic acid ($C_4H_6O_5$) [9], lactic acid ($C_3H_6O_3$) [9]. In order to increase the leaching efficiency, an additional oxidant was also used: $H_2O_2$ [9,14].

Das et al. [13] described the leaching of PCBs from cell phones using inorganic acids, organic acids and bases to select the best leaching agent for each metal present in PCBs. The paper also presents the use of gluconic acid. For organic acid leaching ($C_2H_2O_4$, $C_6H_{12}O_7$ and $C_6H_8O_7$), the PCBs sample and the leaching agent are mixed with a stirrer at 80 °C for 4-5 h. Among all the tested organic acids, it was observed that $C_6H_8O_7$ has a greater ability to extract Pb (1,01 %), Ni (0,73 %), Cu (1,66 %) and Zn (0,28 %). $C_2H_2O_4$ has the highest ability to extract Fe (0,31 %).

Saidan et al. [9] presented the results of PCBs leaching, where organic acids were used - $C_6H_8O_7$, $C_4H_6O_5$, $C_3H_6O_3$, $C_2H_2O_4$ and inorganic acid - $H_2SO_4$. Leaching attempts in this study focused on dissolving metallic copper. A sample with a diameter of 0,35 to 0,72 mm was tested and it contained 34 % Cu, 1,3 % Sn, 0,75 % Pb, 5,2 % Al and 2,8 % Fe. The experiments were carried out at a temp. of 70 to 90 °C for 360 min. After 6 h of leaching at 90 °C, pH = 2, a copper yield of 16,5 % in citric acid, 11 % in malic acid, 4,5 % in oxalic acid, 12 % in lactic acid and 3 % in sulfuric acid was achieved. By extending the leaching time to 33 h, pH = 1,7, a copper yield of 94 % in citric acid was achieved.

Jadhav et al. [10] showed that the combination of organic acid and $H_2O_2$ was as effective in the leaching of PCBs as the use of inorganic acids. The research material in this work were pieces of PCBs from used computers, with dimensions of 4 x 4 cm. $C_6H_8O_7$ with a concentration of 0,5-2 M was used as the leaching liquid, as well as an additional oxidant - $H_2O_2$ with a concentration of 1,45-7,28 %. The experiments were carried out at temp. 30 to 60 °C for 4 h, under static conditions or with agitation of 150 rpm. It has been found that the presence of both $C_6H_8O_7$ and $H_2O_2$ together is essential for the leaching of metals. This work presents the mechanism of metal dissolution with the use of organic acid and $H_2O_2$. Total recovery of metals (Cu, Zn, Sn, Ni, Pb, Fe, Al, Ag, Pd, Au) was achieved by leaching one piece of PCBs in 100 ml of 1 M citric acid and 5,83 % $H_2O_2$ at 30 °C, within 4 h, under static conditions. The use of large pieces of PCBs simplified the metal leaching process compared to using a finer fraction of this material.

Jadhav et al. [14] developed a two-stage PCBs bioleaching process using *Aspergillus niger*. The research material was ground into a fine fraction of 0,299 mm. The PCBs powder was also pre-treated with sodium hydroxide. In the first stage of the research, *Aspergillus niger* fungi were grown to produce organic acid. After 10 days, *Aspergillus niger* had produced citric acid. In the second step, the culture supernatant without fungal cells was harvested and used for the metal leaching process. This helps to avoid fungal toxicity and increase the efficiency of the metal leaching process. The beaker was incubated in a static incubator at temp. 30 °C. The leach efficiency was increased by adding $H_2O_2$ to (0,10 M) $C_6H_8O_7$. The best results were obtained with 3,18 % $H_2O_2$. This resulted in a reduction in the process time from 24 to 2 h with an increase in temp. from 30 to 80 $^oC$ and total leaching of all metals (Cu, Mg, Ti, Mn, Zn, Sn, Ni, As, Sr, Cd, Co, Ag, Al, Si , Pb, Fe, Pd, Au).

