

**DIFFERENTIAL PULSE ANODIC STRIPPING VOLTAMMETRY OF  
CADMIUM, COPPER, LEAD AND ZINC IN THE PRESENCE OF *N,N'*-  
BIS[2-HYDROXYACETOPHENONE]ETHYLENEDIAMINE**

**NUR YASARAH BINTI MOHD YUSOF**

**UNIVERSITI TEKNOLOGI MALAYSIA**

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HYDROXYACETOPHENONE]ETHYLENEDIAMINE

NUR YASARAH BINTI MOHD YUSOF

A thesis submitted in fulfillment of the  
requirements for the award of the degree of  
Master of Science (Chemistry)

Faculty of Science  
Universiti Teknologi Malaysia

OCTOBER 2014

*To my beloved*

## ACKNOWLEDGEMENT

First and foremost, all praise of Allah for his Mercy for answering all my prayers for giving me strength to plod on despite my constitution wanting to give up.

Special thanks go to my supervisor, Prof. Dr. Rahmalan Bin Ahamad, for his knowledge, guidance, supervision, encouragement and supporting me throughout the undertaking of this research. I have gained a lot of knowledge and experience during doing this research.

I owe my most sincere gratitude to Pn. Ramlah, En. Yasin and Pn. Mariam for their kindness to complete my research. They were helping a lot in chemistry analysis lab especially in carrying out the Voltammetry and Atomic Absorption Spectrometer analysis.

Last but not least, I would like to express my love to my family especially my father and mother for their endless love and continuous support for me to complete my research. Thank you so much.

