



UNIVERSITI PUTRA MALAYSIA

***SELECTIVE METAL RECOVERY FROM PRINTED CIRCUIT BOARD
WASTEWATER***

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MASTER OF SCIENCE

UNIVERSITI PUTRA MALAYSIA

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**SELECTIVE METAL RECOVERY FROM PRINTED CIRCUIT BOARD
WASTEWATER**

By

ABD HALIM MD ALI

**Thesis Submitted to the School of Graduated Studies, Universiti Putra
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Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirements for the degree of Master of Science

SELECTIVE METAL RECOVERY FROM PRINTED CIRCUIT BOARD WASTEWATER

By

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Due to the high contain of metals in spent etching waste solution, the disposal of etching waste solution is an economic and ecological concern to electric and electronic manufacturer. This study has been initiated to investigate if metals ions can be recovered selectively in spent etching waste solution. The recovery process is expected to have an enhanced value if the recovered metal can be recycled and thus bring to the cost effective solution method.

In the initial work, acid recovery by solvent extraction method was done in order to increase the pH of the solution to $\text{pH} > 2$. Three different volume ratio of TBP: HNO_3 shows a significant value to extract nitric acid at a significant optimum experimental condition which is 50:50, 60:40 and 70:30.

Based on the effectiveness of extraction versus the optimum usage of volume of TBP used, ratio of 50:50 has an advantage over the ratio of 70:30 in term of the optimisation usage of the overall volume to extract the nitric acid at its optimum condition. Six extraction stages are necessary to increase the pH of the aqueous solution by 50% TBP to $\text{pH} > 2$.

Electrochemical experiments were carried out and showed that the deposition of metals on glassy carbon and graphite electrodes occurred at about the same potential voltage in between -0.60 V to -0.85 V .

Based on scanning electron microscopy images, it can be seen that glassy carbon electrode is a suitable electrode material to recover copper at low potential voltage and graphite electrode work best to recover tin, lead and iron as an aggregate mixtures at higher potential voltage. However, selective recovery is not feasible in this work as the metals recovered formed as aggregates mixtures.

Abstrak tesis yang dikemukakan kepada senat Universiti Putra Malaysia sebagai memenuhi keperluan ijazah Master Sains

**PEMULIHAN BAHAN LOGAM SECARA SELEKTIF DARI AIR SISA
PAPAN LITAR**

By

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Januari 2013

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Kandungan logam yang tinggi di dalam air sisa puniran merupakan faktor kekangan yang menyukarkan proses untuk merawat atau melupuskan air sisa ini dari segi ekonomi dan juga ekologi. Kajian ini dijalankan bagi mengkaji sekiranya logam-logam tersebut dapat diterapkan secara selektif. Proses selidikan ini diharapkan dapat membawa nilai tambah sekiranya logam yang diekstrak dapat diguna semula sekaligus mengurangkan beban kos yang ditanggung oleh pihak pengeluar.

Di awal projek ini, kerja-kerja pengekstrakkan asid dijalankan dengan menggunakan pelarut bagi menaikkan pH air sisa ke paras $\text{pH} > 2$. Tiga nisbah isipadu antara TBP: HNO_3 menunjukkan hasil yang memuaskan untuk mengekstrak asid iaitu antara nisbah 50:50, 60:40 dan 70:30.

Berdasarkan faktor keberkesanan pengekstrakkan dan jumlah larutan yang digunakan untuk pengekstrakkan, nisbah 50:50 didapati mempunyai kelebihan berbanding nisbah 70:30 dari sudut optimisasi penggunaan jumlah larutan untuk mengekstrak asid secara keseluruhan. Enam peringkat pengekstrakan diperlukan untuk menaikkan pH air sisa ke paras $\text{pH} > 2$ dengan menggunakan nisbah 50:50.

Eksperimen elektrokimia kemudiannya dijalankan dengan menggunakan karbon kaca dan juga grafit sebagai elektrod. Dari eksperimen yang dijalankan ini, didapati, logam terenalap di atas elektrod karbon kaca dan grafit pada julat voltan yang agak sama iaitu antara -0.60 V hingga -0.85 V.

