

**ELECTROCHEMICAL BEHAVIOUR OF PESTICIDES AT BARE AND
NYLON 6,6-MODIFIED SOLID ELECTRODES IN DIFFERENTIAL PULSE
CATHODIC STRIPPING VOLTAMMETRY**

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UNIVERSITI TEKNOLOGI MALAYSIA

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6,6-MODIFIED SOLID ELECTRODES IN DIFFERENTIAL PULSE CATHODIC
STRIPPING VOLTAMMETRY

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I dedicate this thesis to my beloved family:

My dearest parents, Mr. Paramalingam & Mrs. Thingalalaky

Jai Sri Maruthi

Om Namashivaya

Mr. Khartigesan & Mrs. Indrani

Mr. Thiyagarajan & Mrs. Gayathry

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ABSTRACT

The study of the voltammetric behaviour of five types of pesticides, namely paraquat dichloride, metsulfuron-methyl, lindane, chlorothalonil and glyphosate were carried out. The electrodes used were hanging mercury drop electrode (HMDE), glassy carbon electrode (GCE), HB pencil electrode (HBPE), boron doped diamond electrode (BDDE) and screen printed electrode (SPE). Due to the toxicity of mercury and to improve the detectivity for the determination of these pesticides, nylon-6,6 was used as modifier to modify the electrodes to produce nylon-6,6-modified glassy carbon electrode (Nyl-MGCE), nylon-6,6-modified HB pencil electrode (Nyl-MHBPE), nylon-6,6-modified boron doped diamond electrode (Nyl-MBDDE), and nylon-6,6-modified screen printed electrode (Nyl-MSPE). All measurements were performed using differential pulse cathodic stripping voltammetry technique (DPCSV) vs. Ag/AgCl (3.0 M KCl). Experimental parameters such as pH of Britton-Robinson buffer (BRB), accumulation time, accumulation potential and initial potential were optimized for the pesticides determination. Linear calibration plots for the paraquat dichloride and metsulfuron-methyl were obtained with the limit of detection (LOD) value of 3.66×10^{-8} M and 8.86×10^{-8} M, respectively on HMDE. The detectivity of DPCSV with nylon-6,6-modified solid electrodes were more effective compared to bare solid electrodes, where the LOD values for paraquat dichloride were 2.75×10^{-8} M (GCE), 6.42×10^{-9} M (Nyl-MGCE), 2.37×10^{-8} M (HBPE), 1.33×10^{-8} M (Nyl-MHBPE), 2.52×10^{-8} M (SPE), 1.05×10^{-8} M (Nyl-MSPE), 2.86×10^{-8} M (BDDE), and 1.54×10^{-8} M (Nyl-MBDDE). The novel sensors, Nyl-MSPE and Nyl-MHBPE were utilized for lindane and chlorothalonil analysis, and the LODs obtained were 4.26×10^{-8} M and 2.13×10^{-8} M, respectively. Efforts to study the electroactivity behaviour of metsulfuron-methyl and glyphosate were unsuccessful at all types of working electrodes that have been assessed in this study except HMDE for metsulfuron-methyl. There was no significant interfering metal ions effect found for voltammetric determination on the selected pesticides. Approximately 90% recovery was achieved for pesticides analyses. It can be concluded that the proposed DPCSV methods with nylon-6,6-modified solid electrodes were efficiently applied in this study and verified in real water samples analysis. The proposed DPCSV methods were also comparatively selective and have good coefficient of determination ($R^2 = 0.995$).

