RECOVERY OF COPPER FROM E-WASTE VIA HYDROMETALLURGY METHOD

NUR AIN BINTI ROSLI

UNIVERSITI SAINS MALAYSIA

2022

RECOVERY OF COPPER FROM E-WASTE VIA HYDROMETALLURGY METHOD

by

NUR AIN BINTI ROSLI

Dissertation submitted in partial fulfilment of the requirements for the degree of

Bachelor of Engineering with Honours

(Mineral Resources Engineering)

Universiti Sains Malaysia

August 2022

DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled Recovery of Copper from E-waste via Hydrometallurgy Method. I also declare that it has not been previously submitted for the award of any degree and diploma or other similar title of this for any other examining body or University.

Name of Student: Nur Ain Binti Rosli Signature:

Date:

Witness by

Supervisor: Dr Suhaina Binti Ismail Signature:

Date:

ACKNOWLEDGEMENT

I would like to convey the gratitude towards my family, both of my parents, Rosli Din and Rozy Azlina for their continuous support although indirectly, have help me in completing the research. I would also like to express my gratitude towards my FYP supervisor, Dr Suhaina Ismail, for guiding me in completing my research, tirelessly and committed in assisting me even after working hour. Her guidance and constant supervision help me tremendously with providing necessary information regarding the project.

My appreciation also goes to the staff of Pusat Pengajian Kejuruteraan Bahan dan Sumber Mineral (PPKBSM). Technical staff and non-technical staff alike, have been a big part in this research. My special thanks in this matter goes to assistant engineers, En. Zulkurnain Hasbollah, and Pn. Haslina Zulkifli, who have provided me with countless help regarding experimental work. The staff has guide me with technical and practical works during my research. They willingly to stay back in helping me to finish my analysis. Their kindness boosts my energy to finish my Final Year Project.

A special dedication to my coursemates and other friends who provided valuable suggestions and offered their assistance both directly and indirectly throughout my studies. Especially, Nadiah Adlin and Ilmadiena who help me with almost everything.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

Page

LIST OF ABBREVIATIONS

PCB	Printed Circuit Board
E-waste	Electronic waste
WPCB	Waste Printed Circuit Board
WEEE	Waste Electric and Electronics Equipment
EEE	Electrical and Electronics Engineering
XRF	X-ray Fluorescence
XRD	X-ray Diffraction
SEM	Scanning Electron Microscope
AAS	Atomic Absorption Microscopy
Cu	Copper
AMD	Acid Mine Drainage
IT	Information Technology
ABS	Acrylonitrile Butadiene Styrene
PC	Polycarbonate
PVC	Polyvinyl Chloride
PTFE	Polytetrafluoroethylene
PE	Polyethylene
PP	Polypropylene
HIPS	High Impact Polystyrene
H_2O_2	Hydrogen Peroxide
H_2SO_4	Sulphuric acid
LCD	Liquid crystal displays
CRT	Cathode Ray Tubes
BFR	Brominated Flame Retardants
CFC	Chlorofluorocarbon
EDTA	Ethylenediaminetetraacetic Acid
MEA	Monoethanolamine Acid

PEROLEHAN TEMBAGA DARIPADA SISA ELEKTRONIK MELALUI KAEDAH HIDROMETALURGI

ABSTRAK

Pengeluaran sisa elektronik semakin meningkat setiap tahun dalam industri elektronik. Sisa elektronik mengandungi kedua-dua logam berbahaya dan logam berharga seperti tembaga (Cu). Jadi, perolehan logam perlu untuk mengurangkan pencemaran alam sekitar dan untuk mendapatkan manfaat daripada logam yang boleh menjadi sumber kewangan untuk negara. Objektif eksperimen ini ialah menentukan ciri fizikal-kimia sisa elektronik melalui analisis XRF, XRD dan SEM, dan untuk membandingkan pemulihan Cu dengan tiga parameter yang berbeza, iaitu suhu, kadar penambahan oksida dan kesan pra-rawatan menggunakan rawatan ultrasonik. Dalam analisis XRF, komposisi terbesar di dalam sisa elektronik ialah SiO_2, CaO dan CuO. Keputusan ini boleh dibuktikan dengan keputusan XRD di mana fasa yang menunjukkan kesan positif bersama puncak tertinggi yang terdapat di dalam sampel ialah CuO serta SiO_2. Analisis SEM juga dilakukan untuk menganalisis kesan pra-rawatan ultrasonik yang menunjukkan pemisahan tembaga yang tinggi daripada elemen yang tidak diperlukan. Parameter tetap dalam larut lesap adalah nisbah S/L (1:10), kepekatan asid sulfurik (1.5M), isipadu asid sulfurik (100ml), saiz sampel larut lesap (di bawah daripada 200μm) dan kadar kacau (300rpm). Sementara itu, parameter yang dimanipulasi yang digunakan untuk mencapai kadar larut lesap yang tinggi adalah suhu (30°C dan 60°C), kadar penambahan oksida (20 ml/jam dan 60 ml/jam) dan kesan pra-rawatan ultrasonik. Keadaan terbaik untuk pemulihan tembaga yang tinggi, 64.36%, adalah 100 ml 1.5M asid sulfurik, dengan penambahan 5% oksida pada kadar 20ml/jam, untuk 10g serbuk PCB dengan nisbah cecair pepejal 1:10 selama 6 jam pada suhu 60°C.

