

Hydrometallurgical recovery of valuable metals from printed circuit boards of obsolete mobile phones



**Thesis submitted in partial fulfillment
for the Award of degree**

Doctor of Philosophy

By

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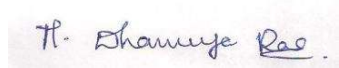
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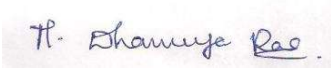
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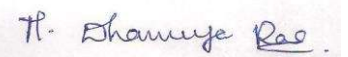
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(Mudila Dhanunjaya Rao)

Dedicated
To
My Beloved Parents
&
Teachers

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List of Abbreviations

Abbreviation	Description
°C	Degree centigrade
°	Degrees
%	Percentage
~	Approximately
θ	Theta
λ	Lambda (wavelength)
β	Beta (Separation factor)
α	Alpha
μ	Micro
ca.	Approximately
α -CD	Alpha-cyclodextrin
¹ H-NMR	Proton- Nuclear Magnetic Resonance Spectroscopy
1°, L1	Primary amide
2°, L2	Secondary amide
3°, L3	Tertiary amide
2-EH	2-ethyl hexanol
2FI	Two factor interaction
AAS	Atomic Absorption Spectrophotometer
ANOVA	Analysis of variance
Aqua regia	1:3 molar mixture of nitric and hydrochloric acid
BET	Brunauer-Emmett and Teller
BPA	Bisphenol-A
BSS	British Standard Sieve
CCD	Central Composite Design
CIC	Carbon-in-Column
CIL	Carbon-in-Leach
CIP	Carbon-in-Pulp
CPU	Central Processing Unit
C.V.%	Coefficient of Variance
D	Distribution coefficient, Dimentional
DBC	Dibutyl carbitol
DCM	Dichloromethane
df	degrees of freedom
DHEHA	N,N-di-hexyl-2-ethylhexainamide
DHOA	N,N-dihexyloctainamide
DOAA	N,N-di-n-octylacetamide
DOE	Design of Experiments
DOLA	N,N-di-n-octyllauramide
DMA	Dimethylacetamide
Ea	Activation energy
EEE	Electrical and Electronic Equipment
E-waste	Electronic waste
Eh	Reduction potential
Emf	Electromotive force
F	Model significant
GSM	Global system for mobile communications

h	hour
HDPE	High Density Poly Ethylene
H ₂ SO ₄	Sulfuric acid
HNO ₃	Nitric acid
HCl	Hydrochloric acid
H ₂ O ₂	Hydrogen peroxide
ICDD	International Centre for Diffraction Data
ICP-OES	Inductively Coupled Plasma-Optical Emission Spectroscopy
k	Reaction rate constant
K	Kelvin
L	Ligand
LIX and ACORGA	Brand names of commercial extractants in solvent extraction
M	Molar
MIBK	Methyl isobutyl ketone
min	minutes
MBHA	N-methyl-N-butylhexylamide
MDMHA	Methyl, dimethyl hexanamide
Mt	Metric ton
MOF	Metal Organic Framework
mm	millimeter
NaBr	Sodium bromide
NaCl	Sodium chloride
NaOH	Sodium hydroxide
NBS	N-bromosuccinamide
nm	nano meter
O/A	Organic/Aqueous
ppm	parts per million
py	pyridine
PID controller	Proportional–Integral–Derivative controller
PIM	Polymer Inclusion Membrane
PCB	Printed Circuit Board
p	Probability
PTFE	Polytetrafluoroethylene
R ²	Correlation coefficient
rpm	Revolutions per minute
RSM	Response Surface Methodology
SEM-EDS	Scanning Electron Microscopy-Energy Dispersive X-ray Spectroscopy
SX	Solvent extraction
USD	United States Dollar
UV-Vis	UV-Visible spectrophotometry
via	By way of
vs	versus
WEEE	Waste Electrical and Electronic Equipment
WPCB	Waste Printed Circuit Board
XRD	X-ray diffraction analysis

