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**Optimization of the Differential Pulse Anodic Stripping
Voltammetry Technique for Determination of Cadmium in
Pengkalan Chepa River, Kelantan**

Dissertation submitted in partial fulfillment for the

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CERTIFICATE

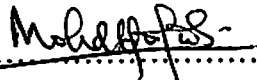
This is to clarify that the dissertation entitled

**“Optimization of the Differential Pulse Anodic Stripping Voltammetry
Technique for Determination of Cadmium in Pengkalan Chepa River,
Kelantan”**

Is the bonafide record of research work done by

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TABLE OF CONTENTS

Chapter	Title	Page
	Acknowledgement	i
	Table of Contents	ii
	List of Tables	iv
	List of Figures	v
	List of Chart	viii
	Abbreviations	ix
	Abstract	1
1	Introduction	
	1.1 Water as general	2
	1.2 Cadmium	4
	1.3 Voltammetry	6
2	Literature Review	9
3	Objectives of study	14
4	Materials and methods	
	4.1 Reagents, Glasswares, Instrumentation and Sample Collection	15
	4.2 Methodology	20

5	Result	
	5.1 Determination Optimum pH of Supporting Electrolyte	25
	5.2 Determination of Optimum Voltammetry Parameters	28
	5.3 Method Validation	41
	5.4 Application for Analysis of Cadmium in Water Samples	46
6	Discussion	51
7	Conclusion	54
	References	55
	Appendix	I-V

LIST OF TABLES

Table No.	Title	Page
4.0	Water sample that collected from Pengkalan Chepa River	19
5.0	Peak potential and peak height of pH series	26
5.1	Peak potential and peak height of scan rate	30
5.2	Peak potential and peak height of deposition potential series	33
5.3	Peak potential and peak height of deposition time series	36
5.4	Peak potential and peak height of equilibrium time series	39
5.5	Peak potential and peak height of standard addition of cadmium	42
5.6	Concentration of cadmium standard solution and their peak heights	42
5.7	Result of cadmium determination in Pengkalan Chepa River water samples	46

LIST OF FIGURES

Figure No.	Title	Page
4.0	Voltammetric System (a) Voltammetry cell of 757 VA Computerace Analyzer (b) Multimode electrode	16
4.1	Metrohm 757 VA Computerace Voltammetric Analyser combined with Multimode Electrode (MME) System	17
4.2	A cyberscan 1000 pH meter	17
4.3	Samples that used in this research, labeled as (from left) 1S, 2S, 3B, 3S, 4B, 4S, 5B and 5S	19
5.0	Voltammogram of 5 ppm cadmium at different pH	25
5.1	Graph of i_p of cadmium standard solution in different pH of supporting electrolyte	26
5.2	Voltammogram of 5 ppm cadmium using optimized initial potential, E_i and final potential, E_f	28
5.3	Voltammogram of 5 ppm cadmium at different scan rate, ν	29

5.4	Graph of i_p of 5 ppm cadmium versus scan rate, ν	30
5.5	Voltammogram of 5 ppm cadmium at different deposition potential, E_{acc}	32
5.6	Graph of i_p of 5 ppm cadmium versus deposition potential, E_{acc}	33
5.7	Voltammogram of 5 ppm cadmium at different deposition time, t_{acc}	35
5.8	Graph of i_p of 5 ppm cadmium versus deposition time, t_{acc}	37
5.9	Voltammogram of 5 ppm cadmium at different equilibrium time, t_{eq}	38
5.10	Graph of i_p of 5 ppm cadmium versus equilibrium time, t_{eq}	40
5.11	Voltammogram of 5 ppm of cadmium standard at various volumes (1 mL, 2 mL, 3 mL, 4 mL and 5 mL)	41
5.12	Graph of i_p versus concentration of cadmium	43

5.13	Voltammogram of sample 1S: Sungai Keladi (surface) with cadmium standard addition method (1 mL to 5 mL are the volumes of cadmium standard)	47
5.14	Voltammogram of sample 2S: Sungai Alor B (surface) with cadmium standard addition method (1 mL to 5 mL are the volumes of cadmium standard)	47
5.15	Voltammogram of sample 3B: Sungai Alor Lintah (Bottom) with cadmium standard addition method (1 mL to 5 mL are the volumes of cadmium standard)	48
5.16	Voltammogram of sample 3S: Sungai Alor Lintah (surface) with cadmium standard addition method (1 mL to 5 mL are the volumes of cadmium standard)	48
5.17	Voltammogram of sample 4B: Sungai Pengkalan Chepa 2 (Bottom) with cadmium standard addition method (1 mL to 5 mL are the volumes of cadmium standard)	49
5.18	Voltammogram of sample 4S: Sungai Pengkalan Chepa 2 (surface) with cadmium standard addition method (1 mL to 5 mL are the volumes of cadmium standard)	49

5.19	Voltammogram of sample 5B: Sungai Pengkalan Chepa (Bottom) with cadmium standard addition method (1 mL to 5 mL are the volumes of cadmium standard)	50
5.20	Voltammogram of sample 5S: Sungai Pengkalan Chepa (surface) with cadmium standard addition method (1 mL to 5 mL are the volumes of cadmium standard)	50

