Comparison of the Effectiveness of Biological and Chemical Leaching of Copper, Nickel and Zinc from Circuit Boards

Dorota Anna Andrzejewska-Górecka*, Agnieszka Poniatowska, Bartłomiej Macherzyński, Dominik Wojewódka, Małgorzata Edyta Wszelaka-Rylik

1 Cardinal Stefan Wyszynski University in Warsaw, Faculty of Biology and Environmental Science, Department of Environmental Biotechnology and Bio-economy, ul. Wóycickiego 1/3, 01-938 Warsaw, Poland
* Corresponding author’s e-mail: d.andrzejewska@uksw.edu.pl

ABSTRACT
The progress of civilization brings with it the development of advanced technologies and increased demand for electric and electronic equipment. That directly influences the increase of produced e-waste, called Waste of Electrical and Electronic Equipment (WEEE). Due to the fact that deficit and critical metals are running out throughout the World, and due to increased demand for those metals, their alternative source and recovery methods have to be found. As an alternative biotechnological methods can be used. The advantage of biological methods over chemical processes is its selectivity in regard to different metal groups, simplicity of technological process, economic effectiveness (lower energy expenditure) and lack of negative impact on environment. The aim of this work was to compare the effectiveness of biological and chemical leaching of copper (Cu), nickel (Ni) and zinc (Zn) from circuit boards (PCBs). The experiment was conducted in variants which included factors such as temperature (24°C and 37°C) and speed of mixing. In case of all metals higher effectiveness was achieved in variants conducted in the temperature of 24°C and faster mixing than in temperature of 37°C and slower mixing. In case of cooper and zinc better results of metal removal were achieved in bioleaching variant. In case of nickel faster result of metal removal were achieved in chemical leaching, but at the end of the experiment the effectiveness of chemical leaching and biological leaching was similar. The maximum efficiency of cooper, nickel and zinc release was adequately 100%, 90%, 65%.

Keywords: bioleaching, chemical leaching, e-wastes, PCBs, heavy metals

INTRODUCTION
The progress of civilization brings about the development of advanced technologies and increased demand for electric and electronic equipment. That directly influences the increase of the produced e-waste, called Waste of Electrical and Electronic Equipment (WEEE). It is estimated that currently 48% of households have a computer. Worldwide, 44.7 million tons of electronic waste was produced in 2016. The greatest amount of electronic waste was produced in Asia (18.2 million tons), followed by Europe (12.3 million tons), then both Americas (11.3 million tons), Africa (2.2 million tons) and Oceania (0.7 million tons). It is predicted that this amount will rise to 52.2 million tons until 2021, with a yearly gain of 3 to 4% [2,7]. WEEE is one of the fastest growing waste streams worldwide and it is estimated that it currently constitutes around 8% of municipal waste stream [7,20]. Unfortunately, in 2016 only 20% of the produced WEEE was collected and recycled. About 80% of the e-waste is not covered by statistics and only 41 countries are collecting this data. At present, Europe recycles 35% of its WEEE which is the greatest amount in the world. Both Americas collect only 17% of produced e-waste, Asia – 15%, and Africa has documented less than 1% of collected and recycled WEEE [2]. An unfavorable tendency to export the e-waste from wealthy countries to developing regions has existed for years now, frequently under the pretext of helping the poorest regions of the world. In those countries, recycling precious metals is carried out using amateur methods without using any technology, frequently without care for the
environment and health of the people [10,19,20]. Currently, there is no unambiguous data on the amount of used electronics sent from wealthy countries to the poor ones. What is positive is the fact that there is an increase in the populace covered with legislation concerning e-waste. In 2016, it was 66% of world population (67 countries), while in 2014 it was 44%. Legislation does not always translate to specific actions and law enforcement [2]. E-wastes contain iron, aluminum, plastics and precious metals, including gold, silver, copper, platinum and palladium. Moreover, it can be the source of rare earth elements and hazardous materials such as heavy metals (mercury, lead, cadmium etc.) and chemicals [2,7,20].

