Recovery of high added-value materials from waste printed circuit boards

Thesis submitted in partial fulfillment
for the Award of Degree

Doctor of Philosophy

By

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It is certified that the work contained in the thesis titled **'Recovery of high added-value materials from waste printed circuit boards'** by **Pushpa Gautam** has been carried out under my supervision and this work has not been submitted elsewhere for a degree.

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Pushpa Gautam

Dedicated

To

My Parents

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List of Abbreviations

Abbreviation	Description
WEEE	Waste electrical and electronic equipments
Mt	Million tonnes
PCBs	Printed circuit boards
wt%	Weight percent
WPCB	Waste-printed circuit board
CuO, Cu(II)O	Cupric oxide, copper oxide
ZnO	Zinc oxide
NiO	Nickel oxide
eV	Electron volt
NPs	Nanoparticles
$Cu(OH)_2/CuO$	Copper hydroxide/copper oxide
EEEs	Electrical and electronic equipments
UNU	United nations university
USD	United States dollar
e-waste	Electronic waste
kg	Kilogram
Cu	Copper
Ni	Nickel
Zn	Zinc
Al	Aluminium
Pb	Lead
Fe	Iron
Sn	Tin
Au	Gold
Ag	Silver
Pt	Platinum
Pd	Palladium
Cd	Cadmium
Hg	Mercury
SiO_2	Silicon dioxide / silica

Al_2O_3	Aluminium oxide
CaO	Calcium oxide
Kt	Kilo ton
ppm	Parts per million
ICSG	International copper study group
IBM	Indian bureau of mines
NMF	Non-metallic fraction
°C	degree Celsius
LNK carbonates	Li_2CO_3 (Lithium carbonate), Na_2CO_3 (Sodium carbonate), K_2CO_3 (Potassium carbonate)
K	Kelvin
CO_2	Carbon dioxide
Sb	Antimony
Bi	Bismuth
HCl	Hydrochloric acid
H_2SO_4	Sulphuric acid
H_2O_2	Hydrogen peroxide
HNO_3	Nitric acid
$HClO_4$	Perchloric acid
EDTA	Ethylene diamine tetraacetic acid
DTPA	Diethylene triamine penta acetate
Cr	Chromium
$FeCl_3$	Ferric chloride
$CuCl_2$	Copper(II) chloride
EoL	End-of-life
TV	Television
LTCC	Low-temperature co-fired ceramic
THSJs	through-hole solder joints
HAVP	High added-value products
EC	Electronic components
IC	Integrated circuit
Ta	Tantalum
CRT	Cathode ray tube

nm	nanometer
PVP	Polyvinylpyrrolidone
HEPES	4-(2-hydroxyethyl)-1-piperazine ethane sulfonic acid
DOPC	1,2-dioleoyl-Sn-glycero-3-phosphocholine
AC	Alternate current
ESM	Electronic scrap material
MLCCs	Multilayer ceramic capacitors
SnO_2	Tin oxide
Si	Silicon
RSCWs	Rejected Solar cell wafers
AgCl	Silver chloride
µm	micrometer
HF	Fluoric acid
RSM	Response surface methodology
MEMs	Micro-electromechanical system
PEG	Polyethylene glycol
RAM	Random access memory
BER	Brominated epoxy resin
DMF	Dimethyl formamide
β-NCD	β-native cyclodextrins
CTAB	Cetyl trimethyl ammonium bromide
$NaBH_4$	Sodium borohydride
PN-PCBs	Polymetallic nanoparticles from Printed Circuit Boards
RB4	Reactive blue 4
NaOH	Sodium hydroxide
NiMH	Nickel-metal hydride
SCM	Supercritical methanol
Cu_2O	Cuprous oxide
SCW	Supercritical water
EK	Electrokinetic
SIM	Subscriber Identity Module
NaOH	Sodium hydroxide

UV-vis	Ultra violet-visible
TiO_2	Titanium oxide
SCWO	Super Critical Water Oxidation
MB	Methylene Blue
P25	Mixed-phase titania commercial photocatalyst
MO	Methyl Orange
H_2O_2	Hydrogen peroxide
AAS	Atomic absorption spectroscopy
P-XRD	Powder X-ray diffraction
FTIR	Fourier transform infrared spectroscopy
ATR	Attenuated total reflectance
SEM	Scanning electron microscopy
EDS	Energy dispersive X-ray spectroscopy
EBSD	Electron backscatter diffraction
HR-SEM	High-resolution scanning electron microscopy
TEM	Transmission electron microscopy
SAED	Selected area electron diffraction
XPS	X-ray photoelectron spectroscopy
BET	Brunauer-Emmett-Teller
BJH	Barrett-Joyner-Halenda
DMA	n,n-Dimethyl acetamide
PTFE	Polytetrafluoroethylene
JCPDS	Joint Committee on Powder Diffraction Standards
v/v	Volume per volume
rpm	Revolutions per minute
M	Molar
CR	Congo Red
MB	Methylene Blue
LED	Light-emitting diode
ACORGA M5640	5-nonyl salicylaldoxine
RhB	Rhodamine blue
HAVPs	High added-value products