LIST OF CHART

Chart No.	Title	Page
4.0	Experimental chart	20

ABBREVIATIONS

AAS	Atomic absorption spectrometry
AdSV	Adsorptive Stripping Voltammetry
AE	Auxiliary Electrode
Ag/AgCl	Silver/silver chloride
ASV	Anodic Stripping Voltammetry
Cd	Cadmium
CSV	Cathodic Stripping Voltammetry
DID	Department of Irrigation and Drainage
DME	Dropping Mercury Electrode
DOE	Department of Environment
DPASV	Differential Pulse Anodic Stripping Voltammetry
E_{acc}	Deposition potential
E_f	Final potential
E_i	Initial potential
E_p	Peak potential
EPA	Environment Pollution Act
HCl	Acid Hydrochloride
HMDE	Hanging Mercury Drop Electrode
HNO ₃	Nitric Acid
ICP-AES	Inductively Coupled Plasma-Atomic Emission Spectroscopy
ICP-MS	ICP-Mass Spectrometry

i_p	Peak current or peak height
LOD	Limit of detection
MME	Multimode Electrode
NaOH	Sodium Hydroxide
ppb	Part per billion
ppm	Part per million
r	correlation coefficient
RE	Reference Electrode
SCE	Saturated Calomel Reference Electrode
SD	Standard Deviation
SMDE	Static Mercury Drop Electrode
SV	Stripping Voltammetry
t	Time
t_{acc}	deposition time
t_{eq}	equilibrium time
v	scan rate
WE	Working Electrode

ABSTRACT

Cadmium is one of heavy metal that can cause river water pollution by waste from factories. Common exposure of human or animal towards cadmium will cause toxicity. In determination of cadmium, voltammetric technique was used since it is highly sensitive, low cost and low limit of detection. This technique was used for qualitative and quantitative determination of cadmium in water samples. Samples were collected from five rivers; Sungai Alor B, Sungai Alor Lintah, Sungai Keladi, Sungai Pengkalan Chepa and Sungai Pengkalan Chepa 2 which are tributaries of main river, Pengkalan Chepa River at different depth (surface and bottom). Differential Pulse Anodic Stripping Voltammetry (DPSAV) technique was carried out using three electrodes, hanging mercury drop electrode (HMDE) act as working electrode, Ag/AgCl/KCl saturated act as reference electrode and platinum electrode act as auxiliary electrode. The supporting electrolyte used was acetate buffer (1.38 M, pH 4.6). The optimum voltammetric parameters to determine cadmium in river water were initial potential (E_i) -1 V, final potential (E_f) -0.2 V, scan rate (ν) 5 mV/s, voltage step 0.005 V, voltage step time 1 s, deposition potential (E_{acc}) -1 V, deposition time (t_{acc}) 60 s and equilibrium time (t_{eq}) 1000 s. Using this optimized parameters, peak potential (E_p) for cadmium standard was found at -0.632 V. The linear range of cadmium was observed over the concentration range 0.26 ppm to 1.32 ppm with correlation coefficient (r) 0.993, standard deviation (SD) 0.500, sensitivity 10.227 nA/ppm and limit of detection 147 ppb. The method had been successfully applied for determination of cadmium in real samples. The results showed that cadmium was absent in all the samples.

CHAPTER 1

INTRODUCTION

1.1 Water as general

According to Water Pollution Control Act, water means surface water or groundwater as it exists in any form (Environment Pollution Act (EPA), 2006.). It is a chemical substance that essential for all living organism to survive. It is form when hydrogen gas burns in oxygen gas (Chang, 2005). Water has chemical and physical characteristics such as tasteless, odourless and colorless liquid. It covers 71% of the earth surface where an ocean covers 97% of surface water, glaciers and polar ice caps 2.4%, and other land surface water such as rivers, lakes and ponds 0.6%.

River is a natural waterway on the earth's surface, which channels freshwater from the mountain to the sea (Department of Irrigation and Drainage (DID), 2008). Rivers has been used to provide water for food and drink of living organism (Adams & Sharpe, 1995), transport or agricultural use (Kobayashi & Ryoichi, 2001). It also played an important role in shaping the landscape of a country like Australia (National Land & Water Resources Audit, 2002) and serve as boundaries between states like in Malaysia (DID, 1999).

According to Subramanian (2008), Asia as a whole region that faces severe stress on water availability due to high population density. Many regions of the continent face severe problems of water pollution on local as well as regional scale. The Water Pollution Control

Act state that water pollution means the introduction into water of substances, biological organisms or forms of energy that alters water quality, impacts the normal use of the water or endangers public health and the living environment (EPA, 2006).

The sources of water pollution is classified into two, point and non-point. Point sources include sewage treatment plants, manufacturing and agro-based industries and animal farms. Non-point sources are defined as diffused sources like agricultural activities and surface runoffs. Thus, it cause problem to human who must drink freshwater in order to survive.

Malaysia has 189 river systems which include from 1,800 rivers and stream with total length 57300 km (DID, 2008). Thus, Department of Environment (DOE) plays a role in establish the status of water quality, detect any changes and identify pollution sources. As in Malaysia, rapid development in recent years has affected the water quality of many rivers due to the wastes that have poured into the rivers (Farah, Norulaini, Al-karkhi & Fatehah, 2008).