Kolenčík M. et al. [12] evaluated the effectiveness of a one-stage e-waste bioleaching process with the use of *Aspergillus niger* and leaching with oxalic acid and citric acid. The e-waste used in this study consisted of powdered parts from desktops and mobile phones. Prior to (bio)leaching, the e-waste sample was sterilized in a hot air oven at 60 °C for 24 h. The bioleaching performance was compared to a 42 day leach with 0,05 M $C_2H_2O_4$ and 0,05 M $C_6H_8O_7$ at a solid solution ratio of 0,3 g/80ml, performed under the same conditions as the bioleaching experiment. The best metal leaching efficiency was achieved using 0,05 M $C_6H_8O_7$ which leached about 67,4 % Cu, 91,4 % Pb, 70,8 % Cd and 92 % Zn from e-waste. Similar results were obtained in [11], where citric acid was also used. While the efficiency of leaching Cu from e-waste was comparable to that of fungus, the chemical leaching of Pb, Zn and Cd was significantly higher with the use of 0,05 M $C_6H_8O_7$. However, the acid extraction using 0,05 M $C_2H_2O_4$ was much lower. $C_2H_2O_4$ was able to leach only 1,8 % Zn, 38,9 % Cd, 7,4 % Pb and 13,3 % Cu.

Wiecka et al. [15] used organic acid as a leaching agents in the first step of leaching of spent automotive converters in order to reduces the amount of non-precious metals (Fe ions, Mg(II), Zn(II)) leached in the second stage. For platinum group metals (PGM) leaching, it is necessary to use more stringent leach solutions.

## EXPERIMANTAL METHODOLOGY

Printed circuit boards from used cell phones were used as research material. They were dismantled manu-

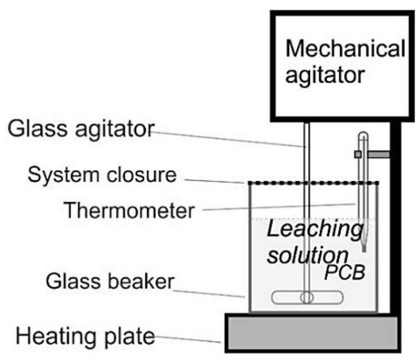


**Figure 1** Scheme of leaching stand

ally, individual elements of the phone were separated from the PCBs. The plates were then cut into smaller pieces and ground in a Retsch SK100 hammer mill to obtain a fine fraction (4-0,045 mm). Figure 1 presents the test stand. The conducted research is shown in the Figure 2.

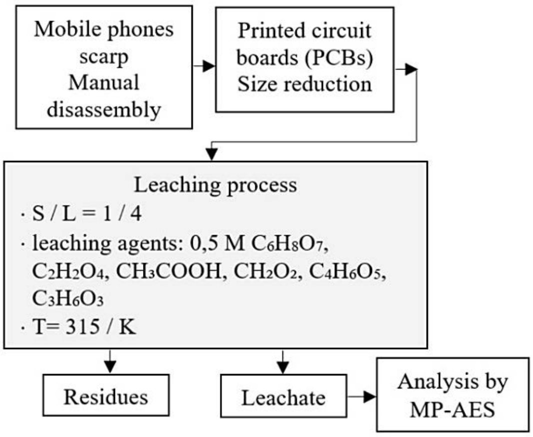


**Figure 2** Scheme of the conducted research with organic acids

The material prepared in this way was subjected to leaching in 0,5 M organic acids - $C_6H_8O_7$, $C_2H_2O_4$, $CH_3COOH$, $CH_2O_2$, $C_4H_6O_5$, $C_3H_6O_3$. Tests were carried out for a constant ratio of solids to liquids (S / L = 1 / 4), at ambient temperature (315 K). The trend was monitored for 4 h. The metal content (Cu, Zn, Sn, Al) was determined by microwave plasma atomic emission spectroscopy (Agilent MP-AES 4200).

## RESULTS OF RESEARCH

The results showed poor leaching of the copper with all the acids used. Therefore, the results are not shown in the chart. The highest obtained result was 0,04 % (0,03 g/dm$^3$) for Cu with the use of malic acid after 4 h of the experiment. Better results were obtained for Sn, which is shown in Figure 3. Citric acid turned out to be the best. When using citric acid, 26 % (1,16 g/dm$^3$) of tin was obtained after 3 h of the experiment and 23 % (1,32 g/dm$^3$) after 4 h of the experiment. It is hard to explain the slight decrease of 3 %. A slightly lower result of 17 % (0,81 g/dm$^3$) was obtained after 4 h with malic acid. When oxalic acid is used, the leaching increases up to 2 h. After 2 h of the experiment, the result was 18 % (0,68 g/dm$^3$), in the following hours a slight decrease was observed. After 4 h of the experiment, 13 % (0,65 g/dm$^3$) of tin was obtained. For malic acid and lactic acid, the longer the leaching time, the greater the degree of Sn leaching. For acetic acid and formic acid, results were below 1 % tin, which are not shown in the graph.

