

**DEVELOPMENT OF AN INTEGRATED TECHNOLOGY FOR
METAL RECOVERY AND GENERATION OF VALUABLE
PRODUCTS FROM E-WASTE**

PRASHANT RAM JADHAO



**DEPARTMENT OF CHEMICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY DELHI**

OCTOBER 2022

© Indian Institute of Technology Delhi (IITD), New Delhi, 2022

**DEVELOPMENT OF AN INTEGRATED TECHNOLOGY FOR
METAL RECOVERY AND GENERATION OF VALUABLE
PRODUCTS FROM E-WASTE**

by

**PRASHANT RAM JADHAO
DEPARTMENT OF CHEMICAL ENGINEERING**

Submitted

In fulfilment of the requirements of the degree of
**DOCTOR OF PHILOSOPHY
TO THE**



**INDIAN INSTITUTE OF TECHNOLOGY DELHI
OCTOBER 2022**

Certificate

This is to certify that the thesis entitled “**Development of an Integrated Technology for Metal Recovery and Generation of Valuable Products from E-waste**” submitted by **Mr. Prashant Ram Jadhao** to the Indian Institute of Technology Delhi, for the award of the degree of **Doctor of Philosophy**, is a record of the original bonafide research work carried out by him. He has worked under my supervision and has fulfilled the requirements, which to my knowledge, has reached the requisite standard for the submission of this thesis. The results contained in this thesis have not been submitted in part or full to any University or Institute for the award of any degree or diploma.



Prof. K. K. Pant

Supervisor

Department of Chemical Engineering

Indian Institute of Technology Delhi



Prof. K. D. P. Nigam

Co-supervisor

Department of Chemical Engineering

Indian Institute of Technology Delhi

Acknowledgements

This gives me immense pleasure to express my heartiest gratitude and a deep sense of respect to **Prof. K. K. Pant** and **Prof. K. D. P. Nigam** under whose able guidance I ventured to undertake this effort. I am grateful to them for their invaluable guidance, valuable suggestions, constructive criticism, constant encouragement, and moral support, without which it had not been possible for me to reach this level of achievement in this work.

I am also thankful to the Head of the Department of Chemical Engineering Indian Institute of Technology, Delhi for providing the necessary facilities and support to carry out research. I would like to extend my sincere gratitude to my research committee members Prof. Shantanu Roy, Prof. Anil Verma, and Prof. S. N. Naik for their valuable suggestions and critical review of my work. I am also thankful to all the members of the Central Research Facility (CRF) for providing me with the facilities to carry out my research work.

I express my special thanks to my senior lab members Dr. Garima Chauhan, Dr. Dinesh Kumar, Dr. Tarak Mondal, Dr. Samuel Kassaye, Dr. Sonal, Dr. Rohit Kumar, Dr. Sonit Balyan, Dr. Ejaz Ahmad, Dr. Ashish Pandey, Dr. Kaushal Parmar, Dr. Sourabh Mishra, Dr. Sonal Asthana, Dr. Arun, Dr. Arindam Modak, Dr. Ashish Bohre, and Dr. Kunwar Pal for their time-to-time outstanding scientific guidance and for making research work more cordial. I would like to thank my lab members Dr. Shireen Qureshi, Mr. Akshay Mankar, Mrs. Uma Dwivedi, Mr. Ramdayal Panda, Mr. Rajan Singh, Ms. Komal Tripathi, Mr. Sagar Dhanushkar, Ms. Snigdha Mishra, Mr. Vaibhav Pandey, Ms. Shreya Singh, Ms. Akshata Ramteke, Ms. Amrita Preetam, Mr. Venkanna, Mr. Pranit, Mr. Avijit, Mr. Marut Jain, Mr. Abhisek Sahoo, Ms. Shally Gupta, Ms. Nidhi, Ms. Aisha, Ms. Neethu, and all other research scholars from Catalytic Reaction Engineering Laboratory for their support, time to time help and encouragement during my research work. I am grateful to my friends and colleagues of

IIT Delhi Dr. Aditya Singh, Mr. Mohit Tiwari, Dr. Bhawan Singh, Mr. Amrish Kumar, Ms. Farah Naaz, and Mr. Aniket Ambekar for their help and support during my research work. I would like to extend my thanks to Mr. Vishesh Kumar, Mr. Krishna Kumar, Mr. Suchit Kumar, and Mr. Vijay Pal for their constant help in every possible way to carry forward my research.