Water pollution can be measured based on Water Quality Index (WQI). The index ranges from 0 to 100, where a 100 represents an excellent water quality condition and analyzed based on six parameters which are dissolved oxygen (DO), biological oxygen demand (BOD), chemical oxygen demand (COD), ammonia-N (AN), total suspended solids (TSS) and pH (Intan & Omar, 2008). Besides two other parameters, heavy metals and bacteria can be used in monitoring water quality (DOE, 2006). Water pollution also can be measured by using Interim National Water Quality Standards for Malaysia (INWQS).

1.2 Cadmium

Cadmium (Cd) is one of heavy metal that can cause river water pollution. Cadmium was found by Fredrich Stromeyer in year 1817 at Gottingen, Germany. Its atomic number is 48. Thus, cadmium is located under group 12, period 5 and transition metal series in the periodic table. It valence electron is +2, atomic weight is 112.4 and silvery grey in color (Chang, 2005). Cadmium is soft, ductile metal, chalcophilic element and does not have a smell and taste. It dissolves in most organic and inorganic acids but not soluble in alkalies (Worthy, 2001).

In nature, cadmium exists as seven stable isotopes and one radioactive isotope. The seven stable isotopes and their abundances are Cd-106 (1.3%), Cd-108 (0.9%), Cd-110 (12%), Cd-111 (13%), Cd-112 (24%), Cd-114 (29%) and Cd-116 (7.5%). The radioactive isotope is Cd-113 (12%) and long half-life (Argonne National Laboratory (EVS), 2005). The most common forms of cadmium found in the environment exist in combinations with other elements such as oxygen, chlorine and sulfur to form cadmium oxide, cadmium chloride and cadmium sulfide. According to EVS (2005), cadmium is found in rare ores such as spalerite, hawleyite (cubic Cds), cadmoselite (CdSe), monteponite (CdO) and greenockite (hexagonal Cds) and it is formed as a byproduct during production of zinc, copper and lead. Cadmium is from mining, smelting, oil and coal combustion and waste incineration.

Cadmium was firstly produced in United State in 1906 from Zn-plant blue powder. Early uses included paint pigments, glassmaking, photography, dying, chemical reagents and low meting alloys. In 1900, nickel-cadmium battery was introduced by Junger and Berg. This battery used as sealed cells in radios, alarms, pacemakers, calculators, motor starters, walkie-talkies and portables appliances (Worthy, 2001). It was also used as an anticorrosive coating for steel and cast iron. It was used in semiconductors, dyes and pigments, as a stabilizer in plastics such as polyvinyl chloride, dental amalgams and as a neutron absorber in nuclear reactor control rods and shields (EVS, 2005).

Cadmium is known as a hazardous environmental pollutant with toxic effects for human and animal (Anke, Ihnat & Stoeppler, 2004). Common exposure of cadmium is by ingestion of heavily contaminated water or food. Water contaminated with cadmium from cadmium waste disposal or hazardous waste, cadmium deposited on land released to water and phosphate fertilizers. Contaminated water leads to residues in drinking water.

Human who drink water contaminated with cadmium for less than 14 days in amounts of 0.05 mg/kg/day can irritate the stomach, causing vomiting or diarrhea. Long term exposure (greater than 14 days) to lower levels of cadmium (0.005 mg/kg/day) may cause kidney disease such as formation of kidney stone and damage lungs (Agency for Toxic Substances and Disease Registry (ATSDR), 1993).

The U.S. Department of Health and Human Services determined that cadmium and certain cadmium compounds were suspected carcinogens which can cause cancer (ATSDR, 1989). Besides that, cadmium toxicity can causes learning disabilities, decreased IQ, motor

dysfunction, hyperactivity and hypoactivity (Greater Boston Physicians for Social Responsibility, 2000). In chronic toxicity, cadmium can causes renal tubular dysfunction by excretion of protein metallothionein.

1.3 Voltammetry

The branch of electrochemistry developed from the discovery of polarography in 1922 by the Czech chemist Jaroslav Heyrovsky (1890-1967). He was received the 1959 Nobel Prize in chemistry based on this finding. Later, polarography was changed name to voltammetry (Kuonaves, 2002). Polarography is a special case of voltammetry referring to the current-voltage measurement acquired using a dropping mercury electrode with a constant flow of mercury drops (Bruce, 2005).

The early voltammetric methods experienced a number of difficulties, making them less than ideal for routine analytical use. However, in the 1960s and 1970s significant advances were made in all areas of voltammetry such as theory, methodology, and instrumentation, which enhanced the sensitivity and expanded the repertoire of analytical methods (Samuel, 2002). The advances made are low maintained cost (Wang, 1985), sensitive, selective (Tsopelas *et al.*, 2002) and low limits of detection (Locatelli, 2002). The advantage of this technique includes high sensitivity where quantitative and qualitative determination of metals, inorganic and organic compounds at traces levels from 10^{-4} to 10^{-8} M (Fifield & Kealey, 2000).

The common principle of all voltammetric techniques is that they involve the application of a potential (E) to an electrode and the monitoring of the resulting current (i) flowing through the electrochemical cell. In many cases the applied potential is varied or the current is monitored over a period of time (t) (Kuonaves, 2002). Normally, there is an interrelationship between all three of these variables; E , I and t (Bond *et al.*, 1989). A plot of current which is directly proportional to the concentration of an electroactive species as a function of applied potential is called a voltammogram. The voltammogram provides quantitative and qualitative information about the species involved in the oxidation, reduction reaction or both at the working electrode (Barek *et al.*, 2001).