RECOVERY OF COPPER FROM E-WASTE VIA HYDROMETALLURGY METHOD

ABSTRACT

E-waste production is increasing by time as the demand of society in electronics grows year by year. Since, e-waste contain both hazardous metals and precious metals such as copper, recovery of the metals are necessary to minimize environmental and to gain benefits from monetary metals. In this work, the pysico-chemical characteristic of Waste Printed Circuit Board (WPCBs) is determined via XRF, XRD and SEM analysis and to compare the recovery of copper with three different leaching parameters, temperature, rate of oxidant addition and effect of ultrasonic pre-treatment. In XRF analysis, the major composition in the e-waste were SiO_2, Ca followed by CuO element. This result was supported by XRD test where the most significant phase with high peak that exist in the sample is copper along with SiO_2. SEM analysis was also done to analyse the impact of ultrasonic pre-treatment which show high copper separation from unwanted particles such as ceramic and plastic. For SEM analysis, the most significant condition was sample that treated with ultrasonic. The fixed parameters in leaching are S/L ratio (1:10), sulphuric acid concentration (1.5 M), volume of sulphuric acid (100 ml), size of leaching sample (below than 200 µm) and stirring rate (300 rpm). Meanwhile, the manipulated parameter used to achieve high leaching rate are temperature (30°C and 60°C), rate of oxidant addition (20 ml/hr and 60 ml/hr) and effect of ultrasonic pre-treatment. The optimum condition for high recovery rate of copper, 64.36%, were addition of 5% hydrogen peroxide at rate 20ml/hr at 60°C.

CHAPTER 1

INTRODUCTION

1.1 Significant of Research Work

Electronic waste or known as e-waste is a term used to describe electronic appliances that have been discard by their owners due to their short lifespan. E-waste is made up of complex and diversified range of material which contains both valuable and harmful materials that contribute to serious environmental problem and cause adverse health effect. Therefore, the treatment of recycle and disposal e-waste need to be done properly, not by ordinary method used for other waste. Presently, e-waste processing involves three major steps namely disassembling which involve removing hazardous or valuable components, upgrading using mechanical or metallurgical technique to recover desirable materials content and refining with purification procedure of recovered materials (Mahapatra et al., 2019).

Recycling of e-waste will be a very important sector in the meantime from economic and environmental aspect as it is rapidly growing disposal problem in worldwide. Recycling Waste Printed Circuit Boards (WPCBs) intend for turning today's waste into environmental friendly, sustainable polymetallic secondary resources (i.e. Urban Mining) with lower carbon footprint for tomorrow. Taking into consideration our decreasing natural resources, this Urban Mining give some benefits which increased energy efficiency and lowers demand for mining of new raw materials (Kaya, 2016). A lot of valuable materials contained in WPCBs make them worth being recycled. As a result, selecting a non-polluting, efficient, and low-cost method for WPCBs recycling can help not only to avoid environmental pollution, but also to recycle valuable resources, all of which are important for the continuous improvement of human living conditions, standards, and resource recycling.

The metallurgical processing of e-waste consists of smelting the components with heat, known as pyrometallurgical processing, or dissolving in the appropriate solvent or liquid, known as hydrometallurgical processing, and then further refining the target metal using its chemical properties (Kaya 2016). As pyrometallurgical processing consume higher energy and require higher cost, hydrometallurgical processing is preferable. Furthermore, adopting the pyrometallurgical approach will result in the production of slag and poisonous fumes, both are harmful to the environment.

Hydrometallurgical method provides high selectivity, lower energy consumption, controlled environment, and high recovery. The initial phase in metal recovery is hydrometallurgy, which involves leaching valuable metals into solutions in an acidic or alkaline media, and then extracting the desired metal from the solution via precipitation, absorption, ion exchange, electrowinning, or solvent extraction (Ashiq et al., 2019).

1.2 Problem Statement

The global production of electronic waste reached approximately 44.7 million tonnes in 2016, with a 17% increase to 52.2 million tonnes in 2021 (Yaashikaa et al., 2022). In Europe, 7.5 million tonnes of waste electrical and electronic equipment (WEEE) are produced each year, accounting for 4% of urban solid waste flow, and the growth trend is expected to increase by 3-5% each year. This trend represents a threefold increase over the average municipal waste growth rate (Andreola et al., 2007). Thailand generated approximately 80,000 tonnes of e-waste per year in 2009, with approximately 20,000 tonnes of electrical and electronic goods. Thailand also faces issues related to a lack of general awareness of e-waste, incomplete e-waste databases and inventories, a lack of environmentally sound management practises, and a lack of e-waste-specific laws and regulations (Suja et al., 2014).

In 2012, total e-waste generated in Malaysia was somewhere between 10-15% of total scheduled waste produced, and its value is estimated to rise once household e-waste collection is fully implemented (Suja et al., 2014). Malaysia generated approximately 688,000 metric tonnes of e-waste in 2008, with a gradual increase to 1.11 million metric tonnes by 2020 (Soo et al., 2013). The low level of public awareness has contributed to Malaysia's e-waste overflow. Previous studies have evaluated various aspects of e-waste management, with the number of studies rapidly increasing in recent years (Ismail & Hanafiah, 2021; Kumar et al., 2017).

Improper disposal of e-waste has been classified as environmental hazard because they contain large amounts of toxic substances such as leaded glass and copper (Nnorom & Osibanjo, 2008). E-waste disposal is a legitimate issue because most of it is often disposed of before it truly becomes useless. In fact, the primary reason for purchasing a new computer is to keep up with rapidly changing technologies rather than to replace a non-functioning system (Adamson et al., 2005). The rapid development of industrial activities produced a wide range of waste products and materials. In addition, the hazardous substances that are found in WEEE, will be prone to both incineration process and landfill which pose a risk to the environment and human health (Andreola et al., 2007).