I would like to thank my friends who became family Ms. Vallari Chourasia, Mr. Khushraj Meena, Mr. Navneet Yadav, Mrs. Ankita, Mrs. Isha Garg, Mrs. Neha Kumari, Ms. Charu Rawat, Mr. Puneet Jha, and Mr. Snehil Pandey for always being there for me and supporting me through tough times. Finally and most importantly, it is my pleasure to express my heartiest appreciation to my beloved family. My abilities and positive attitude towards life are all because of my family. I am thankful to my parents Mr. Ram Ganpat Jadhao, Mrs. Jyoti Ram Jadhao, and sister Ms. Kiran Jadhao for their blessings, constant support, motivation, and being my side throughout my life and career. Their blessings and love always provided me strength and enthusiasm to do something with more perfection. I can't thank them enough for their sacrifices during my research work.

I also want to express my sincere thanks to all those who were directly or indirectly helped me at various stages of this work thereby making it a total success.

At last thanks to the almighty God for his blessing and giving me patience, strength, and peace throughout the journey of life.

Prashant Ram Jadhao

ABSTRACT

Electronic waste (e-waste) is one of the fastest-growing waste streams with an annual growth rate of 3-5%. India is the 3rd largest producer of e-waste and produced around 3.23 million metric tonnes of e-waste in 2019. The huge generation of e-waste, presence of toxic materials, and lack of infrastructure to manage e-waste pose a serious threat to the environment as well as to human health. On the other hand, e-waste is termed as “urban mines” as it contains valuable materials such as metals and plastic which account for 75 wt.% of the total mass. Thus, e-waste recycling provides an opportunity for resource recovery and its simultaneous conservation.

In the present study, attempts have been made to develop an integrated technology for metal recovery and the generation of valuable products from e-waste. Waste printed circuit boards (WPCB) were collected from the local area and were used as a source of e-waste. The pyrolysis of e-waste was performed at lab scale as well as pilot-scale and an experimental setup with a capacity to pyrolyze 10 kg/h of e-waste was used for the pilot-scale study. Initially, the metallic fraction was recovered from WPCB using pyrolysis and chemical-free green ultrasonication technology at the lab scale. Under optimum operating pyrolysis conditions i.e. 400 °C temperature and 20 minutes of pyrolysis time, 60 wt.% solid product was obtained. The solid product was further subjected to a novel ultrasonication process which resulted in 90 wt.% metallic fraction recovery within 30 minutes. Moreover, the transfer of precious metals (Au, Ag, Pd, and Pt) was nearly 100% to the metallic fraction. Furthermore, at the pilot scale study, the yield of solid, liquid, and gaseous products was approximately 75 wt.%, 5 wt.%, and 20 wt.% respectively at the optimized conditions of 500 °C temperature, 10 kg/h feed rate, and 20 min of residence time. The gaseous product mainly consisted of H₂, CH₄, CO, and CO₂, having a heating value of 28 MJ/kg. The liquid product

obtained is majorly comprised of phenol and benzene derivative compounds. The heating value of the liquid product is around 32 MJ/kg which can be used for the generation of energy or as feedstock for the recovery of chemicals. Moreover, the present study has successfully demonstrated the removal of bromine from the liquid product by adding polypropylene during the pyrolysis process.

Metals are the most valuable components of e-waste and for metal recovery, ammonia-ammonium sulfate and methanesulfonic acid (MSA) leaching were used. In the case of ammonia-ammonium sulfate leaching, the maximum recovery of Cu, Ni and Zn was around 100%, 90%, and 75% respectively under the optimized conditions of 90 g/L ammonia, 180 g/L ammonium sulfate, 0.4 M H₂O₂, 4 h of reaction time, L/S ratio of 20 mL/g, 80 °C temperature and agitation speed of 700 rpm. Moreover, electrowinning was employed for the selective Cu recovery which results in the recovery of Cu with nearly 98% purity. In the case of MSA leaching, almost complete extraction of Cu and Zn was achieved whereas 90% Ni was extracted under the optimized process condition of 1 M MSA, 0.6 M H₂O₂, 2 h of reaction time, L/S ratio of 20 mL/g, 50 °C temperature and 500 rpm stirring speed. In addition, the recovery of Cu and Zn was performed using the combination of cementation and electrowinning which resulted in the recovery of Cu and Zn with 99.9% purity. The kinetic study revealed that metal extraction is a diffusion-controlled process.