ABSTRAK

Kajian tingkah laku voltammetri terhadap lima jenis racun perosak, iaitu parakuat diklorida, metsulfuron-metil, lindane, klorotalonil dan glifosat telah dijalankan. Elektrod yang telah digunakan ialah elektrod titisan merkuri (HMDE), elektrod karbon bak kaca (GCE), elektrod pensel HB (HBPE), elektrod berlian didopkan boron (BDDE), dan elektrod cetakan skrin (SPE). Disebabkan oleh ketoksikan merkuri dan untuk meningkatkan pengesanan bagi penentuan racun perosak, nilon-6,6 telah digunakan untuk mengubahsuai elektrod-elektrod tersebut untuk menghasilkan karbon bak kaca terubahsuai nilon-6,6 (Nyl-MGCE), elektrod pensel HB terubahsuai nilon-6,6 (Nyl-MHBPE), elektrod berlian didopkan boron terubahsuai nilon-6,6 (Nyl-MBDDE) dan elektrod cetakan skrin terubahsuai nilon-6,6 (Nyl-MSPE). Semua pengukuran dijalankan dengan menggunakan teknik voltammetri pelucutan katod denyut pembezaan (DPCSV) *vs.* Ag/AgCl (3.0 M KCl). Parameter eksperimen misalnya pH penimbal Britton-Robinson (BRB), masa pengumpulan, potensi pengumpulan dan potensi awal telah dioptimumkan untuk penentuan racun perosak. Lakaran penentukuran linear bagi parakuat diklorida dan metsulfuron-metil diperoleh dengan nilai had pengesanan (LOD) masing-masing adalah 3.66×10^{-8} M dan 8.86×10^{-8} M pada HMDE. Pengesanan DPCSV dengan elektrod pepejal terubahsuai nilon-6,6 adalah lebih efektif berbanding dengan elektrod pepejal biasa, dengan nilai LOD untuk parakuat diklorida 2.75×10^{-8} M (GCE), 6.42×10^{-9} M (Nyl-MGCE), 2.37×10^{-8} M (HBPE), 1.33×10^{-8} M (Nyl-MHBPE), 2.52×10^{-8} M (SPE), 1.05×10^{-8} M (Nyl-MSPE), 2.86×10^{-8} M (BDDE) dan 1.54×10^{-8} M (Nyl-MBDDE). Sensor baharu Nyl-MSPE dan Nyl-MHBPE telah digunakan untuk menganalisis lindane dan klorotalonil dengan LOD yang diperoleh masing-masing ialah 4.26×10^{-8} M dan 2.13×10^{-8} M. Usaha untuk mengkaji tingkah laku elektroaktiviti metsulfuron-metil dan glifosat telah tidak berjaya pada semua jenis elektrod yang digunakan dalam kajian ini kecuali HMDE bagi metsulfuron-metil. Tiada kesan ion logam yang ketara bagi penentuan voltammetri racun perosak yang terpilih. Perolehan semula 90% telah dicapai dalam analisis racun-racun perosak. Dapat disimpulkan bahawa kaedah DPCSV dengan elektrod pejal terubahsuai nilon-6,6 yang dicadangkan telah diaplikasikan dengan berkesan dalam kajian ini dan disahkan dalam analisis sampel air. Secara perbandingan, kaedah DPCSV yang dicadangkan juga selektif dan mempunyai pekali penentuan yang baik ($R^2 = 0.995$).

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LIST OF ABBREVIATIONS

AdSV	-	Adsorptive stripping voltammetry
Ag/AgCl	-	Silver/ silver chloride
APPI	-	Atmospheric pressure photoionization
ASV	-	Anodic stripping voltammetry
APGC-QTOF-MS	-	Atmospheric pressure gas chromatography quadrupole-time-of-flight mass spectrometry
AuNPs	-	Gold nanoparticles
BDDE	-	Boron doped diamond electrode
BiFE	-	Bismuth-film electrode
BRB	-	Britton-Robinson buffer
$C_{12}H_{14}Cl_2N_2 \cdot xH_2O$	-	Methyl viologen hydrate
$C_{14}H_{15}N_5O_6S$	-	Metsulfuron-methyl
$C_3H_8NO_5P$	-	Glyphosate
$C_6H_6Cl_6$	-	Lindane
$C_8Cl_4N_2$	-	Chlorothalonil
$Cd(NO_3)_2 \cdot 4H_2O$	-	Cadmium nitrate
Cd^{2+}	-	Cadmium ion
CE	-	Capillary electrophoresis
CH_2O_2	-	Formic acid
CH_3COOH	-	Acetic acid
CNTs	-	Carbon nanotubes
Conc	-	Concentration
CPE	-	Carbon paste electrode
CSE	-	Copper(II) sulfate electrode
CSV	-	Cathodic stripping voltammetry
$Cu(NO_3)_2 \cdot 3H_2O$	-	Copper(II) nitrate
Cu^{2+}	-	Copper ion