PCB plates, which amount to around 3–5% of WEEE, are the most precious part of e-wastes. The PCB wastes are a heterogeneous mixture of metals, non-metals and toxic substances. They consist of many electronic elements such as resistors, conductors, capacitors and integrated circuits. PCBs contain almost 30% of metals. The preciousness of precious metals in PCBs is more than 10 times higher than that of those coming from mineral sources [8,9,10]. Because of the parts, components and materials that are included in the WEEE, the metals can be a subject of trade on the market of secondary raw materials [17].

Due to the fact that deficit and critical metals are running out throughout the world, and due to the increased demand for those metals, their alternative source has to be found. WEEE recycling conducted in a proper way may be a renewable source of those metals which are contained in the e-waste and called an “urban mine” [13,16,17]. Moreover, the recovery of recyclable materials is less energy-intensive, causes less emission to the environment and is cheaper than production from the primary sources [7,10]. In 2016, an estimated value of all the raw materials present worldwide in the e-waste amounted to around 55 billion euro [2,7]. Because of that the materials which are contained in the used electronics have to be used as much as it can. Introduction of circular economy model throughout the world in which e-waste is considered as resource can help. In the circular economy, there is an increase in the use of the waste-derived resources by improved design the products, recycling, reusing and other means which decrease the pollution [2,7,13].

The traditional techniques of electronic waste recycling, pyrometallurgical as well as hydrometallurgical, frequently require large amounts of energy, are costly, not very efficient and cause significant secondary pollution [10,21]. The biotechnological methods can be used as an alternative. In the course of the last few years, there was a lot of research done on the bioleaching of metals from the wastes. Bioleaching is a process which involves the microorganisms producing organic acids, complexing compounds as well as the bacteria oxidizing the sulfur compounds and creating sulfuric acid. Currently, bioleaching is used not only to recover metals from ores, but also from other sources, such as electronic waste, including PCB [4,11,15]. The advantage of biological methods over chemical processes is its selectivity in regard to different metal groups, simplicity of technological process, economic effectivity (lower energy expenditure) and lack of negative impact on environment [7,12,21]. Currently, the need to continue the research in WEEE bioprocessing is emphasized around the world. This is due to the fact that not all metal leaching mechanisms are fully understood [7].

The aim of this work was to compare the effectiveness of biological and chemical leaching of copper (Cu), nickel (Ni) and zinc (Zn) from circuit boards. The experiment was conducted in variants which included such factors as temperature and speed of mixing. The biological and chemical leaching media contended adequately 1% of sulfate and 1% of sulfuric acid.

MATERIALS AND METHODS

Waste characteristics

Printed circuit boards were used in the research. They were obtained in crumbled (fine) form. The grain fractions were as follows: d < 0.063 mm – 3.1%, 0.063 mm – 1.7%, 0.01 mm – 21.0%, 0.25 mm – 22.4%, 0.5 mm – 3.9%, 1 mm – 10.2%, 2 mm – 37.7%. Metal content in the waste was as follows: Cu – 8870 mg/kg, Ni – 1921 mg/kg, Zn – 1074 mg/kg.

Leaching media

Two types of leaching media were used in the research:

- Bioleaching culture prepared on the basis of the activated sludge coming from a municipal waste disposal facility. The activated sludge was a source of active autotrophic and heterotrophic bacterial strains. The culture consisted of activated sludge and distilled water in 1:1 ratio.
and 1% of dusty sulfur. The process of leaching culture’s adaptation was conducted under the conditions of shaking (120 rpm) and temperature of 24°C in order to achieve pH below 2 and sulfate concentration on the level of 1%.

- Chemical leaching media was 1% sulfuric acid.

### Experimental procedure

Metal leaching from the waste was conducted in 300 ml Erlenmeyer flasks containing 150 ml of leaching media or 1% sulfuric acid and 10 g of waste. The research was conducted in 5 variants. Variant 5 was the control variant consisting of the waste samples in distilled water. The leaching process variants and control variant are shown in Table 1.

