ACETOPHENONE - BENZALDEHYDE ETHYLENEDIAMINE MODIFIED ELECTRODES FOR THE DETERMINATION OF METAL IONS IN AQUEOUS SOLUTIONS

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In the name of Allah, the Most Beneficent and the Most Merciful.

This thesis is dedicated to my beloved parents, Zurida binti Zailani, Zulina binti Zailani, Azhari bin Omar and my siblings Syamim, Amri, Syazwi, Adi, Syafiq, Syakib and Syahid Azim,

for their endless support, love, concern, encouragement and continuous prayer for my success in completing this research.

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ABSTRACT

Concern over the harmful effect of toxic metals in the environment warrants the need of continuous improvement for their determination. Conventional methods such as inductively coupled plasma-mass spectrometry (ICP-MS) and atomic absorption spectrophotometry (AAS) for the determination of metal ions in aqueous solution have several drawbacks such as time consuming manipulation steps, need for sophisticated instruments and high maintenance costs. Alternative methods such as electrochemical technique have been suggested, particularly offering advantages in terms of speed of analysis, low cost, easy operation and ability to directly determine metal ion in complex aqueous samples. In the present study, acetophenone-benzaldehyde ethylenediamine compounds, *N,N'*-bis(2-hydroxyacetophenone)ethylenediamine, bis(4-hydroxybenzaldehyde)ethylenediamine, bis (benzylidene)ethylenediamine and *N,N'*-bis(2-hydroxy-4-methoxyacetophenone)ethylenediamine were synthesized and applied to modify carbon based electrodes for the determination of metal ions using electrochemical techniques. The ligands were used *in-situ* to enhance the detection of cadmium (Cd(II)) and copper (Cu(II)) ions using differential pulse anodic stripping voltammetry (DPASV). Under the optimized conditions the proposed *in-situ* DPASV method for Cd(II) and Cu(II) provides good limits of detection (LOD) and limit of quantification (LOQ) in the range of 0.1 - 1.0 µg L^{-1} and 1.30 - 4.53 µg L^{-1} respectively. The relative recoveries obtained for Cd(II) and Cu(II) in tap water and sea water samples were in the range of 82 - 118%. A composite carbon paste electrode modified with bis(benzylidene)ethylenediamine was successfully fabricated for the determination of Cd(II) using square wave anodic stripping voltammetric technique. The response surface methodological approach employing the Box-Behnken design was utilized to optimize the experimental conditions for the detection of Cd(II). Under optimized conditions, a linear response over a wide range of Cd(II) concentrations (1–500 µg L^{-1}) with low LOD (0.4 µg L^{-1}) and LOQ (1.4 µg L^{-1}) were observed. The electrode employed in this styudy exhibited exceptional recovery results over a wide range of Cd(II) concentrations in the sea and tap water samples. A modified electrode consisting of multi-walled carbon nanotubes (MWCNT), 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim]PF_6), *N,N'*-bis(2-hydroxy acetophenone)ethylenediamine and Nafion was developed on glassy carbon electrode to investigate the electrochemical behaviour and direct determination of silver (Ag(I)) ion using cyclic voltammetry and DPASV. Under optimized conditions, the DPASV calibrations were linear in the range of 0.2 to 200 µg L^{-1}. The LOD and LOQ obtained were 0.07 µg L^{-1} and 0.2 µg L^{-1} respectively. Repetitive measurements revealed good reproducibility with a relative standard deviation value of 0.4%. To prove the applicability of the proposed modified electrode, 10 stations of the river water samples were collected between Malaysia-Singapore Second Link and the Causeway along the Johor Straits and the Ag(I) content was analysed using the developed method. The results were compared to the standard method and were found to be superior to those of conventional methods that have been reported in previous work.