CuSAE	-	Copper solid amalgam electrode
CV	-	Cyclic voltammetry
DDE	-	Dichlorodiphenyldichloroethylene
DDT	-	Dichlordiphenyltrichloroethane
DHE	-	Dynamic hydrogen electrode
DHP	-	Dihexadecylhydrogenphosphate
DME	-	Drop mercury electrode
DME	-	Dropping mercury electrode
DNA	-	Deoxyribonucleic acid
DOE	-	Department of environment
DPCS	-	Differential pulse cathodic stripping
DPCSV	-	Differential pulse cathodic stripping voltammetry
DPV	-	Differential pulse voltammetry
EtOH	-	Ethanol
EU	-	European union
Fe(NO ₃) ₃ ·9H ₂ O	-	Iron (III) nitrate
Fe ³⁺	-	Iron ion
GC	-	Gas chromatography
GCE	-	Glassy carbon electrode
GC–EI-MS	-	Gas chromatography mass spectrometry in electron impact ionisation mode
GC-MS/MS	-	Gas chromatography tandem mass spectrometry
GE	-	Gold electrode
H ₃ BO ₃	-	Boric acid
H ₃ PO ₄	-	Orthophosphoric acid
HBPE	-	HB pencil lead electrode
HCl	-	Hydrochloric acid
HMDE	-	Hanging mercury drop electrode
HPLC	-	High performance liquid chromatography
HPLC-MS/MS	-	High performance liquid chromatography coupled to tandem mass spectrometry
HPMM	-	Heteropolyacidmontmorillonite clay
INWQS	-	Interim national water quality standard
KCl	-	Potassium chloride

LC–MS/MS	-	Liquid chromatography tandem mass spectrometry
LD	-	Lethal dose
LOD	-	Limit of detection
LOQ	-	Limit of quantification
LSV	-	Linear sweep voltammetry
m	-	Mean
m-AgSAE	-	Silver solid amalgam electrode
MALDI-TOF	-	Matrix-assisted laser desorption/ionization time-of-flight
MBDDE	-	Nylon 6,6 modified boron doped diamond electrode
MeOH	-	Methanol
MGCE	-	Nylon 6,6 modified glassy carbon electrode
MSPE	-	Nylon 6,6 modified screen printed electrode
MWCNT	-	Multi-walled carbon nanotube
N ₂	-	Nitrogen gas
NaOH	-	Sodium hydroxide
NGE	-	Nitrogen-doped graphene
NHE	-	Normal hydrogen electrode
NOM	-	Natural organic matter
Nyl-MHBPE	-	Nylon 6,6 modified HB pencil electrode
Pac	-	Polyacetylene
PANI	-	Polyaniline
PAT	-	Poly(3-alkylthiophene)
PAZ	-	Polyazulene
Pb ²⁺	-	Lead ion
Pb ₃ (NO ₃) ₂	-	Lead(II) nitrate
PBD	-	Polybutadiene
PEDOT	-	Poly(3,4-ethylenedioxythiophene)
PFu	-	Polyfuran
PIP	-	Polyisoprene
PITN	-	Poly(isothianaphthene)
PNA	-	Poly(a-naphthylamine)
PPP	-	Poly(p-phenylene)
PPS	-	Poly-p-phenylene-sulphide