The comparative analysis between ammonia-ammonium sulfate leaching and MSA leaching at optimized conditions revealed that the reaction time, temperature, and stirring speed are significantly lower in the case of MSA leaching which makes it a more efficient and economical process. Furthermore, the MSA is contemplated as a biodegradable green solvent and an aqueous solution of MSA does not evolve any toxic compounds under normal conditions. These properties make MSA more suitable to develop an environmentally benign

process for the recovery of metals from WPCB. Therefore, MSA leaching is recommended for the recovery of metals from WPCB over ammonia-ammonium sulfate leaching.

Overall, based on the investigations in the present study an integrated approach consisting of pyrolysis and MSA leaching is recommended for e-waste recycling. The proposed approach can efficiently reduce the problem of e-waste disposal along with the generation of valuable products, energy, and recovery of metals. The economic analysis of the integrated process was carried out for 1 TPD e-waste recycling plant. Based on the economic analysis the payback period for the 1 TPD e-waste recycling plant is around 3.05 years and IRR was calculated as 30.45%. Both processes i.e. pyrolysis and MSA leaching processes are eco-friendly and therefore, the proposed integrated approach will provide a sustainable solution for e-waste management along with metal recovery and generation of valuable liquid and gaseous products.

सारांश

इलेक्ट्रॉनिक कचरा (ई-कचरा) 3-5% की वार्षिक वृद्धि दर के साथ सबसे तेजी से बढ़ने वाले अपशिष्ट पदार्थों में से एक है। पूरी दुनिया में भारत ई-कचरे का तीसरा सबसे बड़ा उत्पादक है और 2019 में भारत ने लगभग 3.23 मिलियन मीट्रिक टन ई-कचरे का उत्पादन किया। ई-कचरे कि बड़े पैमाने पर उत्पादकता, जहरीले पदार्थों की उपस्थिति, और ई-कचरे के प्रबंधन के लिए बुनियादी ढांचे की कमी पर्यावरण के साथ-साथ मानव स्वास्थ्य के लिए भी बेहद हानिकारक है। दूसरी ओर, ई-कचरे को "शहरी खदानें" कहा जाता है क्योंकि इसमें धातु और प्लास्टिक जैसी मूल्यवान सामग्री होती है जो कुल द्रव्यमान का 75 wt.% होती है। इस प्रकार, ई-अपशिष्ट पदार्थों के पुनर्चक्रण से न केवल संसाधन पुनः प्राप्ति होती है वरन इसके संरक्षण का कार्य भी पूर्ण होता है।

वर्तमान अध्ययन में, ई-कचरे से धातुओं तथा अन्य मूल्यवान पदार्थों के उत्पादन के लिए एकीकृत प्रौद्योगिकी विकसित करने का प्रयास किया गया है। अपशिष्ट मुद्रित सर्किट बोर्ड (डब्ल्यूपीसीबी) पास के स्थानीय क्षेत्र से एकत्र किए गए और ई-कचरे के स्रोत के रूप में उपयोग किए गए थे। ई-कचरे का पायरोलिसिस, प्रयोगशाला के साथ-साथ पायलट स्तर पर किया गया था और पायलट स्तर के अध्ययन के लिए 10 किलो प्रति घंटा ई-कचरे को पायरोलाइज करने की क्षमता वाला एक प्रायोगिक संयंत्र प्रयोग किया गया था। प्रारंभ में, प्रयोगशाला स्तर पर पायरोलिसिस और रासायन रहित तथा पर्यावरण अनुकूल अल्ट्रासोनिकेशन तकनीक का उपयोग करके डब्ल्यूपीसीबी से धातु प्राप्त की गई। इष्टतम ऑपरेटिंग पायरोलिसिस स्थितियों यानी 400 °C तापमान और 20 मिनट के पायरोलिसिस समय के तहत, 60 wt.% ठोस उत्पाद प्राप्त किया गया था। ठोस उत्पाद को आगे अल्ट्रासोनिकेशन प्रक्रिया के अधीन किया गया, जिसके परिणामस्वरूप 30 मिनट के भीतर 90 wt.% धातु अंश की प्राप्ति हुई। इसके अलावा, कीमती धातुओं (Au, Ag, Pd, और Pt) का स्थानांतरण धातु अंश में लगभग 100% था। इसके अलावा, 500 °C तापमान, 20 मिनट समय, तथा फ़ीड दर 10 किलोग्राम प्रति घंटा की अनुकूलित परिस्थितियों में,