PREFACE

The rapid global rise in technology, tied in with consumer pressures for upgrades in functionality and design, has generated advanced electrical and electronic equipment with short lifespans. A consequence of this is large production of electronic waste (e-waste) which, in 2019 amounted to 53.6×10^6 metric tonnes (Mt), with a projected annual growth of 3-5%, three times more than for other waste streams. Reports on recycling rates vary, with estimates of around 20-30%. It is estimated that more than 70% of globally produced waste electrical and electronic equipment (WEEE) enter China, Africa and India for re-processing, much of it illegally, and often using crude, hazardous and inefficient processes. Dumping and incinerating large amounts of WEEE has severe impact on human life and the environment, as it leads to the release of toxic heavy elements such as lead, mercury, chromium, cadmium, beryllium, arsenic and antimony into the air, soil and water cycles. An end-of-life printed circuit board (PCB), a valuable part of any e-gadget, may contain up to 60 different chemical elements, and have a metal content as high as 40% by weight. Therefore, it should be viewed as a valuable secondary source of precious and base metals. The metal content of a PCB is typically ten to a hundred times higher than that of conventionally mined ores. It is estimated that recycling one ton of mobile phones could produce on average 130 kg of copper, 3.5 kg of silver, 0.34 kg of gold and 0.14 kg of Pd. On this basis, the global e-waste management market is projected to produce an annual revenue of USD 96 billion by the end of 2028. With an estimated 97% of the world population owning a mobile phone, it can be viewed as a plentiful feedstock for a recycling process. As such, the treatment of e-waste not only helps minimise the environmental impact of our technology-driven society by reducing pollution and energy demands compared to conventional mining practice, it also presents economic drivers for wealth creation and circular economies.

In view of this, we present an economical, eco-friendly and integrated process for the sequential recovery of valuable metals such as copper, nickel, zinc, gold and silver from discarded mobile phone PCBs through hydrometallurgical route. Initially, a chemical pre-treatment process was employed to liberate metallic fractions from non-metallic layers of downsized PCBs. A two-stage acid leaching process was proposed to provide a bulk separation of copper-rich solution in stage-1 and gold-rich solution in stage-2 leaching using liberated metal clads. Subsequent purification of the copper, nickel and zinc from stage-1 leach solution was also studied. Stage-2 leach solution was availed for the selective separation of gold and silver. Finally, the Design of Experimental (DOE) analysis using Response Surface Methodology (RSM) was also undertaken to validate the two-stage leaching process. The proposed work was divided into four major chapters, followed by the scope for future work, references, appendices and a list of publications.

The background representing the e-waste introduction, generation, recycling statistics and metal recovery techniques from waste printed circuit boards (WPCBs) were discussed in the **first chapter**. The detailed discussion of pre-separation processes, chemical techniques for metal recovery such as pyro, hydro and bio-hydrometallurgical processes, purification processes such as solvent extraction, adsorption, precipitation and ion exchange processes used for the recycling of e-waste were discussed with literature background. This chapter also focused on challenges and opportunities in the recovery of metals (particularly gold) and hurdles being faced during recycling. The motivation of the present research work was exploited by this chapter.

The **second chapter** describes the detailed overview of our research strategy, materials used and experimental details. The collection of obsolete mobile phones and pre-processing methods used for the separation of metallic and non-metallic fraction were mentioned initially. The chemical analysis of both non-metallic and metal clads was also

discussed in detail using X-ray diffraction (XRD) analysis, Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy (SEM-EDS), Atomic Absorption Spectroscopy (AAS) and Inductively Coupled Plasm-Optical Emission Spectroscopy (ICP-OES). The experimental methodology used for the leaching, solvent extraction and cementation was also discussed in this chapter.

The results and discussion chapter (**Chapter 3**) was sub-divided into four sections, as mentioned below.

3.1. Two-stage leaching from obsolete mobile phone PCBs: Extraction of copper, nickel and gold

3.2. Separation of copper and nickel from stage-1 leach solution

3.3. Separation of gold and silver from stage-2 leach solution

3.4. Validation of two-stage leaching through Response Surface Methodology (RSM) - A DOE study

In **section 3.1**, an efficient two-stage leaching process was developed. Stage-1 leaching describes the dissolution of copper, nickel and other base metals from obsolete mobile phone PCBs to facilitate the isolation of a gold-rich residue. Chemical pre-treatment of downsized PCBs produced a metallic portion for which the leaching parameters for copper and nickel were optimized, including the type of leaching reagent, temperature, time, pulp density and agitation speed. It was found that quantitative dissolution of base metals (99.9% copper and nickel leaching) occurred using 3 M nitric acid at 30 °C with a 50 g/L pulp density, 2 h residence time, and 500 rpm stirring speed. Under these conditions, no gold was dissolved. In stage-2 leaching, various parameters were optimized for the selective dissolution of gold from the residue obtained from stage-1 leaching. More than 95% gold extraction was observed with 3 M sulfuric acid with the

addition of 3 M sodium bromide at 70 °C. Quantitative leaching of silver and tin was also observed. Finally, the kinetics of leaching process were studied and shown to conform to the kinetic model, with activation energies of 39.7, 18.4 and 22.76 kJ/mol for copper, nickel and gold. Importantly, the leaching process optimized in this section avoids the need for high temperatures and reduces energy consumption and effluent generation, leading to the cleaner processing of obsolete mobile phone PCBs for the separation of copper, nickel and gold.

