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Leaching Cu from e-waste PCB using thiourea solution and oxidizing H_2O_2

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ABSTRACT

Technological advances that occur in developed and developing countries impact increasing the amount of electronic waste (e-waste). In Indonesia, the growth rate of e-waste is predicted to increase by ±23.2% in 2028. The impact that e-waste can have on human health requires processing electronic waste such as printed circuit boards (PCBs) to reduce environmental pollution and economic benefits. PCB waste can be reprocessed because it contains Au, Ag, and Cu metals. The purpose of this study was to determine the effect of size, percent solids, the concentration of oxidizing agent H_2O_2, and the addition of oxidizing volume H_2O_2 to the amount of Cu extracted. The fire assay analysis results show that the mixed PCB waste contains 9.08% Cu. PCB waste leaching was carried out by agitation leaching method using thiourea solution. The leaching process was carried out with a size variation of 80; 100; 120#, a percent solids variation of 10; 15; 20 percent, an oxidizing concentration of H_2O_2 variation of 0.2; 0.4; 0.6 M, and the addition of an oxidizing volume H_2O_2 variation of 20; 28; 36 percent. Leaching was then performed for 6 hours at a rotation speed of 200 rpm, a temperature of 25°C, and a pH of 1-2. The leaching of mixed PCB waste resulted in 3.5% Cu in the leached solution with 10% solids percent and an additional 28% H_2O_2 oxidizing volume. PCB waste with the finest particle size of -120# and concentration of 0.4 M H_2O_2 produces Cu in the leached solution with 0.26%.

ABSTRAK

Kemajuan teknologi yang terjadi pada negara maju maupun negara berkembang berdampak pada meningkatnya jumlah limbah elektronik atau *e-waste*. Laju pertumbuhan limbah elektronik di Indonesia telah diperkirakan akan mengalami kenaikan sebesar ±23,2% pada tahun 2028. Dampak yang dapat ditimbulkan dari limbah elektronik dapat menyebabkan gangguan pada kesehatan manusia, sehingga diperlukan adanya pengolahan limbah elektronik seperti *printed circuit boards* (PCB) untuk mengurangi pencemaran lingkungan serta keuntungan secara ekonomi yang didapatkan. Limbah PCB berpotensi untuk diolah kembali dikarenakan memiliki kandungan logam seperti Au, Ag, Cu, Sn, dll. Tujuan dari penelitian ini adalah untuk mengetahui pengaruh ukuran, persen padatan, konsentrasi oksidator H_2O_2 dan penambahan volume oksidator H_2O_2 terhadap nilai persen ekstraksi Cu. Berdasarkan hasil analisis *fire assay*, limbah PCB campuran mengandung 9,08% Cu. Pelindian limbah PCB dilakukan dengan metode *agitation leaching* menggunakan larutan thiourea. Proses pelindian dilakukan pada variasi ukuran 80; 100; 120#, dengan variasi persen padatan sebesar 10; 15; 20% pada varisai konsentrasi oksidator H_2O_2 0,2; 0,4; 0,6 M serta penambahan volume oksidator H_2O_2 20; 28; 36%. Setelah itu dilakukan pelindian selama 6 jam, dengan kecepatan putaran 200 rpm pada temperatur 25°C dengan pH 1-2. Hasil penelitian pelindian limbah PCB campuran menghasilkan kadar Cu pada larutan hasil pelindian sebesar 3,5% dengan persen padatan 10% dan penambahan volume oksidator H_2O_2 sebesar 28%. Limbah PCB dengan ukuran -120# dengan konsentrasi H_2O_2 0,4 M menghasilkan Cu pada larutan hasil pelindian dengan kadar 0,26%.