Menerusi pemerhatian mikroskopi, elektrod karbon kaca didapati sesuai untuk digunakan sebagai medium enapan kuprum pada penggunaan potensi voltan rendah manakala elektrod grafit sesuai untuk enapan timah, plumbum dan besi pada potensi voltan tinggi. Walaubagaimanapun, enapan secara selektif didapati tidak dapat diperolehi memandangkan logam yang terhasil terenalap secara kumulatif dan bukan secara individu.

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APPROVAL SHEET 1

I certify that an Examination Committee has met on 31st January 2013 to conduct the final examination of Abd Halim Md Ali on his degree thesis entitle “Selective Metal Recovery from Printed Circuit Board (PCB) Wastewater” in accordance with the Universities and University College Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U(A) 106] 15 March 1998. The committee recommends that the student be awarded the Master of Science.

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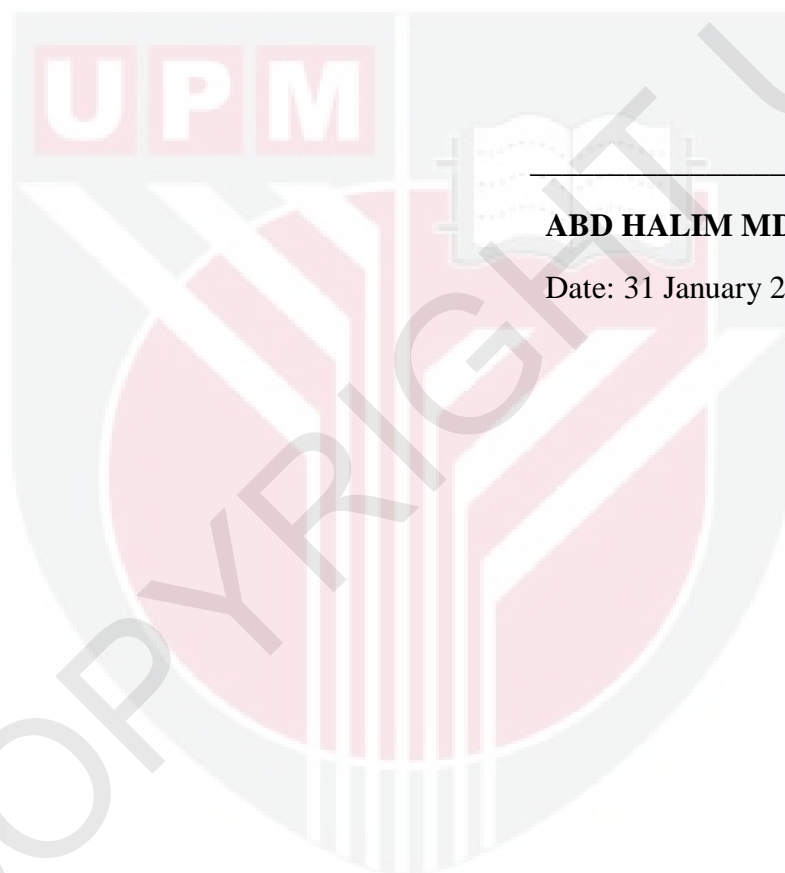
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DECLARATION

I declare that the thesis is my original work except for quotation and citations which have been duly acknowledged. I also declare that it has not been previously, and not concurrently, submitted for any other degree at Universiti Putra Malaysia or at any other institution.