प्रायोगिक पैमाने के अध्ययन में, ठोस, तरल और गैसीय उत्पादों की उपज क्रमशः लगभग 75 wt.%, 5 wt.%, और 20 wt.% थी. गैसीय उत्पाद में मुख्य रूप से H₂, CH₄, CO, और CO₂ होते हैं, जिनका उष्णता मान 28 मेगाजूल प्रति किलोग्राम होता है. प्राप्त तरल उत्पाद में मुख्य रूप से फिनोल और बेंजीन व्युत्पन्न यौगिक शामिल होते हैं. तरल उत्पाद का उष्णता मान लगभग 32 मेगाजूल प्रति किलोग्राम है जिसका उपयोग ऊर्जा उत्पादन के लिए या रसायनों की प्राप्ति के लिए फीडस्टॉक के रूप में किया जा सकता है. इसके अलावा, वर्तमान अध्ययन में पायरोलिसिस प्रक्रिया के दौरान पॉलीप्रोपाइलीन जोड़कर तरल उत्पाद से ब्रोमीन को हटाने का सफलतापूर्वक प्रदर्शन किया है.

धातु ई-कचरे के सबसे मूल्यवान घटक हैं और धातु की प्राप्ति के लिए, अमोनिया-अमोनियम सल्फेट और मीथेनसल्फोनिक एसिड (एमएसए) लीचिंग का उपयोग किया गया था. अमोनिया-अमोनियम सल्फेट लीचिंग के प्रयोग में, 90 ग्राम प्रति लीटर अमोनिया, 180 ग्राम प्रति लीटर अमोनियम सल्फेट, 0.4 मोलर हाइड्रोजन परॉक्साइड, प्रतिक्रिया समय 4 घंटे, एल/एस अनुपात 20 मिलीलीटर प्रति ग्राम, 80 °C तापमान और 700 आरपीएम की आलोड़न गति की अनुकूलित स्थितियों के तहत Cu, Ni और Zn की अधिकतम प्राप्ति क्रमशः लगभग 100%, 90% और 75% थी. इसके अलावा, इलेक्ट्रोविनिंग को चयनात्मक Cu पुनर्प्राप्ति के लिए नियोजित किया गया था जिसके परिणामस्वरूप Cu की लगभग 98% शुद्धता के साथ प्राप्ति हुई. एमएसए लीचिंग के प्रयोग में, 1 मोलर एमएसए, 0.6 मोलर हाइड्रोजन परॉक्साइड, प्रतिक्रिया समय 2 घंटे, एल/एस अनुपात 20 मिलीलीटर प्रति ग्राम, 50 °C तापमान और 500 आरपीएम आलोड़न गति की अनुकूलित स्थितियों के तहत Cu और Zn का लगभग पूर्ण निष्कर्षण हासिल किया गया था, जबकि Ni को 90% प्राप्त किया गया. इसके अलावा, सीमेंटेशन और इलेक्ट्रोविनिंग के संयोजन का उपयोग करके Cu और Zn की रिकवरी की गई, जिसके परिणामस्वरूप Cu और Zn की 99.9% शुद्धता के साथ रिकवरी हुई. गतिज अध्ययन से पता चला कि धातु निष्कर्षण एक प्रसार-नियंत्रित प्रक्रिया है.

अनुकूलित परिस्थितियों में अमोनिया-अमोनियम सल्फेट लीचिंग और एमएसए लीचिंग के बीच तुलनात्मक विश्लेषण से पता चला है कि एमएसए लीचिंग के मामले में प्रतिक्रिया समय, तापमान और आलोड़न की गति काफी कम है जो इसे अधिक कुशल और किफायती प्रक्रिया बनाती है। इसके अलावा, एमएसए को एक बायोडिग्रेडेबल ग्रीन सॉल्वेंट के रूप में माना जाता है और एमएसए का जलीय घोल सामान्य परिस्थितियों में किसी भी जहरीले यौगिक को विकसित नहीं करता है। ये गुण एमएसए को डब्ल्यूपीसीबी से धातुओं की प्राप्ति के लिए पर्यावरण की दृष्टि से अनुकूल प्रक्रिया विकसित करने के लिए अधिक उपयुक्त बनाते हैं। इसलिए, अमोनिया-अमोनियम सल्फेट लीचिंग की तुलना में डब्ल्यूपीसीबी से धातुओं की प्राप्ति के लिए एमएसए लीचिंग प्रभावी साबित हुई है।