Nonetheless, recovery of metals from e-waste provides huge economic benefits due to the valuable substance in e-waste, such as copper (Wu et al., 2017; Yong et al., 2019). As a result, both recovering the valuable metals and protecting the environment from pollution can be succeed. Many developed countries have implemented effective e-waste management method, such as taking pyrometallurgical and hydrometallurgical approaches to manage this monetary value substance in e-waste and extracting them from e-waste. Hydrometallurgy is a successful and preferable technique to recover precious metals from waste materials because it can give high recovery rates at a relatively low cost (Wu et al., 2017).

Leaching of copper is important in effort of recycling WEEE. Copper is the key metal in the production of electronic equipment, about 72% copper metal is procured from the resources available in nature (Yaashikaa et al., 2022). Copper leaching using sulfuric acid results in lower recovery rate without the presence of oxidizing agent such as hydrogen peroxide compared to leaching with oxidant. Copper leaching at elevated temperature also may give higher recovery rate, with or without the addition of oxidant.

Tremendously, acid leaching also contributes to environmental problem which cannot be escape. Therefore, the amount of chemicals used such as acid and oxidant should be reasonably calculated in the leaching process, to avoid excessive acid remaining in the waste liquid and causing impact on the environment. At the same time, proper leaching setup in the fume cupboard must be implied to inhibit hazardous gases from release to the air. Although the hydrometallurgy method could be the potential recovery process of the copper from e-waste, the effects of valuable and main functional components in the e-waste along with the high-value utilization as far as possible should be properly considered (Zhang et al., 2021).

1.3 Objective

The objectives specifically targeting as below:

1. To determine the pysico-chemical characteristic of Waste Printed Circuit Board via XRF and SEM.
2. To compare the recovery of copper with three different leaching parameters, temperature, rate of oxidant addition and effect of ultrasonic pre-treatment.

1.4 Scope of Study

Waste Printed Circuit Boards were collected to recover the copper to minimize the environmental problem from improper handling of it. All the unwanted components were removed from the board manually. Then, WPCBs were crushed and ground until the size passing 3.0mm sieve. Coning and Quartering method was used to do sampling way before grinding process. About 10g of comminuted WPCBs is weighed and leached in sulphuric acid system with addition of hydrogen peroxide (H_2O_2) as oxidant. The feed sample and leaching residue were dried and sent to X-Ray Fluorescent (XRF) and Scanning Electron Microscope (SEM) for characterization procedure. The fraction of copper recovered are analysed using Atomic Absorption Spectroscopy (AAS).

The parameters that were chosen in the project are temperature and oxidants addition rate. There are three different temperatures used in the experiment which are 30℃, 45℃ and 60℃. The type of acid used in this experiment are sulfuric acid

(H_2SO_4). The acid concentration is fixed at 1.5 M and the volume is 100ml. All the parameters are tested simultaneously during the leaching process.

The pre-treatment using ultrasonic analysis was found to give positive effect on recovery of copper. Therefore, two different sample with same leaching condition were used, sample with pre-treatment and sample without pre-treatment was compared to determine sample that give higher recovery of copper. Samples of the leach liquor are taken at interval of 30 minutes, 1 hours, 3 hours and 6 hours.

1.5 Thesis Outline

This thesis is organized into five main chapters which consists of Chapter 1 that introduces briefly about the coverage of the thesis, including the overview of the significant of research work, problem statement, objectives and scope of this research work. Chapter 2 is where the literature review on copper recovery in acid leaching system is briefly discussed. Chapter 3 presents the overall flow of this study and experiment conducted, information about the chemicals, equipment and methodology of the experimental work. Chapter 4 presents and discuss results from the data and result tabulated which also explain the importance of findings and acknowledge any mistake or limitation in experiment. Chapter 5 summarized and draw conclusions for this study and its objective. Also, some recommendation for future work are listed in this chapter.

1.6 Research Gap

Table 1.1 Acid leaching to recover copper from WPCBs from various references

Types	Leaching agent	Methods	Metal recovered	Reference
Acid leaching	H_2SO_4	Oxidative leaching with H_2O_2 with one step addition	99 % Cu	(Birloaga et al., 2014)
	H_2SO_4-HNO_3-H_2O-NaOH, H_2SO_4-HNO_3-H_2O-NO_X	Acid pretreatment, Lix 841 and sulfuric acid as extraction agent	Cu more than 99.9%	(Cui & Zhang, 2008)
	H_2SO_4	Oxidative leaching with 10ml of H_2O_2	Cu	(Yang et al., 2011)
	HNO_3	Electrodeposition of Cu at cathode from solution	Cu, Pb	(Mecucci & Scott, 2002)

According to the past research, leaching of copper with sulphuric acid and hydrogen peroxide as oxidant is the most chosen method as the rate of copper recovery can achieve more than 90% as tabulated in Table 1.1. The oxidant is added with one step addition gives higher recovery instead of many steps addition of oxidant. The most effective leaching time is less than 3 hours as the copper recovery already achieved the highest percentage in that period.

The study of the recovery of copper from e-waste is still lacking in use of ultrasonic pre-treatment which helps to further enhance the recovery of copper. There are many articles that used magnetic separator to liberate the copper from other minerals. Nonetheless, copper is diamagnetic minerals and has lower magnetism. Therefore, ultrasonic pre-treatment that use density properties instead of magnetic properties is studied in this research.