ABD HALIM MD ALI

Date: 31 January 2013

TABLE OF CONTENTS

	Page
ABSTRACT	i
ABSTRAK	iii
ACKNOWLEDGEMENTS	v
APPROVAL	vi
DECLARATION	viii
LIST OF TABLES	xii
LIST OF FIGURES	xiii
LIST OF ABBREVIATIONS	xv
LIST OF NOMENCLATURES	xvi
CHAPTER	
1 INTRODUCTION	
1.1 Background	1
1.2 Printed Circuit Board Manufacturing Process	2
1.3 Spent Etching Waste Solution	4
1.3.1 Past and Current Technology for Treating Etching Waste	4
1.4 Problem Statement	5
1.5 Objectives of the Research	8
2 LITERATURE REVIEW	
2.1 Introduction	9
2.2 Acid Recovery by Solvent Extraction	10
2.3 Theoretical Consideration of HNO ₃ Extraction	
Mechanism Using TBP	11
2.4 Electrochemical Technique for Metal Recovery	13
2.4.1 Electrochemical Technology in Environmental Treatment	13
2.4.2 Electrochemical Techniques for Metal Ion Recovery	16
2.5 Deposition Process	17
2.6 Potentiostatic Current Transient	20
2.6.1 Linear Sweep Voltammetry	21

2.6.2	Cyclic Voltammetry	22
2.6.3	Chronoamperometry	25
2.7	Mechanisms of nucleation growth	26

3 METHODOLOGY

3.1	Reagent	28
3.1.1	Synthetic Spent Nitric Etching Solution	28
3.2	Materials	29
3.2.1	Electrode Materials	29
3.2.2	Glassy Carbon Electrodes	29
3.2.3	Graphite Electrodes	30
3.3	Instruments	31
3.3.1	Inductively Coupled Plasma-Optical Emission Spectrometry	31
3.3.2	Flat Cell System	32
3.3.3	Potentiostat	35
3.3.4	Scanning Electron Microscope	36
3.3.5	Energy-Dispersive Spectrometry	37
3.4	Experiments	37
3.4.1	Solvent Extraction Experiments	37
3.4.2	Electrochemical Experiments	38
3.4.3a	Linear Sweep Voltammetry	38
3.4.3b	Cyclic Voltammetry	39
3.4.3c	Chronoamperometry	39
3.4.3d	Deposit Characterization	40
3.5	Flow Chart of Experimental Design	40

4 RESULTS AND DISCUSSION

4.1	Chemical Characterisation of Synthetic Etching Waste Solution	42
4.1.1	ICP-OES	42
4.1.2	Solvent Extraction of Nitric Acid by TBP	43

4.1.3 Extraction Behavior of Copper, Iron, Tin and Lead Ions by TBP	48
4.2 Electrochemical Experiments	50
4.2.1 Linear Sweep Voltammetry	50
4.2.2 Cyclic Voltammetry Curves	54
4.3 Chronoamperometric Studies	56
4.2.3.1 Current-Time Transients	56
4.4 Deposit Characterisation	64
4.5 Growth Pattern	70
4.6 Diffraction Patterns	73
5 CONCLUSION	77
RECOMMENDATIONS FOR FUTHER STUDY	79
REFERENCES	80
APPENDICES	85
BIODATA OF STUDENT	93
LIST OF PUBLICATION	94

LIST OF TABLES

Table	Page
1.1 Summary of Recovery Techniques	7
2.1 The advantages of electrochemical technology	14
3.1 Chemical composition of synthetic etching waste solution	28
3.2 Properties of glassy carbon electrode	29
3.3 Properties of rigid graphite electrode	30
3.4 Specification of Flat Cell	33
4.1 Composition of synthetic etching waste solution using ICP-OES	41
4.2 pH of the aqueous solution in each stages of extraction isotherm for HNO ₃ using ratio of 50:50 TBP	47
4.3 Potential (V) range and current (A) range at 10 mVs ⁻¹ for linear sweep voltammetry of spent etching waste solution for glassy and graphite electrodes	52
4.4 Selected potentials for choroamperometric studies for glassy carbon electrode based on LSV and CV analysis	54
4.5 Current at which the metals starts to deposit on the electrodes a function of overpotentials	63
4.6 Weight percentage of deposited metals on glassy carbon at each potential deposition	73
4.7 Weight percentage of deposited metals on graphite at each potential deposition	73