ABSTRAK

Kebimbangan terhadap kesan merbahaya logam toksik dalam persekitaran memerlukan usaha berterusan untuk menambahbaik kaedah penentuannya. Kaedah konvensional seperti plasma berganding aruhan-spektrometri jisim (ICP-MS) dan spektrofotometri penyerapan atom (AAS) bagi penentuan ion logam dalam larutan akueus mempunyai beberapa kelemahan seperti langkah manipulasi yang memakan masa, memerlukan peralatan canggih dan kos penyelenggaraan yang tinggi. Kaedah alternatif seperti teknik elektrokimia telah dicadangkan, terutamanya menawarkan kelebihan dari segi analisis yang cepat, murah, operasi yang mudah dan keupayaan menentukan secara langsung ion logam dalam sampel akueus kompleks. Dalam kajian ini, sebatian asetofenon-benzaldehid etilenadiamina, *N*,*N*′-bis(2-hidroksiasetofenon)etilenadiamina, bis(4-hidroksibenzaldehid)etilenadiamina, bis(benzilidena)etilenadiamina dan *N*,*N*′-bis(2-hidroksi-4-mitoksiasetofenon)etilenadiamina telah disintesis dan digunakan untuk mengubah suai elektrod berasaskan karbon untuk penentuan ion logam menggunakan teknik elektrokimia. Ligan digunakan secara *in-situ* untuk meningkatkan pengesanan ion kadmium (Cd(II)) dan kuprum (Cu(II)) menggunakan teknik voltammetri pelucutan anod denyut pembezaan (DPASV). Di bawah keadaan optimum, kaedah *in-situ* DPASV yang dicadangkan bagi Cd(II) and Cu(II) telah menghasilkan had pengesanan (LOD) dan had kuantifikasi (LOQ) yang baik dalam julat 0.1-1.0 μg L^{-1} dan 1.30-4.53 μg L^{-1} masing-masing. Pemulihan semula relatif yang diperoleh untuk ion Cd(II) dan Cu(II) dalam sampel air paip dan air laut adalah dalam julat 82-118%. Elektrod pasta komposit karbon yang telah diubahsuai dengan bis(benzilidena)etilenadiamina telah berjaya difabrikasi bagi menentukan Cd(II) dengan menggunakan teknik gelombang segiempat sama voltammetri pelucutan anod (SWASV). Pendekatan kaedah gerak balas permukaan menggunakan reka bentuk Box-Behnken telah digunakan untuk mengoptimumkan keadaan eksperimen bagi mengesan Cd(II). Di bawah keadaan optimum, ransangan linear pada julat kepekatan Cd(II) yang luas (1-500 μg L^{-1}) dengan LOD (0.4 μg L^{-1}) dan LOQ (1.4 μg L^{-1}) yang rendah telah dicerap. Elektrod yang digunakan dalam kajian ini mempamerkan hasil pemulihan semula yang luar biasa pada julat kepekatan Cd(II) yang luas dalam sampel air laut dan air paip. Sebuah elektrod terubahsuai terdiri daripada nanotiub karbon dinding berganda (MWCNT), 1-butil-3-metilimidazolium heksafluorofosfat ([bmim]PF_6), *N*,*N*′-bis(2-hidroksiasetofenon)etilenadiamina dan Nafion telah dibangunkan pada elektrod karbon berkaca untuk mengkaji tingkah laku elektrokimia dan penentuan langsung ion argentum (Ag(I)) menggunakan voltammetri berkitar (CV) dan DPASV. Di bawah keadaan optimum, penentukuran DPASV adalah linear dalam julat 2 hingga 200 μg L^{-1}. Nilai LOD dan LOQ yang diperoleh adalah 0.07 μg L^{-1} dan 0.2 μg L^{-1} masing-masing. Pengukuran berulang mendedahkan kebolehulangan semula yang baik dengan nilai sisihan piawai 0.4%. Untuk membuktikan kebolehgunaan elektrod terubahsuai yang dicadangkan, 10 stesen sampel air sungai telah dikumpulkan sepanjang Selat Johor di antara Laluan Kedua Malaysia-Singapura dan Tambak Johor, dan kandungan Ag(I) telah dianalisis menggunakan kaedah yang telah dibangunkan. Keputusan kajian telah dibandingkan dengan kaedah piawai dan didapati lebih baik berbanding dengan kaedah konvensional yang dilaporkan dalam kajian terdahulu.