CHAPTER 2

LITERATURE REVIEW

2.1 Copper Background

Pure copper metal is a soft, malleable, and ductile metal that has a high thermal and electrical conductivity making it ideal for many applications (Davis, 2001). Copper is a strategic metal that is used in the construction of buildings, the manufacture of electric and electronic gadgets, the generation and transmission of electricity, transportation equipment, and machinery. The recovery valuable metals such as copper from electronic waste is becoming a more common study topic recently. The advancement of new technology, newly manufactured electronic equipment quickly ages and is replaced by newer models, resulting in significant waste (Kaya, 2016).

Copper can be found naturally as native copper. Copper sulphide, also known as chalcopyrite, is the most common source of copper. The most used metallurgical method for extracting high-grade copper from chalcopyrite is froth flotation. Copper concentrate is produced by froth flotation from unwanted gangue minerals, but it contains trace elements such as Cd, Hg, Pb, Bi, Se, and Te (Cui & Zhang, 2008). These concentrates are then further concentrated using pyrometallurgical methods to increase copper purity and yield high-grade copper metal.

2.2 Industry Demand of Copper

China dominates the global copper market, accounting for 50% of global demand in 2014 and expected to increase to 54% by 2020 (Garside, 2021). Copper has surpassed petroleum as China's second most important strategic raw material (Li et al., 2017). This is due to the country's extensive industrial use of copper such as construction and electrical and electronic manufacturing. According to studies, demand in North America and Western Europe is expected to rise, while India's gains in the copper market are expected to outpace both regions as building construction activity picks up after being slowed by the coronavirus pandemic in 2020.

The total global demand for copper from 2010 to 2050, as well as demand in various sectors for the years 2010, 2025, and 2050 in the four scenarios Market First (MF), Policy First (PF), Security First (SF) and Sustainability First (EF) are shown in Figure 2.1. Copper demand in 2050 is estimated to be 275% (MF), 275% (PF), 213% (SF), and 341% (EF) (Elshkaki et al., 2016). All scenarios would cause significant increases in copper mining and processing and at the same time lessening environmental impact (Elshkaki et al., 2016).

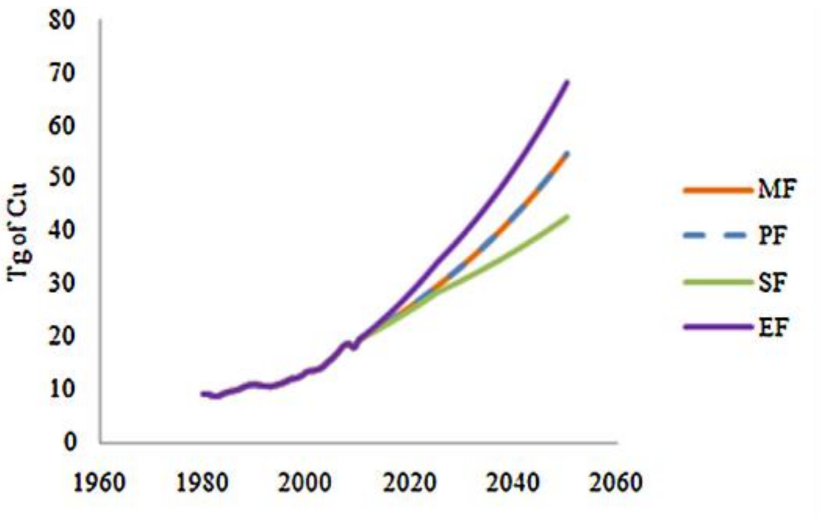

Figure 2.1 Global copper demand for the four GEO-4 scenarios (Elshkaki et al., 2016)

2.3 Quantitative Structure Activity Relationships Studies

Copper is widely used in construction and production of electrical and electronic appliances. Figure 2.2 shows most important end use sector for Cu in infrastructure sector accounting for 25%, 25%, 26%, and 24% of total copper demand by 2050 in the four scenarios respectively, followed by wiring (15%, 15%, 15.5%, and 14.5), industrial EEE (13%, 13%, 12%, and 14%), plumbing (10.5%, 10.5%, 11%, and 10%), built in appliances (10%, 10%, 9%, and 10.5%), consumer electronics (10.5%, 10.5%, 10%, 11%), and motor vehicles (8%, 8%, 9%, 7.8%). Overall, these findings suggest that copper demand could increase by 200-350% over the next four decades (Elshkaki et al., 2016).

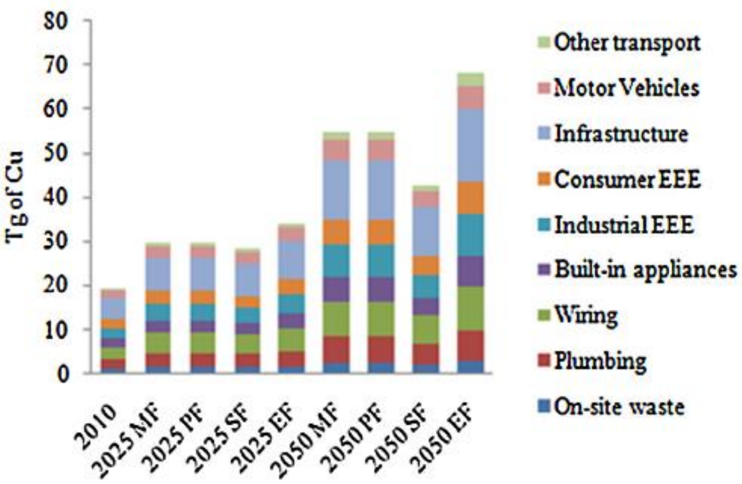

Figure 2.2 Fractional uses of copper in 2010, 2025, and 2050 for the four GEO-4 scenarios (Elshkaki et al., 2016)