### Control analyses

The process lasted for 9 days. After 3, 6 and 9 days, following markings were made:

- Metals content – measurements were conducted using a Shimazu ICPE-9820 plasma spectrometer
- Sulfate concentration – in accordance with the PN-ISO 9280:2002 standard
- pH – in accordance with the PN-90/C-04540/01 standard

At the end of the experiment, the following markings were made (only for bioleaching process):

- General number of bacteria – in accordance with the PN-EN ISO 6222 standard
- Index of sulfur oxidizing bacteria – done using the breeding method on a WR (water on rock) subgrade. The WR medium composition was: (NH₄)₂SO₄ (1.0g), K₂HPO₄ (0.5g), sulfur (10.0g), 1% bromocresol purple solution (0.5 cm³), 10% solution of yeast extract (few drops).

Determination of the elemental composition was performed by ICP-OES plasma spectrometry. It allows for marking several dozen of elements at the same time and is characterized by high sensitivity and precision. In order to mark the metals, the following reagents were used:

- nitric acid of 65% PURANAL purity made by Honeywell,
- deionized water of Mili-Q purity made by Merck,
- argon gas of 99.998% purity.

Working conditions of ICP-OES emission spectrometer are shown below:

- generator sensitivity – 27.12 MHz, generator’s power – 1.20 kW,
- total argon flow – 10.00 L/min.,
- support argon flow – 0.70 L/min.,
- secondary argon flow – 0.60 L/min.,
- exposure time – 30 sec,
- number of expositions – 3,
- duration of system washing – 30 sec,
- rotation of the peristaltic pump – 20–60 rotations/min.

### RESULTS AND DISCUSSION

The results of biological and chemical metal leaching from the printed boards samples are presented on Figures 1–3.

The effectivity of copper release was presented in Figure 1. On the third day of the experiment, the release of magnesium was the highest in the chemical leaching variant at a temperature of 24°C. The effectivity amounted to 60%. The release of metal in bioleaching variant in the same temperature was more than 20% lower. The effectiveness in the biological and chemical leaching variants at a temperature of 37°C was 20% and less than 15%, respectively. The release of metal in the control variant was below 1%.

On the sixth day, the effectiveness increased in all variants. The highest results were achieved in the biological and chemical variants at a temperature of 24°C, and amounted to less than 100% and

### Table 1. The leaching process variants

<table>
<thead>
<tr>
<th>Variants</th>
<th>Temperature, ºC</th>
<th>Speed of mixing, rpm</th>
<th>Type of leaching media</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>24</td>
<td>120</td>
<td>bioleaching culture</td>
</tr>
<tr>
<td>2</td>
<td>37</td>
<td>50</td>
<td>bioleaching culture</td>
</tr>
<tr>
<td>3</td>
<td>24</td>
<td>120</td>
<td>chemical leaching media</td>
</tr>
<tr>
<td>4</td>
<td>37</td>
<td>50</td>
<td>chemical leaching media</td>
</tr>
<tr>
<td>5</td>
<td>24</td>
<td>120</td>
<td>distilled water</td>
</tr>
</tbody>
</table>
90%, respectively. The effectiveness in the biological and chemical leaching variants at a temperature of 37°C was above 30%. The release of metal in the control variant reached 5%.

On the ninth day, the effectiveness decreased in biological and chemical variants at a temperature of 24°C. The effectiveness of both variants amounted to around 30%. The release of metal in the bioleaching variants at a temperature of 37°C increased, by about 10%. There was also 5% of decrease in the chemical leaching variant at the same temperature. The release of metal in the control variant was 10%.

Summing up, the best results were achieved in the biological and chemical leaching variants at a temperature of 24°C and faster mixing on the sixth day of the experiment.

The efficiency of nickel release was presented in Figure 2. On the third day of the experiment, the release of nickel was the highest in the chemical leaching variant at a temperature of 24°C. The effectiveness amounted to over 90%. Higher temperature did not contribute to better results. In the chemical leaching variant at a temperature of 37°C, less than 30% of metal release was achieved. The effectiveness of metal in bioleaching variant was 20% at a temperature of 24°C and 10% at a temperature of 37°C. The release of metal in the control variant was below 1%.

On the sixth day, the effectiveness increased in all variants. The highest results were achieved in the biological and chemical variants at a temperature of 24°C, and amounted to less than 70% and 90%, respectively. The effectiveness of biological and chemical leaching variants at a temperature of 37°C was below 30% and above 40%, respectively. The release of metal in the control variant was 1%.