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LIST OF ABBREVIATIONS

$[bmim]PF_6$	-	1-Butyl-3-methylimidazolium hexafluorophosphate
AAS	-	Atomic absorption spectrophotometry
Ag(I)	-	Silver ion
Ag/AgCl	-	Silver-silver chloride
Al	-	Aluminum
ANOVA	-	Analysis of variance
ASV	-	Anodic stripping voltammetry
BBE	-	Bis(benzylidene)ethylenediamine
BBD	-	Box-Behnken design
BHE	-	Bis(4-hydroxybenzaldehyde)ethylenediamine
BME	-	*N,N'*-bis(2-hydroxy-4-methoxyacetophenone) ethylenediamine
BRB	-	Britton-Robinson buffer
BZE	-	*N,N'*-bis(2-hydroxyacetophenone)ethylenediamine
CCD	-	Central composite design
CD_3OD	-	Methanol
CPE	-	Carbon paste electrode
CV	-	Cyclic voltammetry
Cd(II)	-	Cadmium ions
Cr	-	Chromium
Cu(II)	-	Copper ions
DF		Degree of freedom of different source
DMF	-	Dimethylformamide
DMSO	-	Dimethylsulfoxide
DO	-	Dissolved oxygen

DOE	-	Department of Environment Malaysia
DPASV	-	Differential pulse anodic voltammetry
DPP	-	Differential pulse polarography
DPV	-	Differential pulse voltammetry
F	-	Degree of freedom
FTIR	-	Fourier transform infrared spectroscopy
GFAAS	-	Graphite furnace atomic absorption spectrophotometry
GCE	-	Glassy carbon electrode
HMDE	-	Hanging mercury electrode
ICP-MS	-	Inductively coupled plasma-mass spectrometry
ICP-OES	-	Inductively coupled plasma mass spectrometry
IDR	-	Iskandar Development Region
KBr	-	Potassium bromide
LOD	-	Limit of detection
LOQ	-	Limit of quantification
LSV	-	Linear scan voltammetry
MCM	-	Maximum contaminant levels
Mn	-	Manganese
MS	-	Mean square
MWCNT	-	Multi-walled carbon nanotubes
Ni	-	Nikel
NaOH	-	Sodium hydroxide
NMR	-	Nuclear magnetic resonance
OFAT	-	One factor at a time
P	-	Probability
Pb(II)	-	Lead ions
PHMG	-	Polyhexamethylene guanidine
RfDs	-	Reference dose
RSD	-	Relative standard deviation
RSM	-	Response surface methodology
RTILs	-	Room temperature ionic liquids
SEM	-	Scanning electron microscopy

SS	-	Sum of square
SWASV	-	Square wave anodic stripping voltammetric
TDS	-	Total dissolved solid
TLC	-	Thin-layer chromatography
US-EPA	-	Environmental protection agency
WHO	-	World health organization
Zn(II)	-	Zinc ions

LIST OF SYMBOLS

g	-	Gram
c	-	Concentration
cm	-	Centimeter
cm^{-1}	-	Reciprocal centimeters
E	-	East
E_{acc}	-	Deposition potential
E_f	-	Final potential
E_i	-	Initial potential
E_p	-	Peak potential
h	-	Hour
Hz	-	Hertz
I_p	-	Peak current
M	-	Molar
mM	-	Milimolar
mg	-	Milligram
min	-	Minutes
mL	-	Milliliter
mm	-	Millimeter
mmol L^{-1}	-	Millimole per liter
mV	-	Millivolt
mV/s	-	Millivolt per second
N	-	North
ppm	-	Part per million
R^2	-	Correlation coefficient
mg L^{-1}	-	Milligram per liter

ng L^{-1}	-	Nanogram per liter
s	-	Seconds
t_{acc}	-	Deposition time
V	-	Volt
v/v	-	Volume per volume
w/w	-	Weight per weight
˚C	-	Degree Celsius
δ	-	Delta
v	-	Scan rate
µA	-	Micro ampere
µL	-	Micro Liter
µg L^{-1}	-	Microgram per liter
µM	-	Micro molar