कुल मिलाकर, वर्तमान अध्ययन में जांच के आधार पर ई-अपशिष्ट पुनर्चक्रण के लिए पायरोलिसिस और एमएसए लीचिंग से युक्त एकीकृत दृष्टिकोण उचित माना गया है। प्रस्तावित तकनीक मूल्यवान उत्पादों, ऊर्जा और धातुओं की प्राप्ति के साथ-साथ ई-कचरे के निपटान की समस्या को कुशलता से कम कर सकता है। 1 टीपीडी ई-अपशिष्ट पुनर्चक्रण संयंत्र के लिए एकीकृत प्रक्रिया का आर्थिक विश्लेषण किया गया। आर्थिक विश्लेषण के आधार पर 1 टीपीडी ई-अपशिष्ट पुनर्चक्रण संयंत्र के लिए प्रत्यावर्तन अवधि समय लगभग 3.05 वर्ष है और आईआरआर की गणना 30.45 प्रतिशत के रूप में की गई थी। दोनों प्रक्रियाएं यानी पायरोलिसिस और एमएसए लीचिंग पर्यावरण के अनुकूल हैं और इसलिए, प्रस्तावित एकीकृत तकनीक धातु की प्राप्ति और मूल्यवान तरल और गैसीय उत्पादों के उत्पादन के साथ-साथ ई-कचरा प्रबंधन के लिए एक स्थायी समाधान प्रदान करेगा।

TABLE OF CONTENT

Title	Page No.
<i>Certificate</i>	I
<i>Acknowledgements</i>	II
<i>Abstract</i>	IV
<i>Table of Content</i>	VII
<i>List of Figures</i>	XIV
<i>List of Tables</i>	XX
Chapter 1: Introduction	1
1.1. Background	1
1.2. Composition of e-waste	4
1.2.1. Metal composition of e-waste	5
1.2.2. Plastic content in e-waste	6
1.3. Hazardous effects of e-waste	8
1.4. Research objectives	10
1.5. Overview of the dissertation	11
Chapter 2 : Literature Review	13
2.1. Physical separation	14
2.1.1. Gravity separation	14
2.1.2. Magnetic separation	15
2.1.3. Electrostatic separation	16

2.1.4.	Flotation	18
2.1.5.	Perspective of physical separation processes	19
2.2.	Chemical recycling of e-waste plastic	20
2.2.1.	Pyrolysis of e-waste plastic	20
2.2.2.	Catalytic pyrolysis of e-waste plastic	27
2.2.3.	Gasification of e-waste plastic	34
2.2.4.	Depolymerization of e-waste plastic using supercritical fluids	38
2.3.	Recovery of metals from e-waste	41
2.3.1.	Pyrometallurgy	42
2.3.2.	Hydrometallurgy	45
2.3.2.1.	Cyanide leaching	45
2.3.2.2.	Thiosulfate leaching	47
2.3.2.3.	Thiourea leaching	54
2.3.2.4.	Halide leaching	60
2.3.2.5.	Acid leaching	65
2.4.	Research gaps	69
Chapter 3 : Experimental Details		72
3.1.	Materials	72
3.2.	Recovery of metallic fraction using pyrolysis and ultrasonication	72
3.2.1.	Pre-treatment of WPCB	73
3.2.2.	Pyrolysis of WPCB at lab scale	73

3.2.3.	Recovery of metallic fraction using ultrasonication	75
3.3.	Pilot scale study for pyrolysis of WPCB	75
3.3.1.	Size reduction of WPCB	75
3.3.2.	Pyrolysis of WPCB at pilot scale	76
3.4.	Metal recovery using ammonia-ammonium sulfate leaching	77
3.4.1.	Leaching experiments	77
3.4.2.	Electrowinning of Cu	78
3.5.	Metal recovery using MSA	80
3.5.1.	Metal leaching	80
3.5.2.	Individual recovery of Cu and Zn	81
3.5.2.1.	Recovery of Cu using cementation	81
3.5.2.2.	Recovery of Zn using electrowinning	81
3.6.	Characterization techniques	82
3.6.1.	Microwave plasma atomic emission spectroscopy	82
3.6.2.	Thermogravimetric analysis (TGA)	82
3.6.3.	Fourier transform infrared (FT-IR) spectroscopy	83
3.6.4.	Ultimate analysis	83
3.6.5.	X-ray diffraction (XRD) analysis	83
3.6.6.	Scanning electron microscopy (SEM) and Energy dispersive X-ray (EDX)	83
3.6.7.	Raman spectroscopy	84