Section 3.2 explains the optimization of separation and recovery of copper, nickel and zinc from stage-1 leach solution through two-stage solvent extraction and cementation processes. Copper was selectively extracted in stage-1 solvent extraction (SX1) by leaving nickel rich raffinate. In stage-2 solvent extraction (SX2), selective recovery of nickel was studied from the other minor base metals. An industrial reagent ACORGA M5640 diluted in kerosene was used in both stages. As a first step, copper was selectively separated (99.9%) from the mixed metal leach liquor at pH 2, 30 °C, 1:1 organic (30 vol% extractant in kerosene) to aqueous phase ratio in 20 min. The extracted copper was readily stripped with 4 M sulfuric acid with more than 99% recovered. This results in a purified strip solution comprising 99.9 wt% of the total copper content, along with minor impurities of zinc (5 mg/L) and lead (3 mg/L). A second stage solvent extraction process conducted at pH 8 then permits recovery of the nickel. In this study, the conditions for the optimization of nickel extraction and stripping were explored. Results indicate that the quantitative extraction of nickel (99.7%) can be achieved using a 1:5 organic (10 vol% extractant in kerosene) to aqueous phase ratio at 30 °C in 60 min. The nickel was readily stripped from the extractant, with more than 95% recovered, along with low levels of zinc (1.7 mg/L) and cadmium (0.6 mg/L), following a 0.5 M hydrochloric acid or 1 M nitric acid strip step. Cyclic usage of the extractant organic layer revealed that its

effectiveness to extraction has remained equivalent to the first cycle. In addition, the separation of trace elements such as lead, tin and cadmium from the raffinate of SX2 was also studied by cementation with zinc powder. The study revealed that the removal of these elements and the generation of pure zinc solution could be obtained by adding 300% excess zinc powder (74 μm) at 50 °C with 500 rpm stirring speed in 60 min. The separation of copper in SX1, nickel from copper-free aqueous solution in SX2 and other minor elements from the raffinate of SX2 ensures the proposed process is sustainable and avoids complexity in the sequential metal recovery processes.

Section 3.3 explains the selective recovery of gold and silver from the second stage leach solution. The recovery of Au(III) was carried out using solvent extraction with an organic amide diluted in toluene as an extractant by leaving other elements in the raffinate. Results indicate more than 99% transportation of gold into organic phase was observed with 0.1 M tertiary amide at 1:1 O/A ratio at 20 °C. The extracted Au(III) was stripped out from the toluene solution, with 99.9% recovered with 1 M NaOH as a stripping reagent. The separation of silver from the raffinate was also examined by the chemical precipitation (cementation) with copper powder. Optimum separation of silver (99.9%) was observed at 30 °C, 500 rpm stirring speed and with 300 mg/100 mL solution.

In **section 3.4**, the design of experimental (DOE) analysis using response surface methodology (RSM) was undertaken to validate the two-stage leaching process. Herein, a three-factor, three-coded level (low: -1, centred: 0 and high: +1) central composite design (CCD) based response surface methodology (RSM) was used to validate the optimal conditions for the leaching of copper, nickel and gold. Time (A), concentration of nitric acid (B) and stirring speed (C) were considered as independent variables (factors), with copper and nickel leaching considered as response variables in stage-1 leaching. Similarly, in stage-2, time (A), temperature (B) and stirring speed (C) were

considered as independent variables, with gold leaching as a response variable. The whole process provides the effect of individual and combined parameters on response variables, an analysis of mathematical models for the process optimization, and a check on the adequacy of the model. DOE optimization revealed that the quantitative leaching of copper and nickel were seen at 120 min, using 2.92 M nitric acid, and at 490 rpm stirring speed. Maximum gold leaching (91%) was seen at 60 min, 70 °C with 499 rpm stirring speed. By comparing these data with the experimental optimizations, a similar effect was observed on copper and nickel leaching in the mentioned range of parameters. Thus, the DOE approach has validated the experimental data and interpretation put forward in section 3.1 and clearly establishes that optimal conditions have been met without the need for further classical experimental optimization.

Chapter 4 embodies the major conclusions drawn from the research work and the scope for future work. Bibliography related to the cited references in the context was also given at the end followed by appendices and a list of publications.