LIST OF FIGURES

Figure	Page
1.1 PCB Manufacturing Process Flow	2
2.1 Potentiostatic current transient	20
2.2 Linear sweep voltammetry	21
2.3 Triangular potential excitation signal in cyclic voltammetric experiment	23
2.4 A typical cyclic voltammogram shows the important peak parameters	24
2.5 Potential waveform for chronoamperometry	25
2.6 Stage involve in nucleation growth	26
3.1 K0235 Flat Cell	32
3.2 Steps to prepare the K0235 flat cell	34
3.3 The potentiostat	35
3.4 Flow chart of the experiment design	40
4.1 Effect of TBP concentration on extraction of HNO_3	43
4.2 Effect of TBP concentration on concentration of HNO_3 in organic product	44
4.3 Effect of TBP concentration on concentration of HNO_3 in aqueous product	44
4.4 Effect of TBP concentration on the extraction of metals from synthetic spent etching waste solution	48
4.5 Linear sweep voltammetry for glassy carbon at 10 mVs^{-1} , 20 mVs^{-1} , 30 mVs^{-1} and 40 mVs^{-1}	50
4.6 Linear sweep voltammetry for glassy carbon and graphite electrode of spent etching solution at 10 mVs^{-1}	51
4.7 Cyclic voltammetry of spent etching solution at 10 mVs^{-1} for glassy carbon and graphite carbon electrode	53
4.8 (a) Current-time transient for nucleation of metals on glassy carbon at (a) -0.60 V , (b) -0.65 V and (c) -0.70 V	56
4.8 (b) Current-time transient for nucleation of metals on glassy carbon at (d) -0.75 V , (e) -0.80 V and (f) -0.85 V	57
4.9 (a) Current-time transient for nucleation of metals on graphite at (a) -0.60 V , (b) -0.65 V and (c) -0.70 V	58

4.9 (b)	Current-time transient for nucleation of metals on graphite at (d) -0.75 V, (e) -0.80 V and (f) -0.85	59
4.10	Current-time transient for nucleation of metals based on classical nucleation phenomenon	60
4.11	Current-time transient for nucleation of metals at -0.65 V on (a) glassy carbon, (b) graphite	62
4.12 (A)	SEM images of metals on glassy carbon at different potential and deposition time 60 s with 3K magnification	64
4.12 (B)	SEM images of metals on glassy carbon at different potential and deposition time 60 s with 10K magnification	65
4.13 (A)	SEM images of metals on graphite at different potential and deposition time 60 s with 3K magnifications	66
4.13 (B)	SEM images of metals on graphite at different potential and deposition time 60 s with 10K magnifications	67
4.14	SEM images of metal deposition on glassy carbon as a function of deposition time: (A) 1 s (B) 30 s (C) 100 s	70
4.15	SEM images of metal deposition on graphite as a function of deposition time: (A) 1 s (B) 30 s (C) 100 s	71

LIST OF ABBREVIATIONS

CREST	Centre for Research in Electrochemical Science and Technology
CV	Cyclic Voltammetry
DOE	Department of Environmental
EDS	Energy-Dispersive Spectrometry
EEE	Electric and Electronic Equipment
ICP-OES	Inductively Coupled Plasma-Optical Emission Spectrometry
LSV	Linear Sweep Voltammetry
PCB	Printed Circuit Board
SEM	Scanning Electron Microscopy
TBP	Tributyl-phosphate

LIST OF NOMENCLATURES

M	Molar Mass	g / mol
I	Current	A
E	Potential	V
t	Time	s
D	Distribution coefficient	dimensionless
$[TBP]_{org}$	Concentration of free bound TBP in the organic phase	mol/L
$[TBP.HA]_{org}$	Concentration of free bound TBP in the organic phase	mol/L
$[HA]_{org}$	Concentration of free bound acid in the organic phase	mol/L
$[HA]_{aq}$	Concentration of free bound acid in the aqueous phase	mol/L