3.6.8.	Gaseous product analysis	84
3.6.9.	Liquid product analysis	84
Chapter 4 : Environmentally Friendly Approach for the Recovery of Metallic Fraction from WPCB using Pyrolysis and Ultrasonication		86
4.1.	Introduction	86
4.2.	Result and discussion	86
4.2.1.	Feedstock characterization	86
4.2.1.1.	Elemental composition and ultimate analysis of WPCB	86
4.2.1.2.	Thermogravimetric analysis	87
4.2.1.3.	Fourier Transform Infrared Spectroscopy analysis	89
4.2.2.	Pyrolysis of WPCB	90
4.2.2.1.	Effect of temperature	90
4.2.2.2.	Effect of holding time	92
4.2.3.	Recovery of metallic fraction using ultrasonication	93
4.2.4.	Analysis of solid residue	97
4.2.5.	Mass balance diagram and basis for the pilot scale study	101
4.3.	Summary	102
Chapter 5 : Pilot-scale Study for the Pyrolysis of WPCB and Debromination of the Liquid Product		104
5.1.	Introduction	104

5.2.	Result and discussion	104
5.2.1.	Feed characterization	104
5.2.1.1.	Metal analysis	104
5.2.1.2.	Thermogravimetric analysis	106
5.2.2.	Pyrolysis experiments at pilot scale	107
5.2.2.1.	Effect of temperature on pyrolysis	107
5.2.2.2.	Effect of feed rate	108
5.2.3.	Product analysis	109
5.2.3.1.	Solid product	109
5.2.3.2.	Gaseous product	112
5.2.3.3.	Liquid product	113
5.2.4.	Py-GC/MS analysis and mechanism of WPCB pyrolysis	114
5.2.5.	Effect of PP addition	118
5.2.6.	Mass balance of the pilot scale study	121
5.3.	Summary	122
Chapter 6 : Recovery of Metals from WPCB using Alkali Leaching		123
6.1.	Introduction	123
6.2.	Results and discussion	124
6.2.1.	Extraction of metals from WPCB	124
6.2.1.1.	Effect of ammonia concentration on metal extraction	124
6.2.1.2.	Effect of ammonium sulfate on metal extraction	127

6.2.1.3.	Effect of H ₂ O ₂ on metal extraction	128
6.2.1.4.	Effect of reaction time on metal extraction	130
6.2.1.5.	Effect of L/S ratio on metal extraction	131
6.2.1.6.	Effect of temperature on metal extraction	132
6.2.1.7.	Effect of agitation speed on metal extraction	133
6.2.1.8.	Zn extraction	134
6.2.2.	Kinetic study of metal extraction	135
6.2.3.	Electrowinning of Cu	139
6.2.4.	Comparative study	141
6.3.	Summary	144
Chapter 7 : A Sustainable Route for the Recovery of Metals from WPCB using Methanesulfonic Acid		145
7.1.	Introduction	145
7.2.	Results and discussion	146
7.2.1.	Extraction of metals from WPCB	146
7.2.1.1.	Effect of MSA concentration on metal extraction	146
7.2.1.2.	Effect of H ₂ O ₂ concentration	149
7.2.1.3.	Effect of stirring speed	151
7.2.1.4.	Effect of L/S ratio	152
7.2.1.5.	Effect of time	153
7.2.1.6.	Effect of temperature	154

7.2.2.	Kinetic study	155
7.2.3.	Individual recovery of Cu and Zn metals	159
7.2.3.1.	Cu recovery using cementation	159
7.2.3.2.	Zn recovery	162
7.2.4.	Pollution prevention, resources recovery, and circular economy	164
7.2.5.	Applications and future research prospects	166
7.2.6.	Comparative analysis of alkali leaching and MSA leaching	168
7.2.7.	Proposed integrated approach	169
7.2.8.	Economic analysis	171
7.2.8.1.	Capital and operating cost	171
7.2.8.2.	Net revenue generation	173
7.3.	Summary	175
Chapter 8 : Conclusions and Recommendations		176
8.1.	Conclusions	176
8.2.	Recommendations	179
References		180
Appendix		221
1.	Pilot plant images	221
2.	Pyrolysis product images	222
3.	Metal recovery images	223
Biodata		224

LIST OF FIGURES

Figure No.	Figure Caption	Page No.
1.1	Classification of e-waste	2
1.2	The global quantity of e-waste generated	3
1.3	E-waste scenario in top 10 e-waste producing nations: (a) E-waste produced in 2019 (MMT) (b) E-waste produced kg per capita (c) % E-waste collected and recycled	3
1.4	Overall composition of e-waste	4
1.5	Value of material that can be recycled from e-waste	6
1.6	Plastic composition of e-waste	8
2.1	E-waste recycling using chemical and physical processes	13
2.2	Separation process using corona electrostatic separator	17
2.3	Schematic of eddy current separation process	18
2.4	E-waste plastic conversion technologies	20
2.5	Proposed reaction pathways for thermal degradation of PCBs	25
2.6	Debromination of TBBPA during catalytic pyrolysis	31
2.7	Possible mechanism of Br fixation during catalytic pyrolysis	33
2.8	Application of gasification for e-waste processing	37
2.9	Application of supercritical fluid technology for e-waste treatment	41