On the ninth day, the effectiveness increased in the biological variants and decreased in the chemical variants. The efficiency in bioleaching variants amounted to more than 90% at a temperature of 24°C and more than 60% at a temperature of 37°C. The metal releases of the chemical variants were achieved at about 40%.

![Figure 1. Effectivity of copper release](image1.png)

![Figure 2. Effectivity of nickel release](image2.png)
The release of metal in the control variant was less than 5%.

Summing up, the best result was achieved in the chemical leaching variant at a temperature of 24°C and faster on third and sixth day as well as in the bioleaching variant at a temperature of 24°C and faster in ninth day. The effectiveness of metal release was similar and amounted to about 90%.

The effectiveness of zinc release was presented in Figure 3. On the third day of the experiment, the release of zinc was similar in three variants – bioleaching at a temperature of 24°C, chemical leaching at a temperature of 24°C and 37°C. The effectiveness amounted to about 20%. The effectiveness of metal in the bioleaching variant at a temperature of 37°C was 3%. In the control sample, the release of metal variant was less than 1%.

On the sixth day, the effectiveness increases in the bioleaching variant at a temperature of 24°C. The metal release achieved 55%. In the bioleaching variant at higher temperature, the effectiveness was 10%. The results of chemical leaching did not change so much. In the case of 24°C, the effectiveness increased by 5% and at a temperature of 37°C decreased also by 5%. In the control sample, the release of metal variant was less than 1%.

On the ninth day, also in the bioleaching variant, higher effectiveness was achieved. The metal release reached 65%. In the bioleaching variant at a higher temperature, the effectiveness was 19%. The effectiveness of the chemical leaching variant at a temperature of 24°C amounted to less than 40%. In the case of chemical leaching no change was observed at a higher temperature.

Summing up, the best result was achieved in the bioleaching variant at a temperature of 24°C and faster on the ninth day. The effectiveness of metal release amounted to about 65%.

The sulfate concentration and pH of the leaching solution were also marked. The sulfate concentrations in various variants of leaching media were shown in Figure 4.

The sulfate concentration in the bioleaching variant at a temperature of 24°C was the highest in the third day of experiment. In the next days, a slight decrease was marked. The sulfate concentration was on a level of 2000 mg/l. In the bioleaching variant, at a temperature of 37°C, the sulfate concentration was lower than at a temperature of 24°C. On the third day it was higher and slightly decreased in the following days. The sulfate concentration was on a level of 1200 mg/l. The sulfate concentration of the chemical variants was on a similar stage on the third day.

On the sixth day, the variant at a temperature of 24°C increased to almost 2500 mg/l but at a temperature of 37°C decreased to 1300 mg/l. On the ninth day, an increase was marked in both variants. The sulfate concentration at a temperature of 24°C and 37°C amounted to 2,000 mg/l and 500 mg/l, respectively. The changes of pH in all variants were presented in Figure 5.

The pH value in all variants corresponded with sulfate concentration. The pH was lower in the chemical leaching than in the bioleaching variants except for the ninth day. The pH in the chemical leaching at a temperature of 37°C and slower mixing as well as the biological leaching of 24°C and faster mixing was similar. The pH of the control sample was at a level of 7–8.5.

The research of the microorganism activity in the bioleaching variants consisted of general number of bacteria, index of sulfur oxidizing bacteria on the ninth day. General number of bacteria in leaching culture before adding the sample of waste was $4.2 \times 10^7$ CFU/cm$^3$. On the ninth day, it
was $1.8 \cdot 10^7$ CFU/cm$^3$ at lower temperature and $2.2 \cdot 10^6$ CFU/cm$^3$ at higher temperature. The initial index of sulfur oxidizing bacteria was $10^{-6}$. On the ninth day of bioleaching, it has risen to $10^{-7}$ in the variant with lower temperature and decreased to $10^{-4}$ in the variant with higher temperature. The general number of bacteria and the index of sulfur oxidizing bacteria are shown in Table 2.