PPTA	-	Poly(p-phenylene-terephthalamide)
PPV	-	Poly(p-phenylenevinylene)
PPy	-	Polypyrrole
PQ ²⁺	-	Paraquat dication
Pt	-	Platinum
PTh	-	Polythiophene
PTh-V	-	Polythiophene-vinylene
PTV	-	Poly(2,5-thienylenevinylene)
PVP	-	Polyvinylpyrrolidone
r ²	-	Correlation coefficient
RDE	-	Rotating disk electrode
RHE	-	Reversible hydrogen electrode
RRDE	-	Rotating ring-disk electrode
RSD	-	Relative standard deviation
SCE	-	Saturated calomel electrode
SD	-	Standard deviation
SEM	-	Scanning electron microscope
SHE	-	Standard hydrogen electrode
SPE	-	Screen printed electrode
SPSS	-	Statistical package for the social sciences
SWV	-	Square-wave voltammetry
TGA	-	Thermal gravimetric analysis
TiO ₂	-	Titanium dioxide
TLC	-	Thin layer chromatography
UPLC	-	Ultra high pressure liquid chromatography
UME	-	Ultra-microelectrode
USEPA	-	United States Environmental Protective Agency
UV	-	Ultraviolet
WHO	-	World Health Organization
Zn (NO ₃) ₂ .6H ₂ O	-	Zinc nitrate
Zn ²⁺	-	Zinc ion
ZnO	-	Zinc oxide
ZrO ₂	-	Zirconium Oxide

LIST OF SYMBOLS

m	-	Slope
x	-	x-axis value
c	-	Intercept
y	-	y-axis value
$^{\circ}\text{C}$	-	Degree celsius
μA	-	Microampere
μL	-	Microliter
μm	-	Micrometre
A	-	Absorbance
A	-	Ampere
cm	-	Centimeter
E	-	East
E	-	Potential
E_{acc}	-	Accumulation potential
E_f	-	Final potential
E_i	-	Initial potential
E_p	-	Peak potential
Eq.	-	Equation
E_{sw}	-	Square-wave pulse
g mol^{-1}	-	Gram per mol
g	-	Gram
I_{for}	-	Forward current
I_{net}	-	Net current
I_p	-	Peak current
I_{rev}	-	Reverse current
kV	-	Kilovolt
M	-	Molar

mg L^{-1}	-	Milligrams per litre
mg	-	Milligram
min	-	Minute
mL	-	Millilitre
mM	-	Millimolar
mV s^{-1}	-	Millivolt per second
mV	-	Millivolt
$\text{M}\Omega\text{cm}$	-	Milliohm centimeter
N	-	North
n	-	Number of measurement
nA	-	Nanoampere
nm	-	Nanometer
nM	-	Nanomolar
ppm	-	Parts per million
ppt	-	Part per trillion
R_f	-	Retention factor
s	-	Second
t_{acc}	-	Accumulation time
ν	-	Scan rate
V	-	Volt
vs	-	Versus
w/v	-	Weight to volume
λ	-	Wavelength
$\mu\text{g L}^{-1}$	-	Microgram per litre

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Water operators or waterworks facilities mainly use conventional treatment processes for removing contaminants from the raw water in order to produce safe drinking water, as shown in Figure 1.1. The operator generally determines the combination of treatment processes that is most appropriate to treat the contaminants present in the raw water. The most commonly used processes include coagulation and flocculation, sedimentation, filtration, disinfection, and storage followed by the distribution of the treated water to the consumers (Verlicchi and Masotti, 2001; Berger *et al.*, 2009; Zhou and Haynes, 2010; Chidya *et al.*, 2012; Manda *et al.*, 2016). The conventional water treatment plant has generally been designed and operated to remove mainly the suspended solids and other soluble contaminants including micro-pollutants (Jurate *et al.*, 2010; Zhang *et al.*, 2016).