## ABSTRACT

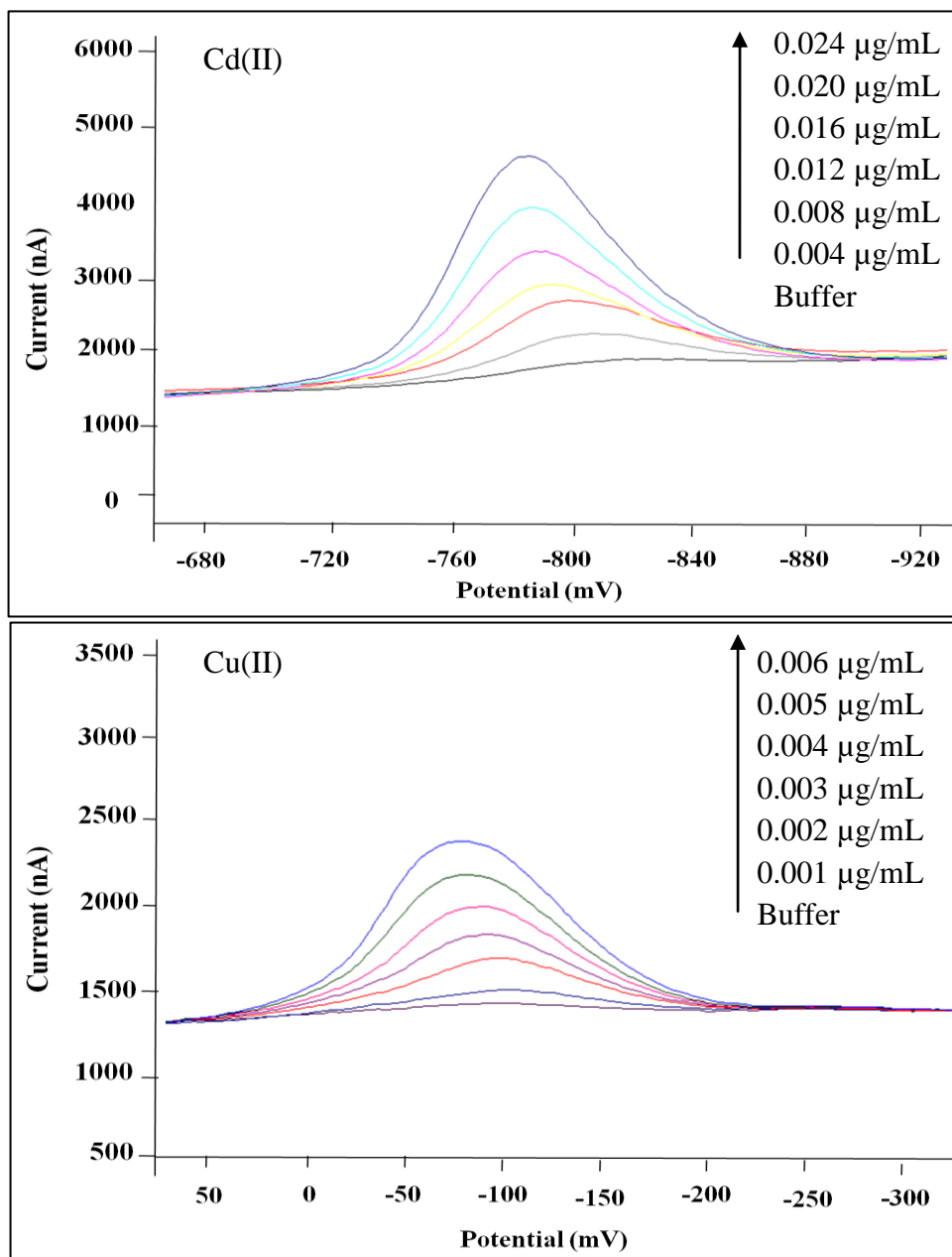
Voltammetry is a low cost and sensitive technique for the detection of heavy metal ions such as Cd(II), Cu(II), Pb(II) and Zn(II). However, the use of glassy carbon electrode as the working electrode suffers from surface fouling that renders poor detection performance towards these metal ions. In the present study, the potential of a Schiff base namely *N,N'*-bis[2-hydroxyacetophenone]ethylenediamine (OAcPh-en) to enhance the sensitivity of voltammetric technique using glassy carbon electrode for the detection of these metal ions were investigated. Complexation ability of OAcPh-en towards these metals was investigated using liquid-liquid extraction with chloroform followed by detection using inductively coupled plasma-mass spectrometry. In this study optimum parameters used for Cd(II) ions; pH 5.0, contact time 120 s, metal concentration 60 µg/mL and OAcPh-en concentration 0.2 M for the complexation of the metal-OAcPh-en was examined. *In-situ* approach was adopted throughout this study for the enhancement of metal ion detection by OAcPh-en using cyclic voltammetry and differential pulse anodic stripping voltammetry. Optimum experimental parameters for Cd(II) ions; pH 8.0, addition of acetonitrile 80 µL, OAcPh-en concentration  $25 \times 10^{-5}$  M, scan rate 10 mV/s, accumulation time 60 s and accumulation potential -0.9 V were obtained. OAcPh-en shows slightly better liquid-liquid extraction for Cd(II) (99.10%) than Cu(II) (89.94%), Pb(II) (78.03%) and Zn(II) (55.93%). The OAcPh-en shows irreversible oxidation peak around +1200 mV vs Ag/AgCl (3.0 M). The relationship between peak current and metals concentration was linear for Cd(II) and Cu(II) in acetonitrile in the range of 0.04-0.68 µg/mL and 0.01-0.24 µg/mL respectively. The detection limit is 0.065 ng/mL for Cd(II) and 0.002 ng/mL for Cu(II) respectively. The newly developed method was successfully applied in the determination of Cd(II) and Cu(II) in mineral water sample and natural tap water.