2.10	Overall approach for recovery of metals from e-waste using chemical recycling	42
2.11	Ronnskar Smelter process for metal recovery	43
3.1	Schematic diagram of the experimental procedure for recovery of metallic fraction	73
3.2	Reactor setup for the pyrolysis of WPCB at lab scale	74
3.3	Process flow diagram of the pyrolysis pilot plant	77
3.4	Typical experimental setup for the leaching of metals	79
3.5	Metal recovery using ammonia-ammonium sulfate leaching	79
3.6	Overall methodology to recover metals from WPCB using MSA leaching	81
4.1	Thermogravimetric analysis of WPCB	88
4.2	FT-IR analysis of WPCB	89
4.3	Effect of temperature on yield of the solid product	91
4.4	FT-IR analysis of solid residue	92
4.5	Effect of holding time on the yield of solid product	93
4.6	Effect of ultrasonication time on the separation of metallic fraction	95
4.7	Raman analysis of the solid residue obtained at optimum process conditions	98
4.8	XRD analysis of solid residue obtained at optimum process	100

	condition	
4.9	SEM image of solid residue obtained at optimum process condition	100
4.10	Mass balance of the process of metallic fraction recovery	102
5.1	Thermogravimetric analysis of WPCB	107
5.2	Effect of temperature on pyrolysis of WPCB	108
5.3	Effect of feed rate on pyrolysis of WPCB	109
5.4	Gaseous product obtained after the pyrolysis of WPCB at 500 °C	113
5.5	Reaction pathway of WPCB pyrolysis based on Py-GC/MS analysis	117
5.6	Effect of PP addition on the removal of bromine from pyrolysis oil	120
5.7	Mass balance of the pilot-scale study for the pyrolysis of WPCB at 500 °C	121
6.1	Effect of ammonia concentration on Cu and Ni extraction (reaction conditions: 100 g/L (NH ₄) ₂ SO ₄ , 1 M H ₂ O ₂ , 20 mL/g of L/S, 3 h, 60 °C, 700 rpm)	126
6.2	Effect of ammonium sulfate concentration of Cu and Ni extraction (reaction conditions: 90 g/L NH ₃ , 1 M H ₂ O ₂ , 20 mL/g of L/S, 3 h, 60 °C, 700 rpm)	128
6.3	Effect of H ₂ O ₂ on extraction of Cu and Ni (reaction conditions: 90 g/L NH ₃ , 180 g/L (NH ₄) ₂ SO ₄ , 20 mL/g of L/S, 3 h, 60 °C, 700	129

	rpm)	
6.4	Effect of reaction time on extraction of Cu and Ni (reaction conditions: 90 g/L NH ₃ , 180 g/L (NH ₄) ₂ SO ₄ , 0.4 M H ₂ O ₂ , 20 mL/g of L/S, 3 h, 60 °C, 700 rpm)	130
6.5	Effect of L/S ratio on extraction of Cu and Ni (reaction conditions: 90 g/L NH ₃ , 180 g/L (NH ₄) ₂ SO ₄ , 0.4 M H ₂ O ₂ , 4 h, 60 °C, 700 rpm)	132
6.6	Effect of temperature on extraction of Cu and Ni (reaction conditions: 90 g/L NH ₃ , 180 g/L (NH ₄) ₂ SO ₄ , 0.4 M H ₂ O ₂ , 20 mL/g of L/S, 4 h, 700 rpm)	133
6.7	Effect of agitation speed on extraction of Cu and Ni (reaction conditions: 90 g/L NH ₃ , 180 g/L (NH ₄) ₂ SO ₄ , 0.4 M H ₂ O ₂ , 20 mL/g of L/S, 4 h, 80 °C)	134
6.8	Schematic of the metal extraction process based on the shrinking core model: (a) and (b) initial state at time = 0, and (c) state at time = t	136
6.9	Shrinking core model for chemical reaction-controlled extraction of (a) Cu and (b) Ni	137
6.10	Shrinking core model for diffusion-controlled extraction of (a) Cu and (b) Ni	138
6.11	Arrhenius plot for calculation of apparent activation energy for extraction of (a) Cu and (b) Ni	139