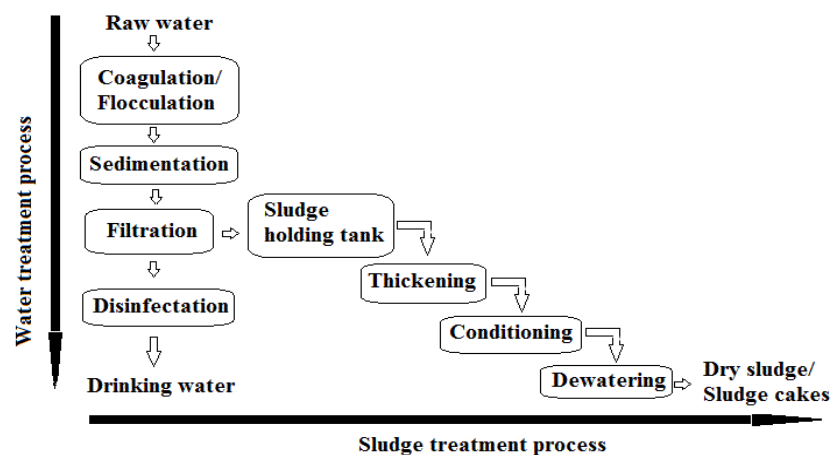


Figure 1.1 Water treatment processes

Micro-pollutants can be defined as the synthetic and natural trace of contaminants that are present in the water at lower concentration. The amount of micro-pollutants (such as natural organic matter (NOM), antibiotics, pesticides and other bioactive chemicals) present in water resources worldwide are rising thus it deteriorates the water quality (Bakouri *et al.*, 2009; Inam *et.al.*, 2013; Writer *et al.*, 2013; Carmona *et al.*, 2014; Luo *et al.*, 2014; Schaidler *et al.*, 2014; Wen *et al.*, 2014; Gavrilesco *et al.*, 2015; Rozman *et al.*, 2015; Knopp *et al.*, 2016;). Some of these chemicals eg; heavy metals are present in the water naturally, however many are synthetic compounds that are produced by human activities which includes industrial chemicals, cleaning agents, medicines, pesticides and flame retardants for furniture and plastics (Rodrigues, 2007; Jin and Peldszus, 2011; Luo *et al.*, 2014; Postigo and Barcelo, 2015). In the treatment process, not all compounds are completely removed and the treated water may contain up to several micrograms per litre of pharmaceutical products (Vieno *et al.*, 2006; Houtman, 2010; Luo *et al.*, 2014; Zhang *et al.*, 2016). Conventional water treatment plants are not able to remove these micro-pollutants efficiently (Abdullah, 2003; Nieto *et al.*, 2009; Benner *et al.*, 2013; Luo *et al.*, 2014).

Agriculture has always been an important sector of Malaysian economy, also it is currently one of the world's primary exporters of palm oil and natural rubber. These together with pepper, pineapple, cocoa and tobacco includes the main crops responsible for the growth of this sector. The pesticide industry is one of the most important industry that supports the agriculture industries which are utilized to secure agricultural or farming products and destroying the pests transmitting risky infectious diseases (Manisankar *et al.*, 2005b; Nieto *et al.*, 2009; Boxall, 2012; Inam *et al.*, 2013; Gill and Grag, 2014; Montory *et al.*, 2016).

Researchers in the pesticide industry are designing new formulations of pesticides to meet the global demand where the pesticides should be biodegradable and eco-friendly to some range and only be toxic to the target organisms (Rosell *et al.*, 2008; Gill and Grag, 2014). Conversely, most of the pesticides are non-specific and may kill the organisms that are harmless and beneficial to the ecosystem. In addition, it has been estimated that only about 0.1% of the pesticides reach the target organisms and the residual substance contaminates the surrounding

environment such as water, air and soil ecosystem (Gill and Grag, 2014). The distribution of pesticides in air, water, soil and organisms is influenced by several physical, chemical and biological factors (Priyantha and Welivegamage, 2008; Raghu *et al.*, 2012). There are different ways by which pesticides can get into water such as industrial effluent, accidental spillage, surface run off and transport from pesticide treated soils including drift into river water, ponds and lakes (Singh and Mandal, 2013; Agarwal *et al.*, 2015). Commonly, the pesticides move from fields to various water bodies by runoff or in drainage induced by rain or irrigation (Larson *et al.*, 2010; Ali *et al.*, 2014).