2.4 Environmental impact from copper mining

Mining for copper ore has environmental consequences such as acid mine drainage (AMD), water basin destruction, deforestation, and other mining impacts (Emmanuel & Dzigbodi, 2018). This is undesirable because regulation for environmental law has devastated and destroying the environment which proven not sustainable for the future livelihood. Recycling secondary products such as e-waste can reduce the negative impact of hazardous wastes while also slowing the depletion of primary metal ores such as copper (Trinh et al., 2020).

2.5 Source of e-waste

Waste electric and electronic equipment (WEEE) or goods that are no longer fit for their original purpose are classified as e-waste. E-waste includes televisions, phones, radios, computers, printers, fax machines, DVDs, CDs, washing machines, refrigerators, dryers, vacuum cleaners, and other WEEEs. Figure 2.3 represents the distribution of e-waste composition (Kaya, 2016). Electrical appliances account for half of all e-waste, while electronic goods account for the other half. Table 2.1 listed the four types of e-waste (Kaya, 2016). The main primary sources of e-waste include small or large home appliances, hospital medical equipment, government office machines (information technology (IT) and telecom equipments), and private sector offices and industrial equipments and machines. The replacement of EEE becomes more frequent, which results in large quantities of e-waste need to be disposed (Zhou & Qiu, 2010).

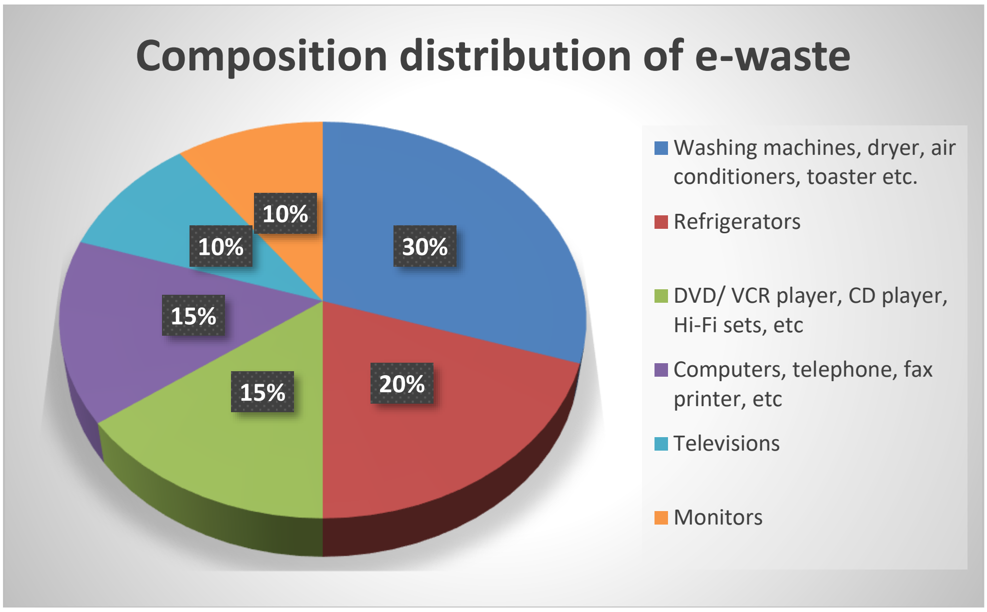

Figure 2.3 Composition distribution of e-waste (Kaya, 2016)

Table 2.1 Four main sources of e-waste (Kaya, 2016)

Home	Hospitals	Government	Private sectors
• PC • TVs • Radio • Cell phone • Washing machine • Microwave oven • CD player • Fan • Electronic iron etc.	• PC • Monitor • ECG device • Microscope • Incubator • X-ray machine etc.	• PC • CPU • Printer • Fax • Photocopy machine • Scanner • Fan • Tube light etc.	• PC • Boiler • Mixer • Signal conditioner • Incubator etc.

2.6 E-waste as source for valuable metal

The annual amount of electronic waste (e-waste) is soaring, because of the high consumption of electronic devices and the rapid advancements in the electronics industry. The global annual production of e-waste is approximately 40 million metric tonnes, accounting for 5% of total solid wastes worldwide (Hazra et al., 2019).

Typically, e-waste contains metal such as Fe, Cu, Al, Pb, Ni, Ag, Au, and Pd as shown in Table 2.2 which is valuable and can be recovered at a profit (Cui & Zhang, 2008).