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Nitrogen (N) containing compounds are among the most widely used ligands that are well known for their importance in pre-concentration of metal ions. (Ghaedi *et al.,* 2009a). The basic reason for utilization of these ligands with metal ions is the reactivity of N donor atoms for binding with electron deficient centres of the metal ions. Thus, this concept was utilized as a modifier in electrode modification for applications in pre-concentration and detection of metal ions from different matrices. In addition, these compounds contain additional donor atoms such as phenolic, thiole or sulphur group participating in coordination which make them an ideal candidates for metal ion complexation (Shehata *et al.,* 2014). The role of chelating ligands is enhancing the selectivity and sensitivity of electrochemical method, which have been studied previously (Gupta *et al.*, 2007, Hassouna *et al.,* 2010a, Prakash and Adhikari 2011, Altmann *et al.,* 2012, Ramezani *et al.,* 2014).

Deterioration of human health due to the exposure to heavy metals has been a major issue of concern worldwide. Heavy metals have been associated with contamination and potential toxicity that negatively affect human health (Locatelli and Torsi 2003). Heavy metals are incorporated into drinking water and various food chains. Heavy metals are non-biodegradable and are considered to be dangerous pollutants. They tend to accumulate in various vital organs with exposure even at trace concentrations of metal ions which will lead to long terms effects.

The concentration range of heavy metal ions present in the environment has a great impact on human health. Thus, the government has imposed environmental regulations and guidelines for toxic pollutant because of the concern over health effects of heavy metal ions. The Malaysian drinking water quality standard stipulates the acceptable value of raw water quality and drinking water standards for cadmium ion (Cd(II)) of 0.003 mg L^{-1}, copper ion (Cu(II)) of 1.0 mg L^{-1} and silver ion (Ag(I)) of 0.05 mg L^{-1} (MOH 2000, DOE 2010a).

Considering the critical condition prevailing around the environment due to the heavy metal ions toxicity, numerous techniques have been developed for detecting low concentrations of heavy metal ions. This includes the development of UV-Vis spectrophotometry (Gouda and Amin 2014), inductively coupled plasma mass spectrometry (ICP-MS) (Beck *et al.,* 2002), inductively coupled plasma optical emission spectrometry (ICP-OES) (Losev *et al.,* 2015) and atomic absorption spectrophotometry (AAS) (Zhao *et al.,* 2015). However, many of these described methods are associated with several drawbacks such as time consuming manipulation steps, the use of sophisticated instruments and high maintenance costs (A. Afkhami *et al.,* 2013).

In an effort to alleviate complications from these methods, the highly sensitive and selective electroanalytical technique for detecting heavy metal ions has been suggested as an alternative (Li *et al.,* 2012b, Luo *et al.,* 2013). Moreover, previous works have highlighted that the intrinsic sensitivity and selectivity of such technique may be attributable to the stripping process, preceding analysis which include anodic stripping voltammetry (ASV) (Beltagi *et al.,* 2011, Giacomino *et al.,* 2011, Li *et al.,* 2012b, Luo *et al.,* 2013). Such pre-concentration step performed prior to analysis elevates sensitivity and selectivity of this method. In this step, the target metal is accumulated on a working electrode followed by stripping step that strip out the metal into the solution (Tarley *et al.,* 2009).

The mercury electrodes including hanging drop mercury, dropping mercury and thin mercury film have been widely used as the working electrode in stripping voltammetry. However, the toxicity of mercury made its applications unfriendly to

the environment, thus numerous attempts have been made to replace it with a new mercury-free and reliable electrode (Hong Lin *et al.,* 2015). Carbon based electrodes have been widely used as an alternative electrode material in electroanalysis due to wider potential window, chemical inertness, low cost, rich surface chemistry and comparative chemical inertness and suitability for various sensing and detection applications (Dong *et al.,* 2014). However, bare carbon electrodes possess some limitations such as poor sensitivity. Thus, it is very important to develop a sensitive, selective, and non-toxic electrode for the determination of heavy metals by stripping methods. Electrode modification might be the most suitable substitute for the ordinary carbon electrodes in the stripping voltammetry. The resulting modified electrodes can benefit environmental analysis through a preferential accumulation of target contaminants, the exclusion of unwanted materials or acceleration of desired electron transfer reactions that enhance both selectivity and sensitivity, improve response time, decrease the overpotential of the analytes in the redox process, and exhibit good stability (Wang 2002).