To date, numerous analytical techniques have been applied for the determination of pesticides in water and other environmental matrices due to their effect towards our ecosystem. This includes the developed techniques of chromatography (Kafilzadeh, 2015; Caldas *et al.*, 2016; Gui *et al.*, 2016; Lang *et al.*, 2016), capillary electrophoresis (Rojano-Delgado and Luque de Castro, 2014; Elbashir and Aboul-Enein, 2015; Chang *et al.*, 2016; Songa and Okonkwo, 2016; Wu *et al.*, 2017), colorimetry (Shi *et al.*, 2013; Bai *et al.*, 2015), spectrophotometry (Sharma *et al.*, 2012; Chen *et al.*, 2015; Takegami *et al.*, 2015) and electrochemiluminescence (Hu, 2015; Marzari *et al.*, 2017). These described methods are associated with some drawbacks such as time consuming involving some manipulation steps and expensive.

Therefore, in an effort to improve difficulties from these methods, the highly detective, quick, simple and selective electroanalytical technique for determining pesticides has been suggested as an alternative. The electrochemical methods which also known as electroanalytical techniques are routinely used in analytical chemistry and they also have been established for measurements in the laboratory regularly for fundamental research (Bard and Faulkner, 2001; Shrivastava *et al.*, 2013). The electrochemical methods can be categorized into three techniques such as potentiometry, coulometry and voltammetry (Wang, 2004; Shrivastava *et al.*, 2013). The voltammetry technique is mostly suitable for the environmental monitoring of pesticides (Tonle and Ngameni, 2011; Fischer *et al.*, 2012; Guziejewski *et al.*, 2012).

The mercury electrodes including hanging drop mercury, dropping mercury and thin mercury film also have been widely used for more than ninety years after their introduction and are probably the best sensors for the determination of pesticides (Fischer *et al.*, 2012; Barek, 2013). However, this method is not popular due to the toxicity of mercury (Fischer *et al.*, 2012; Barek, 2013; Syaza, 2017). According to Barek (2013), the recent trends in the field of electroanalytical chemistry are focused on the development of electrodes or sensors by using various chemical, biological or nanoparticles-based systems. To date, a number voltammetry techniques have been developed for the determination of pesticides (Oudou *et al.*, 2004; Erdogdu and Titretir, 2007; Gaal *et al.*, 2007; Yatmaz and Uzman, 2009; Guziejewski *et al.*, 2012; Chen and Chen, 2013; Garcia *et al.*, 2013; Inam *et al.*, 2013). The use of voltammetric techniques have significant drawbacks due to the non-electroactive behaviour of the analyte, resulting in low analytical sensitivities and reproducibility of the electroanalytical responses (Gaal *et al.*, 2007; Garcia *et al.*, 2013).

Lately, modifications of electrodes for the detection of desired analyte by means of conductive polymers have received considerable attention because of its superior electrical conductivities, good adhesion properties and suitable structural characteristics (Manisankar *et al.*, 2006; Swarupa *et al.*, 2013). In view of this, several modified working electrodes have been proposed in this study to replace mercury based electrodes. This study has also led to the development of highly detective, simple and rapid voltammetric methods for the determination of selected pesticides on modified working electrodes.

1.2 Problem Statement

In the second half of the past century, agriculture practices have been completely modified when synthetic pesticides have been used to control the pests. However, the application of these compounds became a major problem due to the possibility of contaminating the ground and surface waters, also having a consequent

potential impact on the environment and public health. It also caused the regulatory agencies, United States Environmental Protective Agency (USEPA) to establish a maximum concentration of $3 \mu\text{g L}^{-1}$ in natural waters, while the European Community established $0.1 \mu\text{g L}^{-1}$ for the same kind of sample (Springer and Lista, 2010; Wu *et al.*, 2015).