Table 2.2 Composition of valuable metal in e-waste from previous studies (Cui & Zhang, 2008)

E-waste	**Weight%**					**Weight (ppm)**			**Refs**
	Fe	Cu	Al	Pb	Ni	Ag	Au	Pd	
TV board scrap	28	10	10	1.0	0.3	280	20	10	(Hagelüken, n.d.)
PC board scrap	7	20	5	1.5	1	1000	250	110	
Mobile phone scrap	5	13	1	0.3	0.1	1380	350	210	
Portable audio scrap	23	21	1	0.14	0.03	150	10	4	
DVD player scrap	62	5	2	0.3	0.05	115	15	4	
Calculator scrap	4	3	5	0.1	0.5	260	50	5	
PC mainboard scrap	4.5	14.3	2.8	2.2	1.1	639	566	124	(Cui & Forssberg, 2007)
PCBs scrap	12	10	7	1.2	0.85	280	110	-	
TV scrap (CRTs removed)	-	3.4	1.2	0.2	0.038	20	<10	<10	

Electronic scrap	8.3	8.5	0.71	3.15	2.0	29	12	-	(Ilyas et al., 2010)
PC scrap	20	7	14	6	0.85	189	16	3	
Typical electronic scrap	8	20	2	2	2	2000	1000	50	

E-waste has the potential to be a profitable copper source. The value of copper recovery in e-waste is tabulated in Table 2.3 below, assuming 100kg of e-waste for each category above and a current price of copper of RM40 per kilogramme :

Table 2.3 Value of copper in e-waste (Park & Fray, 2009)

E-waste	Cu content (wt %)	Weight of copper in 100kg waste (kg)	Value (RM)
TV board scrap	10	10	400
PC board scrap	20	20	800
Mobile phone scrap	13	13	540
Portable audio scrap	21	21	840
DVD player scrap	5	5	200
Calculator scrap	3	3	120
PC mainboard scrap	14.3	14.3	572
PCBs scrap	10	10	400
TV scrap (CRTs removed)	3.4	3.4	136
Electronic scrap	8.5	8.5	340
PC scrap	7	7	280
Typical electronic scrap	20	20	800

2.6.1 Waste Printed Circuit Boards (WPCBs)

Printed circuit boards (PCBs) are parts of electronic devices that hold and connect other electronic parts electrically. 3% of all the e-waste collected around the world is made up of PCBs (Serhan et al., 2019). The general composition of a typical PCB is roughly 40% metals, 30% organics, and 30% refractory by weight (M Goosey et al., 2009). The organics are most made up of the following polymers, Acrylonitrile Butadiene Styrene (ABS), Polycarbonate (PC), Polyvinyl Chloride (PVC), Polytetrafluoroethylene (PTFE), Polyethylene (PE), Polypropylene (PP), and High Impact Polystyrene (HIPS) (M Goosey et al., 2009). Silica, titanates, alumina, and alkaline oxides are common components of refractory materials (Serhan et al., 2019).

Generally, PCBs are copper-clad laminate consist of glass fibre, reinforced with epoxy resin, plastics, and metals. Figure 2.4 shows the structure of a PCBs that can be multi-layered, double-sided, or single-sided.

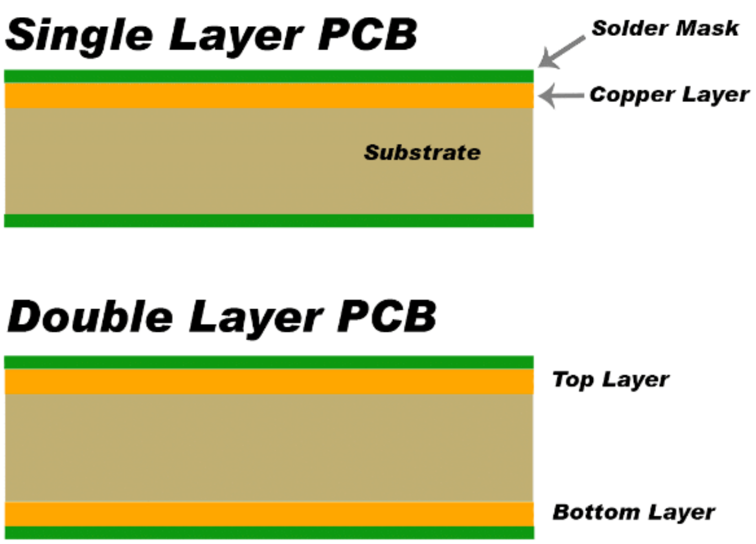

Figure 2.4 Illustration of single and double layer PCBs structure (excerpt from https://www.circuitbasics.com)

WPCBs soldering materials and plastic based components contain toxic substances known as Pb/Sn solder and brominated flame retardants (BFRs) that can be extremely toxic when reacting with oxygen, producing toxic dioxins and furans (Serhan et al., 2019).

2.7 Recycling Waste Printed Circuit Boards (WPCBs)

E-waste comprises a variety of useful resources as well as heavy metals and dangerous elements, making it a desirable polymetallic secondary source as well as an environmental problem (Widmer et al., 2005). E-waste is a rapidly growing disposal issue around the world. Therefore, recycle of valuable metallic and/or non-metallic materials from them are necessary and compulsory in many developed countries.

Table 2.4 shows the occurrences of dangerous substances in WEEE and their potential health effects. Relays, switches, batteries, liquid crystal displays (LCDs), and gas discharge lamps (such as fluorescent tubes in scanners and photocopiers) all contain mercury. The electronics industry consumes around 22% of all Hg generated globally each year. Pb, Cd, Li, and Ni are all used in rechargeable batteries. Pb is found in cone glass, Ba in electron gun getters, and Cd in phosphors in old televisions, personal computers, and cathode ray tubes (CRTs). Solder on PCBs contains Pb, Sn, and Sb, and switches contain Cd and Be. Plastics contain polyvinylchloride (PVC) and brominated flame retardants (BFRs). Cr^{6+} can be found on floppy discs and data formats. Polychlorinated hydrocarbons are found in condensers and transformers. Cooling units and insulation foams contain chlorofluorocarbon (CFC). Smoke detectors contain the element americium (Am). Liquid crystals are sandwiched between thin layers of glass and electrical control elements in LCDs. Liquid crystals are mixture of 10–20 substances which belong to the groups of substituted phenylcyclohexanes, alkylbenzenes and cyclohexylbenzenes. These substances contain O, F, H and C and are suspected to be hazardous.