Summing up, the research of the microorganism activity and sulfate concentration and pH measurement correspond to the effectiveness of metal removal in the bioleaching variants. In the variant with a lower temperature and faster mixing, the metal removal results were better than at higher temperature but slower mixing.

**CONCLUSIONS**

Due to the fast development of the digital technologies, the PCB producing technique has been widely improved [6]. Unsuitable PCBs become wastes. PCBs have a high heavy metals content, which would cause environmental pollution [18]. On the other hand, metals like copper, nickel and zinc can be recovered and used in various industry areas [5]. Moreover, the qualities of these metals are the same as the metals obtained in a traditional way. Bioleaching has been used for the recovery of precious metals and copper for years. However, very limited research was conducted on the bioleaching of metals from electronic waste [3]. There were a few publications concerning the bioleaching of metals from waste in 2019. Intan Nurul Rizki et al. conducted a research on bioleaching of gold from e-waste. The effectiveness of this process amounted to 98%. It is worth mentioning that the scientists used chemical leaching with a 1% sulfuric acid, in order to prepare the sample [14]. An interesting research
on the comparison between the biological and chemical leaching of copper was conducted by Muhammad Arinanda et al. Bioleaching solution consisted of the bacteria originating from the coal tailing storage facility, while for chemical leaching mixing deionized water with Fe\(_2\)(SO\(_4\))\(_3\)·7H\(_2\)O was used. The highest effectiveness of copper release were approximately 85% for bioleaching and 75% for chemical leaching [1]. The results of this work are similar to the newest research. The maximum effectiveness of cooper release in the biological and chemical leaching was less than 100% and 90%, respectively. High results were also achieved in the case of nickel release. The maximum effectiveness of nickel release in the biological and chemical leaching was around 90%. The highest effectiveness of zinc was more than 60% for the bioleaching variant and less than 30% in the chemical leaching variant. In this work, an attempt to find the answer whether the biological methods can be as effective as the chemical ones was made. This information can be useful for preparing the process in technical scale, because the biological and chemical leaching can exist together.

Table 3. Maximum amounts of leached metals in different variants in conversion to mg/kg

<table>
<thead>
<tr>
<th>Variants</th>
<th>Metals content [mg/kg of the waste]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu</td>
</tr>
<tr>
<td>24 °C, 120 rpm bioleaching</td>
<td>8760 (6)</td>
</tr>
<tr>
<td>37 °C, 50 rpm bioleaching</td>
<td>3612 (9)</td>
</tr>
<tr>
<td>24 °C, 120 rpm chemical leaching</td>
<td>7652 (6)</td>
</tr>
<tr>
<td>37 °C, 50 rpm chemical leaching</td>
<td>3149 (6)</td>
</tr>
</tbody>
</table>

The effectivity of chemical leaching at the same temperature was almost a 50% lower.

To sum up, the biological methods may be as effective as the chemical ones. In the near future it would be worthy to investigate the use of both methods to work out an effective and environment friendly process of metal recovery from e-waste.

On the basis of this research, one can formulate the following conclusions:

- The effectivity of metal release from waste depends on the metal. Various metals are characterized by different susceptibility to the biological and chemical leaching.
- The duration of the process depends on metal type and the type of leaching.
- In the case of all metals, higher effectiveness was achieved in the variants conducted at a temperature of 24°C and faster mixing than at a temperature of 37°C and slower mixing. The faster mixing has achieved better results than higher temperature.
- In the case of copper, better results of metal removal were achieved in the bioleaching variant than in the chemical leaching variant. The maximum effectiveness was almost 100%. This situation corresponded with the microorganism activity.
- In the case of nickel, faster metal removal was achieved in the chemical leaching, but at the end of the experiment, the effectivity of chemical leaching and biological leaching was similar. The maximum effectiveness was 90%. This situation corresponded with the sulfate concentration and pH measurement.
- In the case of zinc, better results of metal removal were achieved in the bioleaching variant than in the chemical leaching variant. The maximum effectiveness was 65%. This situation corresponded with the microorganism activity.
- The biological leaching in the same cases is characterized by greater effectiveness.
- The biological and chemical leaching can exist together, as a full scale technical process.
REFERENCES