## ABSTRAK

Voltametri adalah teknik berkos rendah dan sensitif untuk mengesan ion logam berat seperti Cd(II), Cu(II), Pb(II) and Zn(II). Walau bagaimanapun, penggunaan elektrod karbon berkaca sebagai elektrod kerja mengalami kecacatan permukaan yang menyebabkan prestasi pengesanan lemah untuk ion logam ini. Dalam kajian ini, potensi *N,N'*-bis[2-hidroksiasetofenon]etilenadamina (OAcPh-en) untuk meningkatkan kepekaan teknik voltametri menggunakan elektrod karbon berkaca untuk mengesan ion logam ini telah disiasat. Keupayaan mengkompleks oleh OAcPh-en terhadap logam ini telah disiasat menggunakan pengekstrakan cecair-cecair dengan kloroform diikuti dengan pengesanan menggunakan plasma berganding secara aruhan-spektrometri jisim. Dalam kajian ini parameter optimum bagi Cd(II); pH 5.0, masa 120 s, kepekatan logam 60 µg/mL dan kepekatan OAcPh-en 0.2 M untuk mengkompleks logam-OAcPh-en dikaji. Pendekatan *in-situ* telah diguna sepanjang kajian ini untuk meningkatkan pengesanan ion logam dengan OAcPh-en menggunakan voltametri perlucutan anodik denyut pembezaan. Parameter eksperimen optimum yang didapati untuk Cd(II); pH 6.0, penambahan asetonitril 80 µL, kepekatan OAcPh-en  $25 \times 10^{-5}$  M, kadar imbasan 10 mV/s, masa pengumpulan 60 s dan potensi pengumpulan -0.9 V. OAcPh-en menunjukkan pengekstrakan cecair-cecair yang sedikit lebih baik untuk Cd(II) (99.10%) daripada Cu(II) (89.94%), Pb(II) (78.03%) dan Zn(II) (55.93%). OAcPh-en menunjukkan puncak pengoksidaan tidak berbalik pada +1200 mV vs Ag/AgCl (3.0 M). Hubungan antara puncak tunggal dan kepekatan logam adalah linear bagi Cd(II) dan Cu(II) dalam asetonitril masing-masing dalam julat 0.04-0.68 µg/mL dan 0.01-0.24 µg/mL. Had pengesanan untuk Cd(II) ialah 0.065 ng/mL dan 0.002 ng/mL bagi Cu(II). Kaedah yang baharu dibangunkan telah berjaya digunakan dalam penentuan Cd(II) dan Cu(II) dalam sampel air mineral dan air paip semula jadi.

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**LIST OF ABBREVIATIONS**

°C	Degree Celcius
%	Percent
OAcPh-en	<i>N,N'</i> -bis[2-hydroxyacetophenone]ethylenediamine
Cd(II)	Cadmium ions
Cu(II)	Copper ions
NaOH	Sodium Hydroxide
HCl	Hydrochloric Acid
BRB	Britton-Robinson Buffer
GC	Glassy Carbon
FTIR	Fourier Transform Infrared Spectroscopy
NMR	Nucleur Magnetic Resonance
ICP-MS	Inductively Coupled Plasma-Mass Spectrometry
CV	Cyclic Voltammetry
DPASV	Differential Pulse Anodic Voltammetry
R <sup>2</sup>	Correlation Coefficient
LOD	Limit of Detection
LOQ	Limit of Quantification
M	Molar
g	Gram
µg/mL	Micro gram per mililitre
ng/mL	Nano gram per mililitre
mL	Mili litre
µL	Micro litre
min	Minute
rpm	Rotation per minute



## CHAPTER 1

### INTRODUCTION

#### 1.1 General Introduction

Heavy metal ions such as Cd(II), Cu(II), Pb(II) and Zn(II) are known to be toxic to living organisms even at very low concentrations. Exposure of these metal ions to living organisms can occur due to their release by industries into the environment. Cadmium, copper, lead and zinc are frequently used in industrial processes such as metallurgy, mining, painting, smelting, batteries, and alloys industry (Dong et al., 2010, Wang et al., 2003, Li et al., 2007). Accumulation of these metal ions can cause poisoning, premature birth, respiratory problems, cancer and brain damages.