Three electrode systems are used including a working electrode (WE), a reference electrode (RE) and an auxiliary electrode (AE). The three electrodes are connected to the power source for precise controlled the potential applied to the working electrode. A working electrode is used for occurrence of reduction and oxidation process. It can be made positive or negative with the flip of a polarity switch on the instrument (Kenkel, 1994). An ideal working electrode should easy to handle, long term stability, large useful potential range and ideal phase interface for the electrode reaction (Thomas & Henze, 2000).

Working electrode consists of two types; liquid (eg. hanging mercury drop electrode (HMDE), dropping mercury electrode (DME) and static mercury drop electrode (SMDE) and solid (eg. graphite electrode, glassy carbon electrode and platinum electrode) (Thomas *et al.*, 2000). In this experiment, HMDE was used. HMDE is highly reproducible, if the electrode

becomes contaminated before the end of a chromatogram it is immediately renewable and its recovery from an oxygen peak is immediate (Giddings, Giddings, Grushka & Brown, 1991).

Reference electrode is used for the precise control of the potential of the working electrode (Kenkel, 1994). It can be Saturated Calomel Reference Electrode (SCE) or silver-silver chloride electrode. The potential of these electrodes is a function of the activity of the anion presents in a solution (Thomas *et al.*, 2000)

Auxiliary or counter electrode carries the bulk of the current and counters the process that occurs at the working electrode. It is important not to allow the products of the reaction occurring there to interfere with the process occurring at the working electrode (Giddings *et al.*, 1991). Thus, auxiliary electrode is placed in a separate chamber with the fritted glass disc allowing electrical contact with the rest of cell but not allowing diffusion of undesirable chemical species to the working electrode (Kenkel, 1994).

CHAPTER 2

LITERATURE REVIEW

Voltammetry is a refined, clean, simple technique that offers wide limits of detection and the fastest growing analytical technique for trace analysis (Bruce, 2005). Voltammetry is the instrumentation that less expensive than the other analytical methods. It is also available in multi-mode design that offers the analyst the choice of a variety of powerful modes. The compactness of modern polarographic equipment and its low vulnerability to mechanical and electronic breakdown make it the most favorable method for field studies (Vercruyssen, Rokus & De Zeeuw, 1982). Moreover, voltammetry is an oligo-substance method that can run several metals at the same time such as copper, cadmium and iron (Babaei & Badazadeh, 2005). Besides that, voltammetry methods are sensitive, need small sample volume requirement and speciation capability (Salbu & Steinnes, 1995).

The available sensitive analytical methods for determination of cadmium, iron and copper are too expensive. An alternative economic and sensitive method is based on Adsorptive Stripping Voltammetry (AdSV) (Wang, 2000; Shams, Babaei & Soltaninezhad, 2004). Stripping Voltammetry (SV) uses the same instrumentation as traditional polarography but a stationary electrode such as the Hanging Mercury Dropping Electrode (HMDE) is used (Bruce, 2005). The voltammetric measurement is performed on a stationary mercury drop allowing one to achieve considerable increases in sensitivity.

Stripping technique is the most common type of electrochemical detection. The principle used is the analytes are first preconcentrated by electrolytic deposition on the working electrode surface, at a suitable potential. This allows the separation of analytes from the sample matrix prior to the detection stage. Voltammetric stripping enables the very low detection limit and simultaneous determination of several analytes (Trojanowicz, 2000). There are two types of voltammetric stripping instruments; anodic stripping voltammetry (ASV) and cathodic stripping voltammetry (CSV). Differential pulse stripping voltammetry used a square wave voltammetry and provides a shorter analysis time, better sensitivity and preferred in ASV (Trojanowicz, 2000).

The most common applications of differential pulse anodic stripping voltammetry (DPASV) are in determination of metal cations that form amalgams with mercury (Trojanowicz, 2000). It is using a rotating, glassy carbon electrode, mercury film electrode under condition developed to minimize contamination sources and to enhance sensitivity for water matrices has been effectively utilized for determining both the concentration and speciation of copper, plumbum, cadmium and zinc in water (Salbu & Steinnes, 1995). In DPASV, preconcentration is achieved electrochemically and as an integral part of the determination. The first step is the reduction of metal cations with preconcentration in a mercury film electrode and then their oxidation through anodic scanning with various polarization wave forms.

The advantages of ASV are high sensitivity, low maintained costs, rapidity and minimal sample preparation (Wang, 1985). It is also a valid analytical technique that simple, suitable for the determination of any metals and allowing to obtain very low limits of detection

(Locatelli, 2002). The principles involved are deposition step and stripping step. In the deposition step, the target metal is accumulated and preconcentrated by electroreduction of the corresponding ions from aqueous solution usually at mercury electrodes so as to generate an amalgam. In second step, it involved the electrooxidation process of the material deposited in the accumulation step using a potential sweep (Christoper, 1997; Ball *et al.*, 1998).