The effect of time on Zn leaching is observed. An increase in Zn leaching is observed after 0,5 h. The highest results, over 0,1 g/dm$^3$, were obtained with cit-

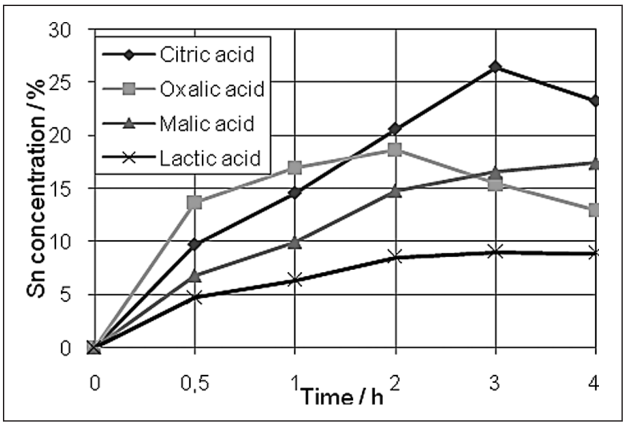


**Figure 3** Tin concentration obtained after leaching of PCBs waste in organic acid solution during 4 hour

ric acid, acetic acid, formic acid and lactic acid, where the leaching degree was 9,64 %, 10,43 %, respectively, 10,90 %, 11,42 %. The results for Zn are shown in Figure 4. Most of the experiments and the acids used showed a decrease in Zn leaching after 2 h. Only in the case of malic acid a slight decrease occurs only after 3 h. It is difficult to explain this situation. Using oxalic acid, no more than 2 % Zn was obtained during the entire experiment.

After one hour of experiment, a sudden increase in Al leaching is observed in oxalic acid. The best result

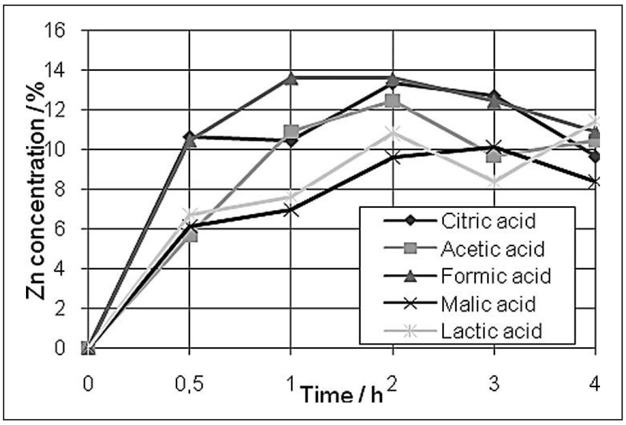


**Figure 4** Zinc concentration obtained after leaching of PCB waste in organic acid solution during 4 hour

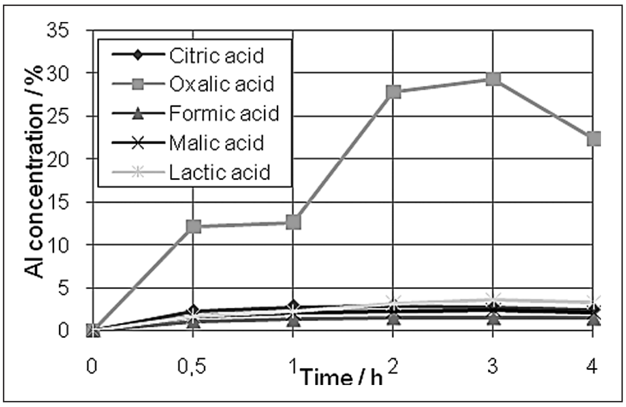


**Figure 5** Aluminium concentration obtained after leaching of PCBs waste in organic acid solution during 4 hour

after 4 h of the experiment for Al was 22 % (2,24 g/dm$^3$) with this acid. When using other acids, the results for Al did not exceed 3 % (0,3 g/dm$^3$). The results for Al are shown in Figure 5.

## CONCLUSIONS

The positive results of using organic acids as a leaching agent in the recovery of metals from electronic waste reported in the literature suggest that organic acids can be substitutes for inorganic acids in hydrometallurgical processes. The recovery of metals from electronic waste using these acids is also still limited. In own research, organic acids were used to recover metals from printed circuit boards from used cell phones, but the acids themselves, without additional oxidants, showed poor leaching properties. The results showed that of the acids used, citric acid and malic acid are the best agents for the leaching of Sn (23 % and 17 %). Oxalic acid, up to 2 h of research, also had effect on tin leaching (18 %), but after 2 h there was a slight decrease (13 %). All acids (citric acid, acetic acid, formic acid and lactic acid), except oxalic acid, have little effect on Zn leaching (9,64 %, 10,43 %, 10,90 %, 11,42 %). In turn, this acid is the only one that has effect on Al leaching (22 %).