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1. Introduction

Electronic waste is one type of waste with a fast growth rate. Around 20-25 million tons of e-waste are generated worldwide [1]. In 2005, the European Union produced about 8.3 to 9.1 million tons of waste electrical and equipment (WEEE). WEE is waste electrical or electronic equipment that is no longer in use and has expired [2]. The growth rate of electronic waste in Indonesia is estimated to increase in 2028 by 49,627,917 if it is not treated properly [3]. Electronic waste contains hazardous materials and toxic elements such as lead, cadmium beryllium, mercury, arsenic, lead oxide, barium, and cadmium [4]. The impact generated from electronic waste containing heavy and toxic metals can cause cancer (carcinogenic) to damage the brain's nervous system. In WEEE, there is electrical and electronic equipment such as televisions, computers, cell phones, and laptops with components called printed circuit boards (PCBs). Currently, PCB waste is one of the most generated electronic wastes, 500 thousand tons of PCB waste that needs to be processed. PCB waste can be reprocessed because it contains metals such as Cu.

In developing countries such as Indonesia, with the largest human population globally, the growth rate of electronic waste is known to be 1 kg per year per capita. In electrical and electronic equipment such as televisions, computers, cell phones, and laptops, there are components called Printed Circuit Boards (PCBs). Generally, PCB waste consists of 40% metal, 30% plastic, and 30% ceramic. PCB itself is coated with a base metal (base metal) in the form of tin, silver, or copper, making it have conductivity properties. There are two types of PCBs, namely PCB FR-4 and PCB FR-2, used in cell phones and computers. PCB type FR-4 is made of a multilayer of fiberglass coated with copper, while PCB type FR-2 is a single layer of fiberglass or cellulose paper coated with a layer of copper [2].

In dissolving precious metals from PCB waste, the method that can be used is the hydrometallurgical method by leaching. The main stage in the hydrometallurgical process is the leaching process. Leaching is extracting a soluble material from a solid through a solvent [5]. The leaching process uses chemical solutions or reagents to dissolve materials such as PCB (Printed Circuit Boards); waste is thiourea. Thiourea is one of the reagents that can be used in the PCB waste leaching process because thiourea leaching can reach 99% and has a low cost, and is more friendly to the environment [6]. Leaching using thiourea requires the presence of an oxidizing agent in the form of Fe^{3+}. Thiourea is unstable and easily decomposes in an alkaline environment, so the reaction requires an acidic medium. The leach solution used is thiourea (NH_2CSNH_2). The use of thiourea solution is because thiourea has a low environmental impact, easier handling, and greater selectivity to metals. Leaching using thiourea solution requires the presence of an oxidizing agent in the form of Fe^{3+}. The oxidizing agent Fe^{3+} plays a role in accelerating the leaching reaction by increasing its potential. In addition, the reduction reaction of Fe^{3+} and thiourea ions is quite slow to form complex compounds that are relatively stable in acidic solutions. There has been no further research on the variation of oxidizing agents used in the PCB leaching process, one of which is using H_2O_2 oxidizing agents, which are relatively more environmentally friendly. Therefore, this research is quite important to be carried out to find out other alternatives in the use of oxidizing agents in the Cu metal extraction process using electronic waste raw materials.

2. Research Methodology

The mixed printed circuit boards (PCB) waste originating from Tangerang was first carried out in the dismantling stage or the separation stage of the components in the PCB and a comminution process to reduce particle size using a hammer mill. Then it is separated magnetically and sifted with the appropriate size. After the pretreatment stage on PCB waste, initial characterization was carried out using X-Ray Fluorescence (XRF) and fire assay to determine the elements contained. The PCB waste leaching process was carried out with an agitation speed of 200 rpm, with a pH of 1-2 at a temperature of 25°C for 6 hours. The concentration of thiourea used was 0.5M, with the addition of an oxidizing volume of $Fe_2(SO_4)_3$ 20% of 0.01 M [7]. PCB sample size variations were carried out starting from 80#, 100#, and 120#.