1.2 Problem Statement

Due to the toxicity of heavy metals, there is a considerable interest in their determination in environmental matrices. The direct determination of the trace metals in aqueous sample solution with a complicated matrix by AAS, GFAAS and ICP-MS is often difficult due to their extremely low concentration and matrix interferences. Pre-concentration of the sample is needed to separate analytes from sample matrix and to concentrate them in a small volume. Sergio *et al.* (2007) reported that the pre-concentration procedures include conventional liquid-liquid extraction, which present some limitation, such as the use of extensive toxic solvents. Due to this, it tends to be avoided (Sérgio L. C. Ferreira *et al.,* 2007).

On the other hand, electrochemical methods such as voltammetry offer advantages such as simplicity, low cost, high sensitivity, easy operation and ability of analysing 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 (Wang 1985, Kalcher *et al.,* 1995, Luo *et al.*, 2010).

For many years, mercury was the choice of electrode material (van den Berg *et al.,* 1986, Perez-Marin *et al.,* 2000, Gupta *et al.,* 2005, Saleh *et al.,* 2008, Rofouei *et al.,* 2009). Nevertheless, the toxicity of mercury and the limited anodic range have restricted the use of mercury electrode. Therefore, alternative electrode materials are highly desired in electrochemical studies. There are several solid materials that can be used as a 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. Owing to its physical and chemical properties, glassy carbon has become an interesting and widely applied electrode material. The often-cited advantages of glassy carbon electrode are inert and have great potential windows in anodic and cathodic electrochemistry (Oztekin *et al.,* 2010a). Unfortunately, carbon electrode lacks in sensitivity for the determination of metal ions due to fouling effects. Therefore, the development of modified electrodes that provides high conductivity, selectivity, sensitivity, stability and reusability for pollutant need to be studied extensively.

Interestingly, electrochemical analysis based on modified electrodes has proven to be a sensitive and selective method for the detection of various organic and inorganic pollutants (Hamsawahini *et al.,* 2015). 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 (salicylidenimine) (Bastos *et al.,* 2000) has been previously reported for the determination of heavy metal ions such as Cu(II), Cd(II), Pb(II), Zn(II) and Ag(I) ions using voltammetry stripping techniques. However, most of these chelating ligands exhibit limitations such as low linear range, high detection limit and response time. Following the attempts of other researchers to fabricate new selective electrodes without such limitations, ligands containing mixed O and N donor atoms

and imine group was synthesized and applied (Ghaedi *et al.,* 2012). The use of these ligands provide excellent electrochemical platforms for heavy metal analyses due to strong adsorptive and complexing capability of the ligands with metal ions (Janegitz *et al.,* 2011).

By employing the synthesized ligands with new derivatives, this enhances the selectivity and sensitivity of heavy metal detection on carbon based electrode through ligand complexation and electrode modification. Thus, this study reports on the development of a sensitive electrochemical method for the detection of heavy metal ions using glassy carbon electrode by *in-situ* addition of ligand, modification of carbon paste and glassy carbon electrode. The functional groups of ligands are expected to make effective coordination with heavy metal ions. This enables a new, simple and precise stripping voltammetry technique for the ultra-trace determination of heavy metal ions in aqueous solution.

1.3 Objectives

The present study aims to develop an acetophenone-benzaldehye ethylenediamine based electrode modifiers for rapid determination of metal ions in aqueous solutions with the following objectives:

1. To synthesize and characterize tetradentate ligands, derived from acetophenone, benzaldehye, ethylenediamine and electroanalytical screening of six metal ions (Cadmium(II), Copper(II), Chromium(III), Lead(II), Silver(I) and Zinc(II)) able to form a metal-complex using the cyclic voltammetry technique.

2. To study the electrochemical behaviour of the synthesized ligands on glassy carbon electrode and develop a method for the determination of cadmium and copper ions in tap water and sea water by differential pulse anodic stripping voltammetry technique.

3. To apply the Box-Behnken optimization approach for detection of cadmium ions using a carbon paste electrode modified with Bis(benzylidene)ethylenediamine (BBE) in tap water and sea water by square wave anodic stripping voltammetry technique.