A study on determination of Copper, Iron and Cadmium in water by using DPASV method was done (Babaei & Badazadeh, 2005). The instrument used was a multi mode electrode using a HMDE, a platinum auxiliary electrode and an Ag/AgCl as the reference electrode. Differential pulse voltammetry experiments were carried out with pulse amplitude of 50 mV, scan rate of 20 mVs⁻¹ and a pulse interval of 0.3 s. pH measurements were performed with a Methrom 744 pH meter using a combined glass electrode and the optimum pH was 9.5 using an ammonia buffer. The accumulation potential that applied was -0.4 V and accumulation time was 60 s. Finally, the result that obtained was the reduction peak potentials for copper, iron, cadmium were -0.28 V, -0.46 V and -0.65 V respectively. These reduction currents increased linearly with increasing metal concentration.

Grzybowski in his study stated that the stability constants of cadmium and lead complexes with humic substances of different molecular weight isolated from Baltic Sea water can be determined by DPASV (Grzybowski, 2000). The parameters used were pH 7, deposition potential -0.1 V, pulse height 0.5 mV, deposition time 30 min and nitrogen purge every 10 min.

Flow voltammetric analysis method was used on determination of cadmium, copper, lead and zinc in drinking water (Jakumnee, Suteerapataranon, Vaneesorn & Grudpan, 2001). Mercury film working electrode was prepared by on line mercury deposition on a glassy carbon electrode. Cadmium, copper, lead and zinc were monitored simultaneously by ASV after drinking water sample was flowed through the electrochemical cell for deposition of the metals on mercury film. The electrochemical cell used was acetate buffer 1 M at pH 4.6. Detection limits for cadmium was 4 ppb for deposition time of 20 s. Linear range of calibration graph for metal was up to 100 ppb.

Another study on determination of zinc, cadmium, lead and copper in blood samples of children aged between 3 months and 6 years was reported by using ASV (Mahajan, Walia & Sumanjit, 2005). The instrumentation that used was consists of HMDE, platinum auxiliary electrode and Ag/AgCl saturated with KCl electrode. 20 mL of ammonium acetate buffer at pH 8.3 was used. The voltammetric parameters that set up was scan rate 4 mV/s, pulse amplitude 50 mV and preconcentration time 180 s. The result obtained was concentration of cadmium in the infants remained lower because placenta acts as fairly effective barrier to cadmium. It was also found that, the accumulation of cadmium in the body increase with age. In comparison of different gender, cadmium is higher in boy.

In Germany, a research was conducted by using chelating agent, 1-Phenylpropane-1-Pentylsulfonylhydrazone-2-Oxime in determination nickel, cobalt, cadmium, lead and copper in river water samples (Iliadoua, Girousia, Dietzeb, Ottob, Voulgaropoulos & Papadopoulos, 1997). The instrumentation used was adsorptive voltammetry. Result showed that various

buffers were suitable to analyze cadmium such as phosphate, acetate, ammonia and borate buffers. The optimum condition and parameters for cadmium was pH 3, deposition potential -0.8 V, deposition time 240 s and ligand concentration $12.4 \times 10^{-6} \text{ mol dm}^{-3}$. The voltammogram was recorded that cadmium peak appear at -0.60 V. The concentration of cadmium detected in river water samples were in range 1 ppb to 5 ppb.

Besides that, the determination of traces of cadmium and zinc was done by using adsorptive stripping voltammetry (Shemirani, Rajabi, Asghari & Milani-Hosseini, 2005). The samples used were natural water obtained from tap water, spring water and under ground water. Cadmium and zinc ions were complexes with ligand 5-phenyl-1,2,4-triazolo-3-tion (PTT). Result showed the optimal conditions were pH 9.0, PTT concentration $3.5 \times 10^{-5} \text{ M}$, initial potential -0.5 V, final potential -1.2 V, deposition potential 0.1 V, deposition time 30 s, scan rate 12 mV/s and pulse height 50 mV. The peak of cadmium was appeared at -0.665 V that correspond to the reduction of Cd (II) complexes with PTT. The limit of detection of cadmium was 1.1 ng/mL.

CHAPTER 3

OBJECTIVES OF THE STUDY

The objectives of this study are:

- 3.1 To optimize voltammetric method for the analysis of cadmium in river water samples using Differential Pulse Anodic Stripping Voltammetry technique.
- 3.2 To find the optimum pH of supporting electrolyte for the analysis of cadmium in river water samples.
- 3.3 To find the optimum voltammetric parameters for the analysis of cadmium in river water samples.
- 3.4 To determine cadmium qualitatively and quantitatively in river water samples.

CHAPTER 4

MATERIALS AND METHODS

4.1 Reagents, Glasswares, Instrumentation and Sample Collection

4.1.1 Reagents

For preparing the supporting electrolyte, 8.26 gm of sodium acetate and 6 ml glacial acetate acid was used to prepare 1.38 M acetate buffer, $\text{CH}_3\text{COOH}-\text{CH}_3\text{COONa}$ (pH 4.6). In adjusting the pH, 1 M acid hydrochloride (HCl) and 1 M sodium hydroxide (NaOH) was used. The standard solution of cadmium (1000 mg/L^{-1} , Merck, Germany) used to prepare 5 M of cadmium standard solution. Deionized water was used for reagent and sample preparation. 1% nitric acid (HNO_3) was used in cleaning the glassware followed with rinsing by distilled water.