Table 2.4 Hazardous substances in WEEE (Widmer et al., 2005)

Substances	Occurrence in WEEE	Possible adverse effects
Lead (Pb)	CRT screens, batteries, PCBs	Vomiting, diarrhea, convulsions, coma or even death, appetite loss, abdominal pain, constipation, fatigue, sleeplessness, irritability and headache
Mercury (Hg)	Fluorescent lambs, some alkaline batteries, switches	Brain and liver damage
Chromium VI (Cr^{6+})	Data tapes, floppy-discs	Irritating to eyes, skin and mucous membranes, DNA
Barium (Ba)	Getters in CRT	Brain swelling, muscle weakness, damage to the heart, liver and spleen
Cadmium (Cd)	NiCd batteries, fluorescent layer (CRT screens), printer inks and toners	Symptoms of poisoning (weakness, fever, headache, chills, sweating and muscle pain), lung cancer and kidney damage
Arsenic (As)	Gallium arsenide in light emitting diodes (LED)	Skin diseases, decrease nerve conduction velocity, lung cancer
Americium (Am)	Smoke detectors	Radioactive element
Antimony (Sb)	Flame retardants in plastics	Carcinogenic potential
Chlorofluorocarbon (CFC)	Cooling units, insulation foams	Deleterious effect on the ozone layer, increased incidence of skin cancer and/or genetic damages
Polychlorinated	Condensers, transformers	Cancer, effects on the immune

biphenyls (PCB)		systems, reproductive system, nervous system, endocrine system and other health effects
PBDEs, PBBs	Flame retardants in plastics	Hormonal effects, under thermal treatment possible formation of dioxins and furans

2.8 Pre-treatment Method

Recovery of copper and valuable metal from e-waste typically begin with pre-treatment method followed by processing or concentration process using hydrometallurgical methods and recovery or purification process using solution purification, cementation and other methods. Manually disassembling the electronic components on Waste Printed Circuit Boards is the pre-treatment method (WPCBs). The WPCBs were crushed in a knife mill with a 6 mm grid and a hammer mill with a 1mm grid, according to (Mahapatra et al., 2019). Smaller particles are needed to ensure complete liberation and to avoid copper encapsulation in WPCBs. A dry magnetic separator was used to separate nonmagnetic metals from magnetic minerals. Finally, the non-magnetic minerals were separated from magnetic minerals and processed further to recover the copper.

2.9 Comparison between Pyrometallurgy, Hydrometallurgy and Biological Method

PCB recycling technologies are improving as research advances, and traditional methods are no longer used (Yaashikaa et al., 2022). Recycling techniques can be pyrometallurgical, hydrometallurgical, or biological, depending on the process. PCB treatment methods include direct, primitive, and advanced recycling. Incineration and landfill are two direct methods of PCB recycling that use no or little energy. Metallic fractions are recycled in primitive recycling techniques, while non-metallic fractions are disposed of or subjected to fewer treatment processes (Hadi et al., 2015). Separation without causing damage to non-metallic fractions, followed by recycling or altering non-metallic fractions, is an example of advanced treatment (Kaya, 2016). Microbes are used in the leaching process of metallic substances from printed circuit boards in advanced techniques (Vermeşan et al., 2020). The advantages and disadvantages of physical, chemical and biological methods of recovery is explained in Table 2.5.

Table 2.5 Advantages and disadvantages of different recovery approach (Yaashikaa et al., 2022)

Type of recovery method	**Advantages**	**Disadvantages**
Physical	• Low operational cost • Absence of chemical usage • Low or nil energy requirement • No pre-treatment required • Solvent contamination is neglected • Minimal cost for consumables	• Time consuming • Labor intensive process • Low efficiency • High capital cost • Incomplete metal recovery
Chemical	• Rapid • High recovery • No gaseous pollutants emission • Relatively inexpensive • Less sensitivity to base metals	• High cost of reagents • Limited availability • Requirement of high temperatures • High toxicity • Environmental issues
Biology	• Economic and simple • Eco-friendly process	• Relatively slow process • Dependant on operational conditions

	• Produces less pollution • Leaching of low concentration of metals • Wide range of metal leaching • Less energy requirement	• Low pulp density • Microbial inhibition by microorganisms

2.9.1 Pyrometallurgical method

Pyrometallurgy is one of the common methods used for recovery of nonferrous metals as well as valuable metals from WEEE due to its capability to accept any forms of scrap as the feed. Thus, WEEE can be used as a part of raw materials in the pyrometallurgy process (Kaya, 2016).

Pyrometallurgical operation involves pre-treatment of WEEE (i.e. dismantling, shredding and physical processing using magnetic separation etc.) as the first step and followed by smelting process of enriched metal product to obtain copper in WEEE. Then, the extracted metal is being further treated to purification stage which is electrolytic refining to produce higher purity copper and eliminate any volatile matters while slimes collected from copper electrorefining are further refined to recover other precious metals including Ag, Au, Pt, Pd, Rh, Ru and Ir.