CHAPTER 1

INTRODUCTION

1.1 Background

The demand for production of electric and electronic equipment (EEE) dramatically increasing from year to year. Technological innovation and intense marketing are the factors accelerating the update rate of EEE and shortening the lifespan of EEE (Park & Fray, 2009). In recent years, it has been reported that the average rate of worldwide printed circuit board (PCBs) manufacturing increases by 8.7% with total value of 51.5 billion USD worldwide and this number is higher in Southeast Asia by 10.8% (Huang et al., 2009; WECC global PCB production report for 2008, 2009)

In 1994, it was estimated that approximately 20 million of PCB for personal computers (PC) alone were produced and this figure was increased to over 100 million in 2004 (Billy, 2009). The production of EEE is one of the fastest growing sectors of the manufacturing industry in the world as the use of electronic devices such as PCs, mobile telephones and entertainment electronics were discarded due to the technological innovation and accelerating the update of rate of EEE and the production trend was exponentially from year to year.

1.2 Printed Circuit Board Manufacturing Process

The printed circuit board manufacturing process is highly complicated and uses large quantities of water and chemicals as shown in Figure 1.1 (Sage & Schnitzer, 1995; Dao, 2006; Scott et al., 1997; Bairs et al., 2005). The chemical process themselves results in the generation of a significant volume of effluent that needs costly treatment before it can be discharged.

The production begins with laminating a sheet of plastic with a thin layer of copper foil and adhered over the entire board. Holes are then drilled through the board and these holes are used to mount the electronic components on the board (Bair et al., 2005).

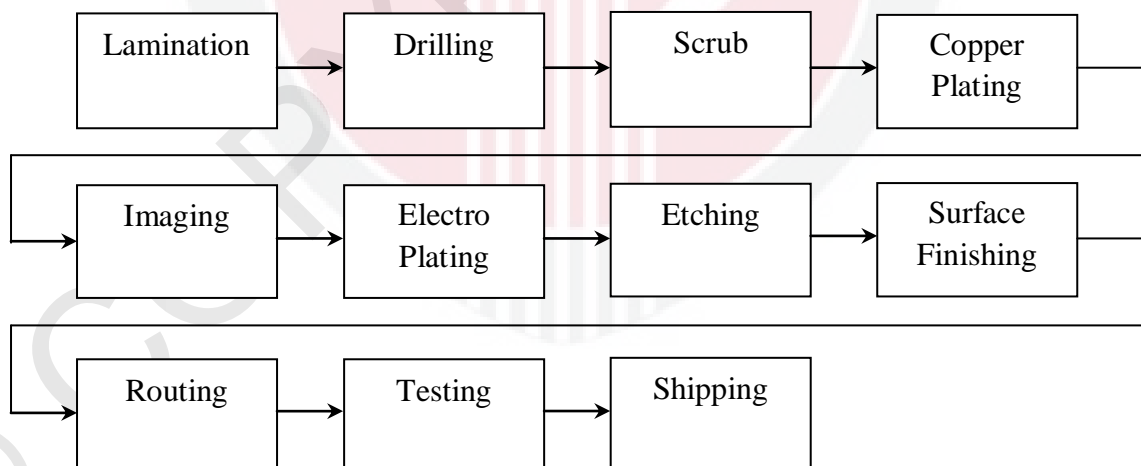


Figure 1.1 : PCB Manufacturing Process Flow

Following drilling process, the board is scrubbed to remove unwanted fine copper left by the drilling process using sodium or potassium permanganate. After being

scrubbed, the board is plated with an additional layer of thin electroless copper over the surface of the board and through the holes. These electrodes copper plating is employed to provide the intended interconnection between layers since the holes are not conductive.

Following electroless plating process, a plating resist is applied to the panel and panel will undergo a photo-imaged process called photoresist that revealed the circuit design (Iordache, 2009). Copper is then electroplated on the board to its final thickness together with adhering a thin layer of tin-lead solder over the copper as an etch resist.

After adhering a thin layer of tin-lead solder, the plating resist is then removed to expose the non-useful base copper which is not a part of the final circuit pattern by nitric acid based etching solution. In PCB manufacturing, etching process is the most crucial process and spent nitric etching waste solution with composition of 250 g/L HNO_3 , 30-40 g/L Cu, 30-40 g/L Sn, 30-40 g/L Pb and 20-25 g/L Fe is produced (Lee et al., 2003).