The government has imposed environmental regulations and guidelines pertaining to toxic pollutant because of the concern over health effects of toxic metal ions. For example, the Malaysian standard for sewage and industrial effluents industrial waste water discharges stipulated the maximum concentration of Cd(II) (0.01  $\mu\text{g/mL}$ ), Cu(II) (0.2  $\mu\text{g/mL}$ ) Pb(II) (0.1  $\mu\text{g/mL}$ ) and Zn(II) (1  $\mu\text{g/mL}$ ) (DOE, 2010a) and Drinking Water Quality Standard Cd(II) (0.003  $\mu\text{g/mL}$ ), Cu(II) (1  $\mu\text{g/mL}$ ), Pb(II) (0.01  $\mu\text{g/mL}$ ) and Zn(II) (3  $\mu\text{g/mL}$ ) (MOH, 2000, DOE, 2010a).

Due to risks to human health and some environmental problems, there is a need for continuous improvement in the detection and determination of heavy metal ions in the environment. UV-Vis spectroscopy, inductively coupled plasma-mass spectrometry (ICP-MS), inductively coupled plasma-atomic emission spectroscopy (ICP-AES), atomic absorption spectroscopy (AAS) and neutron activation analysis

(NAA) are the most commonly used techniques for detection of heavy metal ions (Ouyang et al., 2011). However, these methods are mostly time consuming, require highly qualified technicians and involve laborious sample preparation. Besides, the concentrations in natural waters are frequently lower than the limits of detection especially by spectrometric techniques, and therefore require pre-concentration procedure (Yokoi et al., 1995).

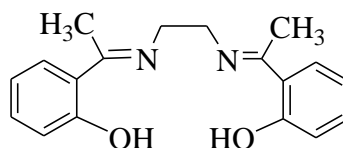
Voltammetry techniques especially stripping voltammetry with improved sensitivity and selectivity have been promoted for the development of various electrochemical method for ultra-trace metal ions measurement (Safavi and Shams, 2000). Voltammetry system inherently simple and low cost such that determination of heavy metal ions at very low concentrations can be carried out directly on-site which can significantly reduce cost and shorten the duration of analysis time. Moreover, this technique has been proven for excellent accuracy, precision and potential for simultaneous determination of several metal ions in one operational condition.

Conventionally, voltammetric technique utilizes mercury as the working electrode material. Due to toxicity of mercury, the focus of research in this area has been diverted towards non mercury electrode material particularly carbonaceous material such as glassy carbon and carbon paste. Glassy carbon is particularly interesting because of several advantages including serving broad potential window, low cost, chemical inertness and easy surface modification procedures (Van der Linden and Dieker, 1980). Chemical modifications of bare glassy carbon electrodes offer significant advantages in the design and development of electrochemical technique in terms of reducing overpotential and overcoming the slow kinetics of the electrode processes. Furthermore, chemically modified electrodes is less prone to surface fouling compared to bare electrodes (Ensafi et al., 2009).

Various enhancement techniques to improve the chemical functionalities of the glassy carbon electrode have proposed specific chemisorptions, pre-treatment, covalent bonding and non-specific physical sorption using self-assembled monolayers (Oztekin et al., 2011a, Oztekin et al., 2011b). The precise alterations on

the surface of electrodes and the mechanisms for the activation sites at extreme potentials remain unknown, but primarily involve the presence of surface functional groups, especially species of the carbon-oxygen types such as the carbonyl and hydroxyl groups in the form of carboxylic acid, quinone, lactone, phenol and others have been implicated as the species (Prabhu et al., 2009, Bowers and Yenser, 1991).

Schiff base is a class of compounds important to chelate metal ions in chemical analysis. Schiff base ligand is able to coordinate many different metals and stabilize them in various oxidation states (Singh et al., 2010). Metal complexes with Schiff base ligands have been extensively investigated as catalyst for a number of organic redox reactions and electrochemical reduction process (Rodríguez et al., 2010, Samide and Peters, 1998). These compounds are derived from the reaction of aromatic aldehydes and aliphatic or aromatic amines represent an important series of widely studied organic ligands. One of the examples of this ligand is *N,N'*-bis[2-hydroxyacetophenone]ethylenediamine (OAcPh-en) (Figure 1.1) which is derived from the reaction of 2-hydroxyacetophenone with ethylenediamine.