Al_2O_3	Aluminum Oxide
SiO_2	Silicon Dioxide
MgO	Magnesium Oxide
CaO	Calcium Oxide
BaO	Barium Oxide
NOx	Nitrogen Oxides
$Cu(NO_3)_2$	Copper Nitrate
$Cu(OH)_2$	Copper Hydroxide
FWHM	Full Width at Half Maximum
$O_2^{-\cdot}$	Superoxide radical
$OH^{\cdot}$	Hydroxyl radical
h^+_{VB}	Hole in valence band
e^-_{CB}	Electron in conduction band

PREFACE

Due to the rapid development in electronic industries and high consumer demand for upgrades in functionality and design, electrical and electronic equipment have a shorter lifetime in developed and developing countries markets, leading to tonnes of electronic waste. According to global transboundary e-waste flows monitor 2022, the worldwide generation of waste electrical and electronic equipment (WEEE) reached 41.8 million tonnes (Mt) in 2014, which increased to 44.7 Mt in 2016 and 53.6 Mt in 2019, and is expected to reach 74.7 Mt by 2030 and 110 Mt by 2050. Researchers have found that only 20% of the e-waste produced is being recycled every year and 80% is informally recycled, dumped, or incinerated, causing loss of valuable resources and environmental hazards. Printed circuit boards (PCBs), a valuable part of any e-gadget, contain up to 60 different elements and a significant metal content (40 wt%), should be viewed as valuable secondary resources. Their treatment not only reduces environmental impact compared to mining but also offers economic opportunities and promotes circular economies. Recycling with the only objective of waste management is not a striking scenario in emergent nations where economic interests oust environmental liabilities. Hence, it is essential to consider remanufacturing products in the process of WPCB recycling to re-utilize the recovered metals as starting material for production of commercially valuable products, e.g. nanomaterials. This would help acquire the goal of circular economy by closing the materials loop, decreasing inputs, reusing, minimizing waste, and efficiently recycling huge quantity of scrap electronics, creating wealth and reducing pollution. In this direction, nanotechnology has also been recently used to recover base metals, toxic metals, and precious metals in different sizes and morphologies. Oxides of transition metals, such as CuO, ZnO, NiO exhibit typical photocatalytic and catalytic attributes. Monoclinic cupric oxide, Cu(II)O, a p-type semiconductor, has a bandgap range of 1.2–1.8 eV. CuO offers diverse potential applications in fields of catalysis due to its thermal stability, superconductivity, and photocatalytic behaviour.

In view of this, we present an eco-friendly and integrated process for the recovery of valuable metals from discarded computer motherboard PCBs via a hydrometallurgical route. Chemical pre-treatment liberates metallic fractions from PCB layers, followed by nitric acid leaching to obtain a copper-rich solution. We synthesize copper oxide nanoparticles (CuO NPs) from the reclaimed copper, adding value to the recovered material. Furthermore, the recovered value-added material is explored as a potential photocatalyst for degradation of textile dyes in the presence of visible light.

The thesis is structured into seven chapters:

- Chapter I: Reviews e-waste generation, composition, and recycling techniques, emphasizing high-value materials recovered from electronic waste.
- Chapter II: Details the experimental methodology used for recovery steps.
- Chapter III: Discusses the characterization and leaching of bare PCBs from computer motherboards, achieving high leaching efficiency for copper and zinc.
- Chapter IV: Illustrates the recovery of copper as copper oxide nanoparticles from the leach liquor of waste PCBs of computer motherboards by precipitation followed by calcination route and details the structural analysis.
- Chapter V: Focuses on evaluating the photocatalytic properties of the synthesized nanoparticles for degrading textile dyes Congo Red and Methylene Blue.
- Chapter VI: Explores the recovery of $Cu(OH)_2/CuO$ and CuO nanostructures, via alkaline precipitation and low-temperature aging methods using the strip solution originated from laboratory-scale spent mobile phone printed circuit board recovery process and demonstrated their photocatalytic activity by evaluating Rhodamine Blue degradation.
- Chapter VII: Summarizes conclusions, outlines future work, and provides a

bibliography and publication list.

This integrated approach not only extracts valuable metals but also explores their applications, offering a sustainable solution to electronic waste management while contributing to environmental and economic benefits.