After the etching process, circuit board will undergo the final stage in manufacturing PCB process with surface finishing, routing, testing and inspection and its ready for the shipping.

1.3 Spent Etching Waste Solution

1.3.1 Past and Current Technology for Treating Etching Waste

Due to the high contain of heavy metals in spent nitric etching waste, the disposal of etching waste solution is an ecological problem for the EEE industry. Conventionally, spent nitric etching waste solutions resulting from the etching process are neutralized by adding sodium hydroxide and the neutralized sludges are incinerated (Lee et al., 2003; Shin, et al., 2009). Due to the emitted of nitrogen monoxide during the incineration and the leaching of heavy metals from the dumped residues, the spent nitric etching solutions are managed as hazardous wastes. (Lee et al., 2003; Keskitalo et al., 2007).

At present, spent nitric etching solution are treated by several commercial systems to remove the heavy metals from the solution. The current treatments available are ion exchange technique process, evaporation technique process and electrowinning technique process (Recovery and recycling of bath chemicals; Electroplating tip sheet, 2006).

These current treatments bring a significant way to move towards a more sustainable methodology to treat the spent nitric etching waste solution as the amount of waste generated is minimized and potentially large volumes of heavy metals can be reclaimed from waste instead of being consigned to landfill.

1.4 Problem Statement

The recent international growth in the electronics industry has generated a drastic increase in the amount of waste PCBs with profound environmental impacts such as soil and groundwater contamination. Until now, the waste acid resulting from the use of etching solution has been subjected neutralization without any proper treatment as the cheapest disposal action resulting environmental problems (Lee et al., 2003; Shin et al., 2009; Keskitalo et al., 2007).

Eventhough the current treatment available for treating the spent nitric etching brings a promising technique to treat the waste etching solution, yet, it has its own advantages and disadvantages as listed in Table 1.1.

Based on Table 1.1, electrowinning process is a well reasonable approach compared to with the rest of treatment technique but the information of electrowinning technique in treating spent nitric etching waste are scarce.

Due to the significant method to recover metals from the spent nitric etching waste solution by electrowinning process, the high metal concentrations in the spent nitric etching waste solution make them viable candidates for recovery and it has more advantages compared with other techniques available.

In electrowinning recovery techniques, the heavy metal in spent nitric etching solution can be reclaimed in a pure form and can eliminate energy demand and costly

furnace refining together with a high degree of control and process monitoring compared to conventional and current available treatment (Ottewill et al., 2005)

Based on the limitation of information regarding the feasibility study of electrowinning deposition technique in metals recovery from spent etching waste, this work will attempt to investigate the electrowinning deposition technique for selective recovery of different metals, e.g. copper, tin, lead in PCB spent etching waste solution.



Table 1.1: Summary of Recovery Techniques

Technique	Advantages	Disadvantages
<ul style="list-style-type: none">Evaporators	Reliable technology Simple to operate Can exceed bath concentration	Energy intensive May require pH control Returns bath and impurities Most evaporators designed for steam heating Multi-stage counter current rinsing essential Additional treatments may be needed to control impurities
<ul style="list-style-type: none">Ion Exchange	Low energy demand Handles dilute feed Returns metal as metal salt solution	Limited concentration ability Excess regenerate required Requires tight operation and maintenance May require evaporation to increase concentration Require close monitoring of feed concentration
<ul style="list-style-type: none">Electrowinning	Recovers only metals Energy efficient Low Maintenance Eliminates metal ion Results in salable non-hazardous product	Must constantly monitor solution concentration Fumes may form and require hood scrubbing system

1.5 Objectives of the Research

This study embarks on the following objectives:

1. To investigate the effective volume ratio between TBP and nitric acid for extraction process.
2. To determine the effects of electrode potentials, deposition time and types of electrodes on metal deposition.
3. To characterize the deposited metals and profile current potentials.

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