4.1.2 Glasswares

Glass pipette 10 mL, glass pipette 5 mL, micropipette 1 mL, pipette tip, pipette filler, beaker 50 mL, volumetric flask 50 mL, volumetric flask 100 mL, glass rod, voltammetric cell and amber bottle were used. Before and after used, the glasswares were cleaned using HNO_3 to prevent any metal contamination especially cadmium.

4.1.3 Instrumentation

In determination of cadmium in river water, Metrohm 757 VA Computerace Voltammetric Analyser combined with Multimode Electrode (MME) System was used as shown in Figure 4.0 and 4.1. The electrodes used were:

- 1) Working electrode : Hanging Mercury Drop Electrode
- 2) Reference electrode : Ag/AgCl/KCl saturated
- 3) Auxiliary electrode : Platinum electrode

The voltammetric parameters were optimized first. The voltammetric parameters include initial potential, final potential, voltage step, voltage step time, sweep rate, pulse amplitude, pulse time, deposition potential, deposition time and equilibrium time.

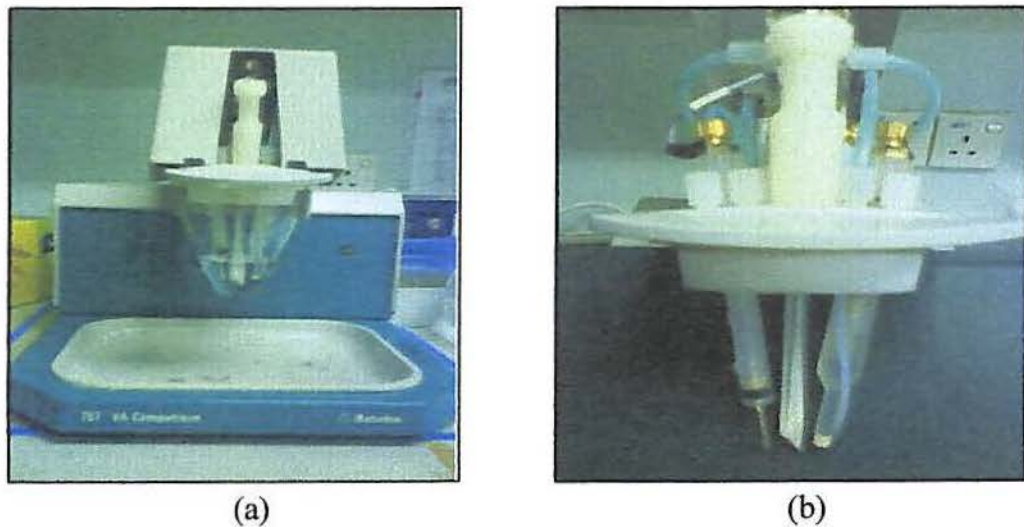


Figure 4.0 Voltammetric System (a) Voltammetry cell of 757 VA Computerace Analyzer
(b) Multimode electrode



Figure 4.1 Metrohm 757 VA Computerace Voltammetric Analyser combined with Multimode Electrode (MME) System

A Cyberscan 1000 pH meter (figure 4.2) was used to check the pH value of supporting electrolyte in voltammetric cell in all performed analysis.

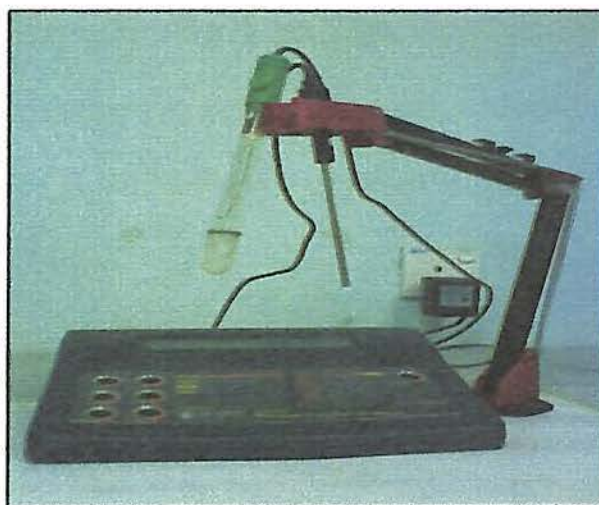


Figure 4.2 A cyberscan 1000 pH meter

Ekman Dredge is a device that was used to collect water sample from difference deeper level. It has a heavy, brass scope that held open with spring wires. It was closed by dropping a heavy, round object called messenger that hits the top causing it to close. Thus, water sample can be collected and brought up to the surface.

4.1.4 Sample collection

In this research, water samples were collected from Pengkalan Chepa River. Located at $6^{\circ}10'20.15''\text{N}$ $102^{\circ}16'46.24''\text{E}$, the catchments comprises of the main river, Pengkalan Chepa River, and its five tributaries namely Sungai Alor B, Sungai Pengkalan Chepa 2, Sungai Alor Lintah, Sungai Pengkalan Chepa and Sungai Keladi.

Eight water samples were collected which six samples were collected at bottom and surface level from three rivers (Sungai Pengkalan Chepa 2, Sungai Alor Lintah and Sungai Pengkalan Chepa) and two samples were collected only at surface level from Sungai Alor B and Sungai Keladi (Figure 4.3). Water samples at surface level were collected from 10 to 15 cm from surface while water samples at bottom level were collected from 15 to 25 cm from base of river.