4. To develop a *N,N'*-bis(2-hydroxyacetophenone)ethylenediamine (BZE)-multi-walled carbon nanotubes-ionic liquid-nafion modified glassy carbon electrode for silver ion detection in different real water samples by using differential pulse anodic stripping voltammetry technique and applying the modified electrode for the determination of silver ion in coastal waters in the Johor Straits.

1.4 Scope of Study

In this study, tetradentate ligands were derived by the condensation reactions of benzaldehyde and acetophenone derivatives with ethylenediamine. This organic compound has been selected as the ligand owing to the fact that it can coordinate with metal ions *via* azomethine nitrogen. The presence of azomethine group with lone pair electrons on the nitrogen atoms provides a binding site for coordination with a metal ion forming metal ligand complexes which have high stability under a variety of oxidative and reductive conditions. To confirm the structure of the ligands, characterizations using the Nuclear Magnetic Resonance spectroscopy (^{1}H-NMR, ^{13}C NMR) and Fourier Transforms Infrared spectroscopy (FTIR) were carried out.

The preliminary study of all ligands with several metal ions (Ag(I), Cd(II), Cr(III), Cu(II), Pb(II) and Zn(II) was carried out using cyclic voltammetry (CV) which is widely used for initial characterization of electrochemically active systems. It provides useful information regarding reduction and oxidation potentials as well as the reaction mechanism involving the electrode, modifier and metal ions. The selection of these metals was based on the possibilities of the metals to complex with ligand according to the Pearson theory wherein hard acids prefer to co-ordinate with hard bases and soft acids to soft bases. Ag(I), Cd(II), Cr(III), Cu(II), Pb(II) and

Zn(II) are soft Lewis acids and as a rule, their interactions with soft bases would be favoured. On the other hand, these metals were also classified as toxic heavy metals whose presence in the environment has been of increasing concern. Once absorbed, these metals can be accumulated in the body and greatly threaten human health.

The determination of heavy metals was carried out using an electrochemical stripping analysis which has been well-recognized as a powerful tool for trace metals determinations because of its low cost, easy operation, and portability. The stripping techniques were focused on differential pulse anodic stripping voltammetry (DPASV) and square wave anodic stripping voltammetry (SWASV). Carbon based electrodes (glassy carbon and carbon paste) were used as the working electrode in this study. The ability of carbon based electrode to form strong covalent bonds with a variety of materials for modification has been chosen as a solid working electrode in this study.

In-situ approach, carbon paste and drop casting modification were investigated and comprehensively optimized for the enhancement of the metal ion detection. Applications to real samples were focused on aqueous samples such as sea water, lake water, river water, tap water and drinking water. The results were compared with those obtained using an inductively coupled plasma-mass spectrometry (ICP-MS) as the conventional method.

1.5 Significance of Study

Common methods adopted for the concentration assessment of heavy metal ions are mainly focused on the use of an atomic absorption or inductively coupled plasma (ICP) atomic emission spectroscopy and ICP-mass spectrometry. However, owing to the ponderous and sophisticated instrumentation, the spectroscopy methods are fairly cumbersome and not suitable for *in-situ* measurements. On the contrary, the electrochemical techniques have attracted increasing levels of interest. This is owing to the fact that electrochemical methods possess relatively low detection limit,

good selectivity in a wide concentration range, show a fast response and non-destructive analysis, low cost, and provide easy construction and manipulation.

Stripping voltammetric techniques are well known in providing a powerful tool for the determination of metal ions. In general, the performance of anodic stripping voltammetry (ASV) is strongly affected by the electrode material. Carbon based has been an excellent choice to be used as a working electrode because of the advantages it brings such as allow scans to more negative potentials than platinum or gold, wider anodic potential windows, and low porosity which can help produce a smooth surface after polishing to give rise to minimised substrate double layer current. It is also preferred to platinum or gold because the electrochemistry of water is highly polarised on carbon and the carbon surface offers better affinity than platinum or gold for attaching carbon and any organic based materials.