The variation of percent solids was carried out at 10%, 15%, and 20%. Variations in addition to the volume of H2O2 oxidizing agents were added by 20%, 28%, and 36%, with variations in H_2O_2 concentrations of 0.2, 0.4, and 0.6 M., The characterization of PCB sample content resulting from leaching in the form of the filtrate, was analyzed using inductively coupled plasma-optical emission spectrometry (ICP-OES) to determine Cu levels. Previous research has carried out leaching of PCB waste using thiourea solution with the addition of an oxidizing agent $Fe_2(SO_4)_3$, which has been carried out by Lonela Birloaga using two leaching steps, namely dissolving the base metal first (Cu), then dissolving the noble metal (Au and Ag). While in this study, PCB waste was leached using a thiourea solution with the addition of an oxidizing agent H_2O_2 mixed with an oxidizing agent $Fe_2(SO_4)_3$¬ and did not use two leaching steps, the leaching step in this study was only carried out in 1 step by dissolving the base metal and the noble metal simultaneously. [8].

3. Results and Discussion

The slag depressant is first characterized for raw materials and then several variations to obtain a higher compressive strength value. Raw materials are paper sludge, slag blast furnace, and limestone as the main component of slag depressant.

3.1. XRF Characterization

Initial characterization of printed circuit boards (PCB) waste samples was carried out to determine the chemical elements' composition. The characterization results using X-Ray fluorescence (XRF) can be seen in Table 1. Table 1 shows six compositions of chemical elements contained in PCB waste, but the Cu element has not been seen due to its small concentration. Initial characterization of printed circuit boards (PCB) waste samples was carried out to determine the chemical elements' composition. The characterization results using X-Ray fluorescence (XRF) can be seen in Table 1. Table 1 shows six compositions of chemical elements contained in PCB waste, but the Cu element has not been seen due to its small concentration.

Sn elements with high levels are metal elements used as solders in PCB waste. Then the elements of Ca and Ba are non-metals used as raw materials for coating on PCB waste in the form of fiberglass. In PCB waste, the Fe element is used as a contact on the board and magnetic core in transformers and chokes, while the Sb element is usually used in PCBs because of its ability to reduce the flammability of electronics [9].

Table 1. Chemical composition of PCB waste

No	Element	Rate (% *wt*)
1	Fe	6.073
2	Ca	13.184
3	Sb	1.154
4	Sn	26.113
5	Rb	2.041
6	Ba	2.006

3.2. Fire Assay Characterization

Initial characterization using fire assay analysis on Printed Circuit Boards (PCB) waste is needed to determine the metal content with a small concentration value. Table 2 shows the analysis results using the fire assay method on PCB waste. The initial characterization results with the element fire assay method with the highest content obtained in Cu metal of 9.08%. The element of Cu with the highest content is usually used as the main layer that forms the structure on the PCB so that Cu elements are usually found at the bottom of the PCB surface [10].

Table 2. The findings of the fire assay analysis

Element	Rate	Unit
Cu	9.08	%

3.3. Microscope Observations

The purpose of microscopic examination of PCB waste is to establish the type of PCB. Based on the microscope findings at a zoom of 10x, it is possible to observe extremely visible fiberglass fibers in Figures 1a, 1b, and 1c, indicating that the PCB employed in this research is the FR-4 PCB.

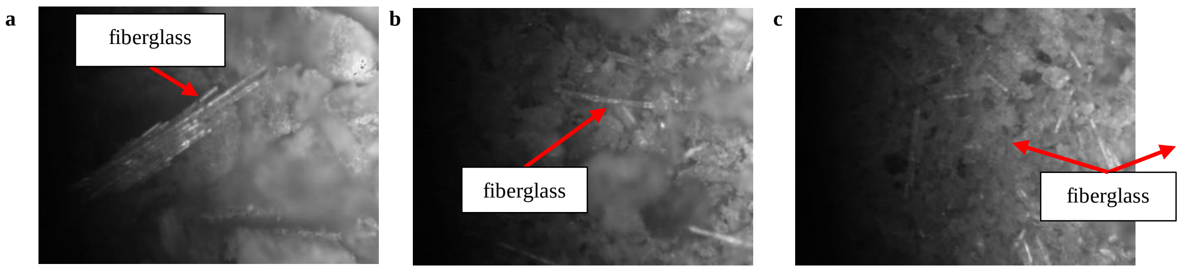

Figure 1. The findings of the PCB microscopy analysis (a) size -70+100# (b) siza 100+120# (c) size -120+140# (zoom 10x).