Further experiments with organic acids and additional oxidants (e.g. $H_2O_2$ or $O_3$) and other process parameters are needed to allow recovery of Cu and other metals.

## Acknowledgements:

This article was financed by Silesian University of Technology as a part of Statutory Research 11/020/BK_21/0080 and co-financed by the Ministry of Education and Science, Poland (grant No. 0912/SBAD/2110).

## REFERENCES

[1] M. Lisińska, M. Saternus, J. Willner. Research of leaching of the printed circuit boards coming from waste mobile phones, Arch. Metall. Mater. 63 (2018) 1, 143-147.

[2] L. Canda, T. Heput, E. Ardelean. Methods for recovering precious metals from industrial waste, IOP Conf. Series: Mat. Sci. and Eng. 106 (2016) 012020, 1-9.

[3] G. Chauhana, R.P. Jadhaob, K.K. Pantb, K.D.P. Nigamb. Novel technologies and conventional processes for recovery of metals from waste electrical and electronic equipment: Challenges & opportunities – A review, J. Environ. Chem. Eng. 6 (2018), 1288-1304.

[4] M. Kaya. Recovery of metals and non-metals from electronic waste by physical and chemical recycling processes, Waste Manag. 57 (2016), 64-90.

[5] X. Chen, C. Luo, J. Zhang, J. Kong, T. Zhou. Sustainable recovery of metals from spent lithium-ion batteries: a green process, ACS Sustain. Chem. Eng. 3 (2015), 3104-3113.

[6] R. Golmohammadzadeha, F. Farajia, F. Rashchia. Recovery of lithium and cobalt from spent lithium ion batteries (LIBs) using organic acids as leaching reagents: A review, Resour. Conserv. Recycl. 136 (2018), 418-435.

[7] L.P. He, S. Sun, Y.Y. Mu, X. Song, J. Yu. Recovery of lithium, nickel, cobalt, and manganese from spent lithium-ion batteries using L-tartaric acid as a leachant, ACS Sustain. Chem. & Eng. 5 (2017), 714-721.

[8] L. Rocchetti, F. Vegliò, B. Kopacek, F. Beolchini. Environmental impact assessment of hydrometallurgical processes for metal recovery from WEEE residues using a portable prototype plant, Environ. Sci. Technol. 47 (2013), 1581-1588.

[9] M. Saidan, B. Brown, M. Valix. Leaching of Electronic Waste Using Biometabolised Acids, Chin. J. of Chem. Eng. 20 (2012) 3, 530-534.

[10] U. Jadhav, C. Sua, H. Hocheng. Leaching of metals from large pieces of printed circuit boards using citric acid and hydrogen peroxide, Environ Sci. Pollut. Res. 23 (2016), 24384-24392.

[11] F.R. Xiu, F.S. Zhang. Electrokinetic recovery of Cd, Cr, As, Ni, Zn and Mn from waste printed circuit boards: Effect of assisting agents. J. Hazard. Mater. 170 (2009), 191-196.

[12] M. Kolenčík, M. Urík, S. Čerňanský, M. Molnárová, P. Matúš. Leaching of zinc, cadmium, lead and copper from electronic scrap using organic acids and the *Aspergillus niger* strain, Fresenius Environmental Bulletin 22 (2013) 12, 3673-3679.

[13] D. Das, S. Mukherjee, M.G. Chaudhuri. Studies on leaching characteristics of electronic waste for metal recovery using inorganic and organic acids and base, Waste Manag. Res, 20 (2020) 10, 1-8.

[14] U. Jadhav, C. Sua, H. Hocheng. Leaching of metals from printed circuit board powder by an *Aspergillus niger* culture supernatant and hydrogen peroxide, RSC Adv. 6 (2016), 43442-43452.

[15] Z. Wiecka, M. Rzelewska-Piekut, M. Regel-Rosocka. Recovery of platinum group metals from spent automotive converters by leaching with organic and inorganic acids and extraction with quaternary phosphonium salts, Sep. Purif. Technol. 280 (2022) 119933.

**Note:** The responsible for English language is Franciszek Krolak