After bringing up, the water samples were filtered and a few drops of HCl were added to preserve their original status. Then, they were transferred into polyethylene bottles, stored in ice compartment and placed into a refrigerator for a day.

Table 4.0 Water sample that collected from Pengkalan Chepa River

Sample	River	Level
1S	Sungai Keladi	Surface
2S	Sungai Alor B	Surface
3B	Sungai Alor Lintah	Bottom
3S		Surface
4B	Sungai Pengkalan Chepa 2	Bottom
4S		Surface
5B	Sungai Pengkalan Chepa	Bottom
5S		Surface

(S = Surface, B = Bottom)

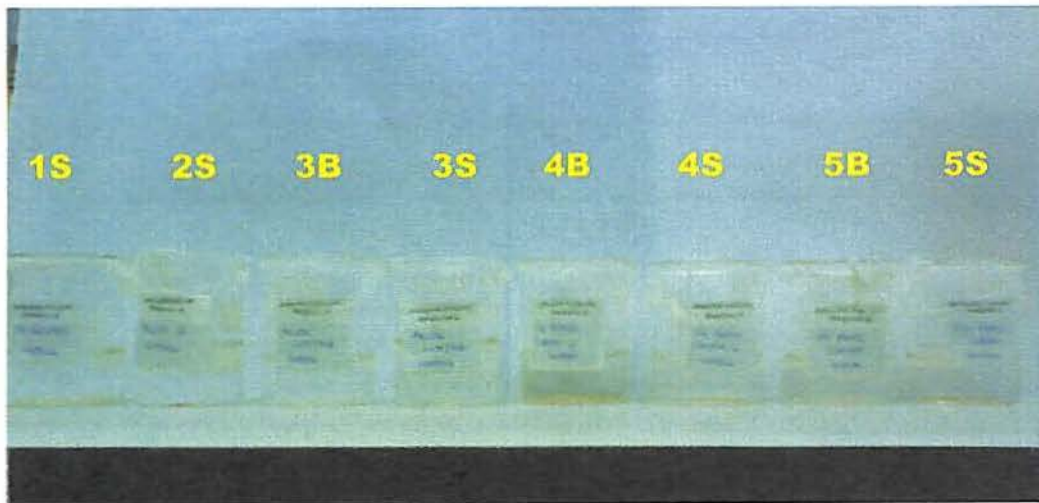


Figure 4.3 Samples that used in this research, labeled as (from left) 1S, 2S, 3B, 3S, 4B, 4S, 5B and 5S

4.2 Methodology

The method that used for determination of cadmium in river water was shown in chart 4.0 below.