Modifying electrodes' surfaces has been one of the most active areas of research interest in electrochemistry. Ligands derived from oxygen and nitrogen containing compounds have played an important role as electrode modifier for metal ion determination due to the flexible nature and easy proton donating property. These ligands show a number of sites for binding that lead to a higher coordination and cause greater kinetic and higher stability. Possessing such properties make this group of compounds as excellent ligands to be used as a potential chelating agent and modifier in the field of electrochemistry.

Upon all the points mentioned above, in this study, a new modified carbon based electrode employing organic ligands derived from acetophenone and benzaldehye as a chelating ligand and electrode modifier was developed for determination of heavy metal ions using an electrochemical technique. The novelty of this research can be summarized as follows:

a) New modified electrode utilizing the use of ligands as the modifier to enhance the detection performance of the electrode to at least 50% more than the unmodified electrode for determination of heavy metal ions in environmental aqueous samples.

b) New ideal modified carbon paste electrode by employing the Box–Behnken design approach for optimization process which possess qualities such as simple, sensitive, selective, simplified sampling and pre-concentration method, good mechanical properties, wider potential window, low background current and ease of reproduction of the electrode.

c) Fabrication of new multi-walled carbon nanotubes-*N,N'*-bis(2-hydroxy acetophenone)ethylenediamine-ionic liquid composite modified glassy carbon electrode that exhibited high sensitivity, excellent reproducibility and good stability for the detection of silver ion in aqueous solutions.

1.6 Thesis Outline

This thesis consists of seven chapters. Chapter 1 describes in detail the research background, problem statement, objectives, scope as well as significance of the study. Chapter 2 compiles the literature review of analysis of conventional heavy metal determination techniques, electroanalytical techniques, carbon base material for modified electrodes, electrode modifier and the details of heavy metal ions.

Chapter 3 describes the synthesis, characterization and electroanalytical studies of ligands; ((*N,N'*-bis(2-hydroxyacetophenone)ethylenediamine, Bis(4-hydroxybenzaldehyde)ethylenediamine, Bis(benzylidene)ethylenediamine, *N,N'*-bis(2-hydroxy-4-methoxyacetophenone)ethylenediamine). Characterizations of the ligands were carried out by ^{1}H-NMR, ^{13}C NMR and FTIR. Preliminary screenings of six metal ions (silver, cadmium, chromium, copper, lead and zinc) which are prone to form a metal-complex were carried out using the cyclic voltammetry (CV) technique.

Chapter 4 describes the methodology and discusses on *in-situ* glassy carbon electrode (GCE) modification with ligands using CV and differential pulse anodic stripping voltammetry (DPASV) technique for the analysis of copper and cadmium

ions in sea and tap water samples. Several important parameters such as pH, ligand concentration, deposition time and deposition potential were optimized.

Chapter 5 reports the results on carbon paste electrode (CPE) modification with Bis(benzylidene)ethylenediamine (BBE) for Cd(II) ions detection by CV and square wave stripping voltammetry technique (SWASV). The response surface methodological approach employing the Box-Behnken design (BBD) was used for optimizing conditions *viz.* pH, time, percentage ligand and detecting Cd(II) ions by using CPE modified with BBE. The attained optimized conditions using BBD were used in detecting Cd(II) ions in tap and sea water samples.

Chapter 6 describes a novel modification of glassy carbon with multi-walled carbon nanotubes (MWCNTs), 1-Butyl-3-methylimidazolium hexafluorophosphate ([bmim]PF_6), *N,N'*-bis(2-hydroxyacetophenone)ethylenediamine (BZE) and Nafion to form a BZE-MWCNT-[bmim]PF_6-Nafion-GCE for silver (Ag(I)) ion detection. The electrochemical behaviour of the modified electrode on Ag(I) ion detection was studied using CV and DPASV. Experimental parameters that were optimized during this study are, pH value of supporting electrolyte, influence of Nafion, MWCNTs, BZE and ([bmim]PF_6) concentration, the deposition potential and time. The developed electrode was applied for the analysis of Ag(I) ion in sea water, tap water, lake water, drinking water and 10 sampling points of river water along the Johor Straits. The physicochemical properties (temperature, pH, conductivity, total dissolved solids, salinity, dissolved oxygen and turbidity) were also investigated.

Finally, Chapter 7 summarizes the overall results obtained with suggestions for future work.

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