3.4. Effect of Size on PCB

The size of the PCB used during the leaching process can affect the percent Cu recovery. The experimental results are shown in Figure 2. Based on Figure 2, the results of the leaching of Cu elements. The largest extraction percentage, 0.26594%, was obtained by leaching using PCB at a size of -120 + 140#. Following the research conducted by [11], the smaller the PCB particle size, will increase the Cu recovery during leaching. The condition occurs because the smaller the size, the greater the degree of release, resulting in a large surface area exposed to the solution, maximizing the leaching outcomes.

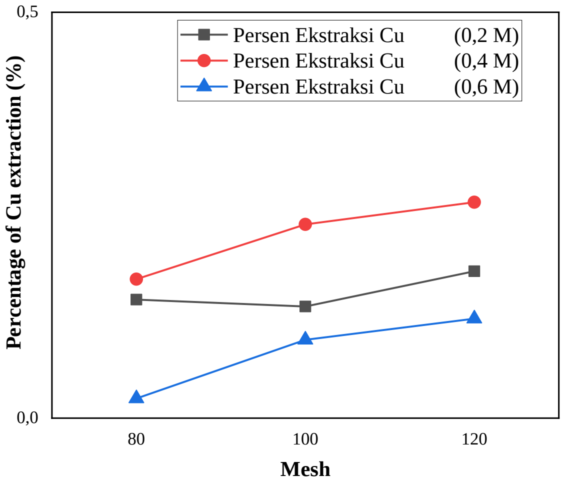

Figure 2. Effect of PCB size on % Cu extraction.

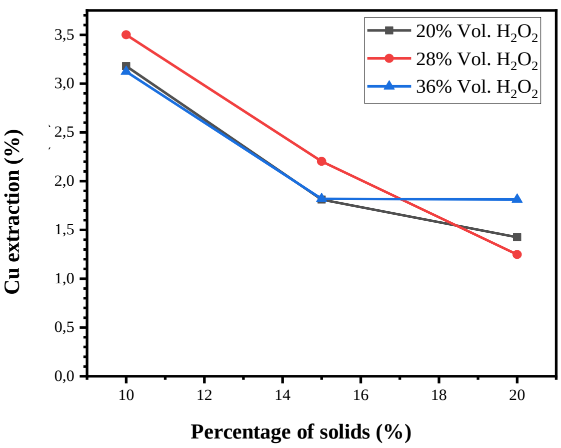

Figure 3. Effect of % solids on % Cu extraction.

3.5. The effect of solids percentage on PCB

One factor that affects the leaching process is the percentage of solids. The percentage of solids is the ratio of solids to pulp weight, where pulp weight is the total of solids and water. The lower the solids used, the higher the extraction percent obtained. With the low percent solids used, the chance of reacting between Cu metal and thiourea will be easier so that the percent extraction yield will be higher. Figure 3 shows the effect of percent solids on percent Cu extraction. Figure 1 shows the highest percentage of Cu extraction was obtained at 10% solids condition. In conditions of 10% solids percent, the highest Cu extraction percent value was 3.5%, and there was a decrease with the increase in the percentage of solids used.

3.6. Effect of H_2O_2 concentration

The concentration of H_2O_2 used during the leaching process can affect the percent recovery of Cu produced because the addition of H_2O_2 in the leaching process functions as an oxidizing agent to obtain a higher percentage of Cu recovery. The experimental results are shown in Figure 4. In the experiment conducted by Wang et al., namely the extraction of copper from PCB waste using hydrochloric acid (HCl) and hydrogen peroxide (H_2O_2) as an oxidizing solution, the concentration of concentration was shown H_2O_2 affected the percent copper extraction.

The higher the concentration of H_2O_2 used, the higher the percentage of copper extraction that will be obtained [12]. However, in contrast to the leaching process with HCl, in the leaching with thiourea solution that has been carried out, it can be seen in Figure 4 that the highest percentage of Cu element extraction is at a concentration of 0.4 M H2O2, which is 0.26594%. The condition happens because the leaching of Cu using H_2O_2 is less stable, so it is necessary to add chlorine ions ($CuCl_2$) to make it stable [13].