6.12	EDX analysis of the recovered Cu	140
6.13	SEM image of recovered Cu, inset shows the magnified view	140
7.1	Effect of MSA concentration on Cu, Zn and Ni extraction (reaction conditions: H ₂ O ₂ : 1 M, stirring speed: 500 rpm, time: 3 h, temperature: 40 °C, L/S ratio: 20 mL/g)	148
7.2	Eh-pH diagrams of Cu-H ₂ O, Zn-H ₂ O, and Ni-H ₂ O systems under similar extraction conditions (40 °C, 101 kPa)	149
7.3	Effect of H ₂ O ₂ concentration on Cu, Zn, and Ni extraction (reaction conditions: MSA: 1 M, stirring speed: 500 rpm, time: 3 h, temperature: 40 °C, L/S ratio: 20 mL/g)	151
7.4	Effect of stirring speed on the extraction of Cu, Zn, and Ni (reaction conditions: MSA: 1 M, H ₂ O ₂ : 0.6 M, time: 3 h, temperature: 40 °C, L/S ratio: 20 mL/g)	152
7.5	Effect of L/S ratio on the extraction of Cu, Zn and Ni (reaction conditions: MSA: 1 M, H ₂ O ₂ : 0.6 M, stirring speed, 500 rpm, time: 3 h, temperature: 40 °C)	153
7.6	Effect of time on the extraction of Cu, Zn and Ni (reaction conditions: MSA: 1 M, H ₂ O ₂ : 0.6 M, stirring speed, 500 rpm, L/S ratio: 20 mL/g, temperature: 40 °C)	154
7.7	Effect of temperature on the extraction of Cu, Zn and Ni (reaction conditions: MSA: 1 M, H ₂ O ₂ : 0.6 M, stirring speed, 500 rpm, L/S ratio: 20 mL/g, time: 2 h)	155

7.8	Shrinking core model for chemical reaction controlled extraction of (a) Cu, (b) Zn, and (c) Ni	157
7.9	Shrinking core model for diffusion-controlled extraction of (a) Cu, (b) Zn, and (c) Ni	158
7.10	Arrhenius plot to calculate activation energy for extraction of (a) Cu and (b) Zn and (c) Ni	159
7.11	EDX and SEM analysis of the recovered Cu	162
7.12	EDX and SEM analysis of the recovered Zn	164
7.13	Proposed flow sheet for the recovery of metals from WPCB using MSA leaching	167
7.14	Schematic of the proposed integrated approach for e-waste recycling	170
A1	E-waste pilot plant images	221
A2	Images of the products obtained from the pyrolysis at pilot scale	222
A3	Images of the products obtained after ultrasonication	222
A4	Images of the leaching solution (a) initial and (b) during cementation of Cu	223
A5	Photos of recovered (a) Cu and (b) Zn	223

LIST OF TABLES

Table No.	Table Caption	Page No.
1.1	Hazardous substances present in e-waste and their harmful effect on human health	9
2.1	Difference in densities of different components of e-waste	15
2.2	Summary of research work on the pyrolysis of e-waste in a fixed bed reactor	26
2.3	Research work carried out on catalytic pyrolysis of e-waste	33
2.4	Pyrometallurgical approach for metal recovery	44
2.5	Recovery of metal using cyanide leaching from e-waste	47
2.6	Thiosulfate leaching for metal recovery from e-waste	50
2.7	Recovery of metals using thiourea leaching from e-waste	57
2.8	Halide leaching for metal recovery from e-waste	63
2.9	Acid leaching for metal recovery from e-waste	67
4.1	Elemental composition and ultimate analysis of WPCB	87
4.2	Recovery of metallic fraction from WPCB	97
5.1	Elemental and ultimate analysis of WPCB	105
5.2	The metal analysis of solid product obtained after pyrolysis	111
5.3	Liquid product composition obtained at 500 °C pyrolysis	114

	temperature	
5.4	Volatile compounds obtained using Py-GC/MS analysis at 500 °C	116
6.1	Comparison with previous studies	141
7.1	The standard electrode potential for Cu, Zn, Ni and H ₂ O ₂	148
7.2	Assumptions for economic analysis	171
7.3	Capital cost for 1 TPD e-waste recycling plant	172
7.4	Operating cost of 1 TPD e-waste recycling plant/annum	173
7.5	Gross income from the sales of products per annum	174