**Figure 1.1:** Structure of *N,N'*-bis[2-hydroxyacetophenone]ethylenediamine (OAcPh-en)

The chemistry between Schiff base and metal ions give different complexes with different geometries which are potentially biologically active. The complexation abilities of these ligands have a remarkable attention in inorganic chemistry due to their great versatility displaying borderline characteristics between hard and soft Lewis bases (Aslantaş et al., 2009). Metal-Schiff base complexes containing nitrogen donors has been devoted through the years because of the potential applications as chelating agents, catalyst, drug synthesis and biological activity (Bhattacharjee et al., 2012, Saxena et al., 1981).

Organic solvents such as acetonitrile, chloroform and dimethylformamide have been included into the electrochemical systems to enhance chemical functionality of carbon surface and electrochemical oxidation of amine-containing compounds. The reaction mechanism of the electro-oxidation of the metal complexes in organic solvents normally involves one electron transfer to form a stable ion (Kapturkiewicz and Behr, 1983).

## 1.2 Problem Statement

Although metals such as copper at trace levels are essential to human body function, heavy metals such as lead and cadmium are known to be toxic and excessive intake of these metals will cause health problems such as anemia, brain and kidney damage. Heavy metal ions discharged by industrial effluents usually find their way into receiving water sources such as rivers, lakes and streams leading to increasing amounts of these pollutants in the environment (Crompton, 2007).

Through the years, sensitive methods for determination of ultra-trace amounts of metal ions have received much attention and have been developed to improve the analysis measurements. Most commonly used sensitive and selective techniques are inductively coupled plasma-mass spectrometry (ICP-MS), inductively coupled plasma-atomic emission spectroscopy (ICP-AES), atomic absorption spectroscopy (AAS) and neutron activation analysis (NAA). However, most of these methods are time consuming, including sophisticated equipments and require high maintenance cost (Afkhani et al., 2012, Philips et al., 2012, Abbasi et al., 2010).

On the other hand, electrochemical methods such as voltammetry offer advantages such as simplicity, low cost, high sensitivity, easy operation and ability of analyzing element of different species (Cobelo-García and Prego, 2004). In particular, stripping techniques are widely recognized due to the unique ability to pre-concentrate the target metal ions during the accumulation step (Luo et al., 2010, Kalcher et al., 1995, Wang, 1985). Mercury based electrodes have long been used for

the determination of ultra-trace metal ions by stripping voltammetry technique. However, the high toxicity of mercury and occupational health consideration has render restrictions to the use of mercury (Wu et al., 2008, Hu et al., 2003, Economou and Fielden, 1998).

In view of mercury toxicity, the development for alternative electrode materials including solid electrodes has shown innumerable performance for stripping voltammetry. There are several solid materials that can be used as working electrode such as gold, platinum and carbon. In particular, carbon including graphite (German et al., 2012), glassy carbon (GC) (Wang et al., 2000, Oztekin and Yazicigil, 2009) and carbon nanotubes (Yao and Shiu, 2008) demonstrate superior electrochemical properties. The entire carbon electrode mentioned above seems highly promising for electrochemical systems because of inertness, good conductivity and wide potential window suitable for electrochemical detection.

The extended application of glassy carbon electrode in the detection of ultra-trace metal ions has led to the sensitivity enhancement directly on the electrode surface with specific compounds. For example, complexing ligands with functional groups have been used as dopant or modifier to increase sensitivity and selectivity toward the target species. Some treatments on the surface of bare solid electrodes are needed to activate its surface and provide enhanced electrochemical signals. Modification procedures improve the selectivity, increase the electrocatalysis effect, decreases kinetics over potential and avoid surface fouling (Ensafi et al., 2010, Arduini et al., 2010).