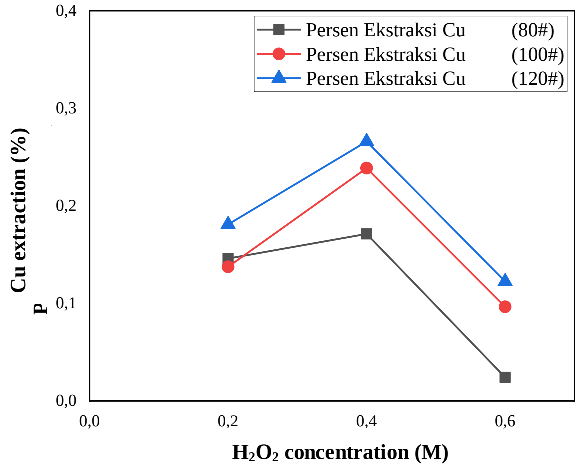

Figure 4. Effect of H_2O_2 concentration on % Cu extraction

3.7. Effect of increasing the volume of H_2O_2

The addition of oxidizing volume H_2O_2 to the oxidizing agent $Fe_2(SO_4)_3$ in thiourea solution has an important influence on the PCB waste leaching process because it can help increase Fe^{3+} ions the extraction percent value produced is high. Figure 3 shows the results of Cu leaching using thiourea solution with variations in the addition of H_2O_2 oxidizing volume. It can be seen in Figure 3, the highest percentage of Cu extraction was obtained when the oxidizing volume was added by 28%, namely 3.5%. The addition of H_2O_2 volume was used to increase the availability of low Fe^{3+} ions and maintain Fe^{3+} ions. Fe^{3+} ions assist in leaching with thiourea because Fe^{3+} ions can form complex, relatively stable compounds in acidic solutions [14]. The use of an oxidizing volume that is too high can result in a decrease in the percent value of Cu extraction because PCB waste does not only consist of Cu, but also other metals such as Fe, Ni, Au, Ag, and Pd as well as other fractions, thus requiring an oxidizing agent that can hold stable so that the extraction percent value obtained is high.

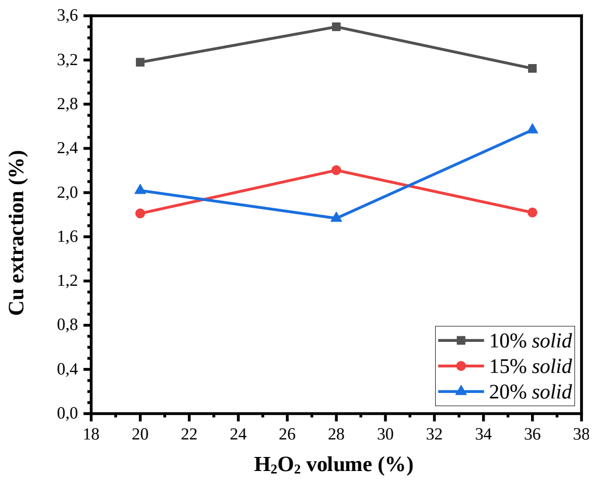

Figure 5. Effect of additional volume of H_2O_2 on % Cu extraction.

4. Conclusion

Leaching PCB waste with 10% solids condition and adding 28% volume of oxidizing agent H_2O_2 using 0.5 M thiourea solution produced Cu with a percentage extraction value of 3.5%. The lower the percent solids used, the higher the extraction percent value. The addition of 28% H_2O_2 oxidizing volume was able to extract Cu. The smaller the size (-120+140#), the higher the percentage of Cu extraction, 0.26%. The lower the concentration of H_2O_2, the higher the percentage of Cu extraction, which is 0.26%. The results obtained by leaching by agitation leaching on PCB waste using a thiourea solution and an oxidizing agent H_2O_2 were able to dissolve Cu metal for 6 hours. Metal extraction by recycling PCB waste can be an alternative future metal raw material amidst Indonesia's declining metal mineral reserves. PCB waste can also be used as a product with high added value and reduce the environmental impact caused by the increasing amount of PCB waste produced.

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