The advantages of pyrometallurgy method are it give fast result and require shorter operation time compared to hydrometallurgical and biological method. However, each method has their own drawbacks where pyrometallurgical method is require high energy consumption higher cost. The smelting process which uses heat to extract the metal from the ore generate large amount of slag and fumes of heavy metals (Kaya, 2016). Besides, if the feed contains PVC or plastic element, it may lead to formation of dioxins and furans, volatile metals and dust which cause severe environment problems (Tuncuk et al., 2012). The lack of metal recovery on individual species make pyrometallurgical method unpreferable (Ashiq et al., 2019).

2.9.2 Hydrometallurgical method

The hydrometallurgy process is an alternative to the pyrometallurgy route in which the hydrometallurgical approach is more selective toward metal recovery from WPCBs or pre-treated PCBs (Ashiq et al., 2019). It is easier to control and has fewer environmental consequences than the pyrometallurgical route. The large amount of base metal in WPCBs cause significant impact on the process's economics in the recovery of base metal in WPCBs. Furthermore, recovering base metals ensures that precious metals are enriched in the solid residue, making them easier to leach out later (Ghosh et al., 2015). Hydrometallurgical processes are primarily used for the recovery of metallic-ferrous elements where the extraction of the metal content is profitable and low-cost operation is required. Different hydrometallurgical processes are used depending on the substrate material (ceramic, glass, or polymer) (Li et al., 2017). A large amount of liquid is used in the hydrometallurgical process, which produces sludge, which must be disposed of carefully to reduce environmental hazards. The disadvantage of this process is the slow leaching kinetic, which can take days or months to complete the leaching reaction. Electro-oxidation leaching can help reduce acid consumption while recovering valuable metals without loss.

2.9.3 Bioleaching method

Metals from e-waste can be recovered using a bioleaching method developed in the 1980s. This method's mechanism involves the interaction of microorganisms and e-waste to recycle metals. The microorganisms involved in the interaction are classified as either autotrophic bacteria or heterotrophic bacteria. Acidithiobacillus thiooxidans (At. thiooxidans) and Acidithiobacillus ferroxidans (At. ferroxidans) are autotrophic bacteria, while Aspergillus niger and Penicillium simplicissimum are heterotrophic bacteria (Liang et al., 2013). When compared to traditional pyrometallurgy and hydrometallurgy operations, the bioleaching process has lower costs, causes less severe environmental issues, consumes less energy, and is easier to control. However, the bioleaching method has a limited application in industrial systems and is only suitable for small-scale operations. Even though the bioleaching method recovers more metals from e-waste, it takes a long time due to the time required for the microorganisms to react.

Many research have shown high recovery of metals from WPCBs using bioleaching method despite its disadvantages recently. A study using autotrophic bacteria which involve Acidithiobacillus thiooxidans (At. thiooxidans) and Acidithiobacillus ferroxidans (At. ferroxidans) to leach copper from WPCBs shows a leaching rate of greater than 90% was achieved (Wang et al., 2009). The leaching rate of copper, nickel, zinc, and lead increased dramatically when mixed cultures of Acidithiobacillus thiooxidans (At. thiooxidans) and Acidithiobacillus ferroxidans (At. ferroxidans) were applied compared to individual cultures (Liang et al., 2013). They concluded this bioleaching approach enhanced the redox potential and lowered pH value in the case of mixed culture.

2.10 Hydrometallurgical Method

Different type of leaching such as cyanide leaching, acid and alkali leaching, thiosulfate leaching, thiourea leaching and halide leaching, have their own advantages and disadvantages which will be discuss below. The summary of the chemical reaction in each leaching type was presented in Table 2.6.

Table 2.6 Summary of chemical reaction in each leaching type (Pant et al., 2012)

Chemical Leaching	**Chemical Reaction**
Cyanide Leaching	Gold dissolution: $4Au + 8CN^{-} \rightarrow 4Au(CN)_2^{-} + 4e^{-}(Anode)$ $O^2 + 2H_2O + 4e \rightarrow 4OH^{-}(Cathode)$ $4Au + 8CN^{-} + O^2 + 2H_2O \rightarrow 4Au(CN)_2^{-} + 4OH^{-}(overall\ reaction)$ Silver dissolution: $4Ag + 8\,CN^{-} + O_2 + 2H_2O \rightarrow 4AgCN + 4OH^{-}$ Palladium dissolution: $4Pd + 4CN^{-} + O_2 + 2H_2O \rightarrow 4Pd(CN)_2^{-} + 4OH^{-}$ Platinum dissolution: $4Pt + 8CN^{-} + O_2 + 2H_2O \rightarrow 4Pt(CN)_2^{-} + 4OH^{-}$
Sulfuric acid Leaching	Cu dissolution: $Cu + 2H^{+} + H_2O_2 \rightarrow Cu^{2+} + 2H_2O$ Cu dissolution with oxidant(ferric ion): $Cu + Fe_2(SO_4)_3 \rightarrow CuSO_4 + 2FeSO_4$ Cu dissolution with oxidant(oxygen) $Cu + 1/2\ O_2(g) + H_2SO_4(aq) \rightarrow CuSO_4 + H_2$
Nitric acid Leaching	Copper dissolution: $4HNO_3 + 3Cu \rightarrow 3Cu(NO_3)_3 + 2NO + 4H_2O$ Lead dissolution: $Pb + 2HNO_3 \rightarrow Pb(NO_3)_2 + H_2$ Tin dissolution: $Sn + 4HNO_3 \rightarrow H_2SnO_3 + 4NO_2 + H_2O$