The use of functional ligands such as 2-carboxy-20-hydroxy-50-sulfoformazyl benzene (Zincon) (Taher et al., 2008), cyclopentanone thiosemicarbazone (Mahajan et al., 2006), 5,5-dimethylcyclohexane-1,2,3-trione 1,2-dioxime 3-thiosemicarbazone (Díaz et al., 2006), dimethylglyoxime mixed with catechol (Cobelo-García et al., 2005) and *N,N*-ethylenebis(salicylideneimine) (Bastos et al., 2000) have been previously reported for the determination of heavy metal ions using voltammetry stripping techniques. However, most of the reported works on the use of ligands to enhance selectivity and sensitivity of metal ion detection involve the

use of mercury electrodes. The use of these ligands to enhance selectivity and sensitivity of solid electrodes other than mercury for the detection of metal ions is still lacking.

The present study reported on the development of a sensitive DPASV method for the detection of heavy metal ions using glassy carbon electrode by *in-situ* addition of *N,N'*-bis[2-hydroxyacetophenone]ethylenediamine (OAcPh-en). The functional groups of OAcPh-en are expected to make effective coordination with heavy metal ions to enable a new simple and precise stripping voltammetry technique for the ultra-trace determination of Cd(II), Cu(II), Pb(II) and Zn(II) in aqueous solution.

### 1.3 Objective

The objectives of this study are:

1. To investigate the complexation ability of OAcPh-en and heavy metal ions, Cd(II), Cu(II), Pb(II) and Zn(II) in aqueous solution by using liquid-liquid extraction.
2. To investigate the electrochemical behaviour of OAcPh-en and heavy metal ions using cyclic voltammetry with glassy carbon electrode.
3. To develop and optimize a stripping technique for the determination of heavy metal ions under various experimental parameters such as pH, addition of acetonitrile, ligand concentration, scan rate ( $\nu$ ), accumulation time ( $t_{acc}$ ) and accumulation potential ( $E_{acc}$ ).
4. To apply the developed stripping voltammetry methods for the determination of Cd(II) and Cu(II) in mineral water and tap water.

#### 1.4 Scope of Study

This research involved liquid-liquid extraction in a preliminary study and electrochemical measurement of Cd(II), Cu(II), Pb(II) and Zn(II) detection using glassy carbon electrode. The investigation involves the following:

1. Liquid-liquid extraction (LLE) studies on the complexation ability of OAcPh-en towards these metal ions by using inductively coupled plasma-mass spectrometry (ICP-MS) with emphasis on the effects of pH, contact time, ligand concentration and metal concentration.
2. Cyclic voltammetry (CV) studies on electrochemical behavior of OAcPh-en towards these metals under different changing parameters such as pH, ligand concentration and scan rate ( $v$ ).
3. Investigation on the differential pulse anodic stripping voltammetry (DPASV) technique for the determination of the metal ions with optimization of parameters such as pH, addition of acetonitrile, ligand concentration, scan rate ( $v$ ), accumulation time ( $t_{acc}$ ) and accumulation potential ( $E_{acc}$ ).
4. Application of the optimized parameters to investigate the effect of increasing concentration of metal ions to the peak current ( $I_p$ ). From the graph, regression equation,  $R^2$  value, linearity range, limit of detection (LOD) and limit of quantification (LOQ) can be obtained.
5. Investigation on the interference of metal ions such as As(II), Fe(II) and Ni(II), on the differential pulse anodic stripping voltammetry (DPASV) technique.
6. Application of the differential pulse stripping voltammetry (DPASV) for determination of metal ions in real sample. The recovery studies were carried out and the results were compared with FAAS.

## 1.5 Significance of Study

A new developed *in-situ* electrochemical technique based on differential pulse anodic stripping voltammetry of metal complex with OAcPh-en ligand has the potential to be an alternative method to improve the development of a rapid analysis, low cost and environmentally friendly analysis. This ligand is expected to be a modifier ion to enhance the sensitivity and selectivity of glassy carbon electrode in electrochemical detection of heavy metal ions.



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