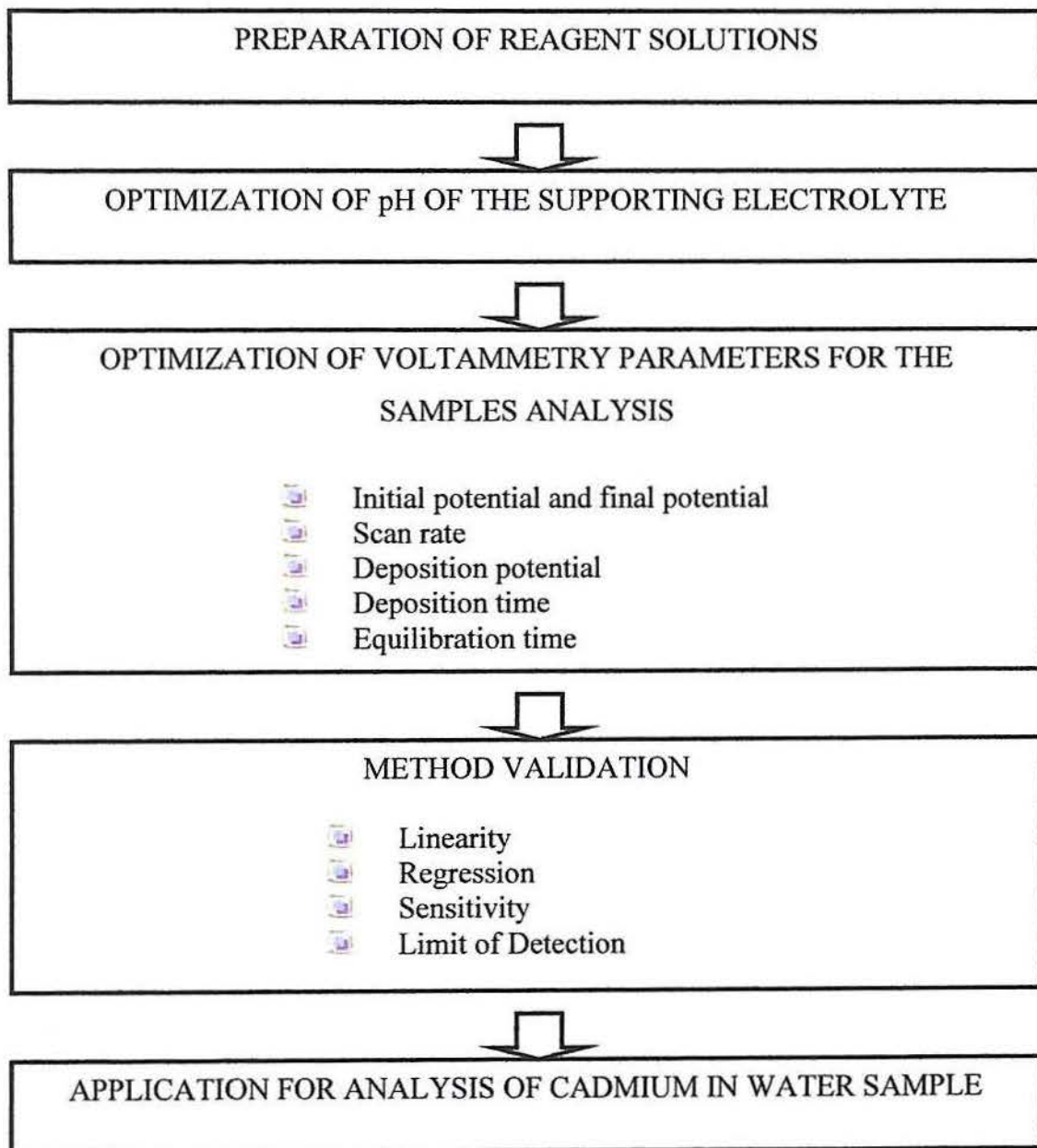


Chart 4.0 Experimental chart

4.2.1 Preparation of solutions

4.2.1.1 Acetate Buffer (pH 4.6)

Acetate buffer was prepared by using 8.26 g of sodium acetate in distilled water. 6 mL glacial acetate acid was added and makes up to 100 mL with distilled water. The pH was measured.

4.2.1.2 HCl, 1 M

9.8 mL of 32% HCl was added to 100 mL volumetric flask. Then, distilled water was filled up to 100 mL mark and this solution was transferred into an amber bottle.

4.2.1.3 NaOH, 1 M

4 g of NaOH powder was dissolved into 100 mL of distilled water. The solution was transferred into an amber bottle.

4.2.1.4 Supporting electrolyte

19 mL of acetate buffer was used for optimization procedure and sample analysis. 1 mL of cadmium standard (5 ppm) was used. The pH condition for this supporting electrolyte was adjusted by using 1 M of HCl and 1 M of NaOH solution.

4.2.2 Determination Optimum pH of Supporting Electrolyte

19 mL of acetate buffer was added into voltammetric cell and scanned as blank after purging with nitrogen for 500 minutes. 1 mL of cadmium standard (5 ppm) was added. pH of supporting electrolyte was adjusted from 2 to 9 by adding HCl or NaOH into the solution. Then, the supporting electrolyte was rescanned using the same parameter as blank scanning. For peak appeared was recorded for each pH. The highest peak was taken as optimum pH.

4.2.3 Determination of Optimum Voltammetry Parameters for Sample Analysis

19 mL of acetate buffer was transferred into voltammetric cell and scanned as a blank. 1 mL of 5 ppm cadmium standard solution was added. All analysis was performed at the pH which had been selected during the determination optimum pH of supporting electrolyte. The parameters which here optimized include:

4.2.3.1 Initial Potential, E_i and Final Potential, E_f

The parameter for E_i and E_f were optimized to get highest and most significant peak of cadmium. The optimized E_i was the potential that exclude hydrogen potential and the optimized E_f was the potential before the mercury reduction potential.

4.2.3.2 Scan Rate, ν

The optimized ν was obtained by analyzing cadmium standard solution with a series of scan rate; 5, 10, 20, 30, 40 and 50 mV/s. The findings were presented in i_p versus ν graph. ν with the highest value of i_p was selected as the optimum scan rate.

4.2.3.3 Deposition Potential, E_{acc}

The optimized E_{acc} was obtained by analyzing a series of selected deposition potential which were, 0, -0.1, -0.2, -0.4, -0.6, -0.8, -1.0 and -1.2 V. The findings were presented in i_p versus E_{acc} graph. E_{acc} with the highest value of i_p was selected as the optimum deposition potential.

4.2.3.4 Deposition Time, t_{acc}

The optimized t_{acc} was obtained by analyzing a series of selected deposition time which were 0, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60 and 65 s. The findings were presented in i_p versus t_{acc} graph. t_{acc} with the highest value of i_p was selected as the optimum deposition time.

4.2.3.5 Equilibrium time, t_{eq}

The optimized t_{eq} was obtained by analyzing a series of selected equilibrium time which were 0, 50, 100, 150, 200, 250, 300, 350, 400, 600, 1000 and 1300 s. The findings were presented in i_p versus t_{eq} graph. t_{eq} with the highest value of i_p was selected as the optimum equilibrium time.

4.2.4 Method Validation

19 mL of acetate buffer was transferred into voltammetric cell and scanned as blank using optimized parameters and nitrogen gas was purged for 500 min. Then, a series of addition of different volumes, 1, 2, 3, 4 and 5 mL from cadmium standard solution of 5 ppm were analyzed. The calibration curve was drawn using i_p of cadmium standard solution versus series of standard solution. The linearity, regression, sensitivity and limit of detection were calculated.

4.2.5 Application for Analysis of Water Sample

Eight collected water samples were analyzed. 1 mL of sample was added to 19 mL of acetate buffer and analysis was performed by using the optimum voltammetric parameters. The method above was repeated with other samples. Triplicate measurements were completed for each sample analysis.