On the other hand, voltammetry technique offers advantages for pesticides determinations such as simplicity, high sensitivity and easy operation. Besides, stripping techniques are usually accredited due to the exceptional ability to preconcentrate the target pesticides through the accumulation step (Syaza, 2017). Mercury based electrode was the choice of electrode material for many years and it has been extensively used in voltammetry studies. Nonetheless, the toxicity of mercury and have restricted the use of mercury electrode (Deylova *et al.*, 2011; Syaza, 2017). Thus, an alternative electrode materials are highly preferred in voltammetry studies.

The development of “green sensor”, which aims to reduce or eliminate the use of substances hazardous to ecosystem is always essential. Therefore, some “green sensors” which are safe, detective and simple have been proposed in this study for the determination of pesticides with the main target of avoiding the use of mercury. By modification of the working electrodes using polymer, it also enhances the detectivity of electrodes for pesticides determination. Hence, this study reports on the development of highly detective, rapid and simple stripping voltammetry technique for the pesticides determination in water samples.

1.3 Objectives of Study

The aim of this research is to develop new electrochemical sensors for determination of selected pesticides in water samples with the following objectives:

- i. To study the voltammetric behaviour of selected pesticides on different types of working electrodes using differential pulse cathodic stripping voltammetry (DPCSV).
- ii. To optimize the voltammetric operating parameters for the determination of pesticides.
- iii. To develop “green sensors” for the determination of selected pesticides by utilizing nylon-6,6 as modifier.
- iv. To apply the developed methods for determination of selected pesticides in real water samples.

1.4 Scope of Study

The determination of pesticides was carried out using DPCSV which has been well-recognized as dominant tools for pesticides determinations because of its simplicity and easy operation. Although mercury is toxic, hanging mercury drop electrode (HMDE) was used to compare with carbon based electrodes (glassy carbon electrode (GCE), HB pencil lead electrode (HBPE), screen printed electrode (SPE) and boron doped diamond electrode (BDDE)) were used as the working electrodes in this study. Five type of pesticides; paraquat dichloride, glyphosate, metsulfuron methyl, lindane and chlorothalonil were selected as the target compounds in this study.

The first part of this study was focused on the determination of electrochemical behaviour of pesticides at various pH using DPCSV. The HMDE, GCE, HBPE, SPE and BDDE were applied as the working electrodes to carry out this analysis. The operating parameters such as pH of Britton-Robinson buffer, accumulation time, accumulation potential and initial potential were optimized in this study.

The second part of this study was about the application of nylon 6,6 modified solid electrodes (glassy carbon electrode (Nyl-MGCE), HB pencil lead electrode (Nyl- MHBPE), screen printed electrode (Nyl- MSPE) and boron doped diamond electrode (Nyl-MBDDE) for the selected pesticides determination. The potential of nylon 6,6 to enhance the detectivity of the proposed methods was evaluated.

In the third part, the optimized parameters were used to analyse pesticides in real water samples. The interferences studies was also conducted to observe the matrix effects toward determination of the pesticides. Several metal ions such as Cu^{2+} , Cd^{2+} , Fe^{3+} , Pb^{2+} and Zn^{2+} were used for this interference analysis. The efficiency and precision of the newly developed voltammetric methods were compared with an analytical method (UV-vis spectrophotometry).

1.5 Significance of Study

Pesticides are widely used throughout the world, they are reported to be highly toxic and its presence in the environment poses several serious problems due to long-term exposure. Hence, the prevention of their negative effect requires a systematic control of its content persistent in the agricultural products, food, soil and water. Techniques, such as thin layer chromatography (TLC), high performance liquid chromatography (HPLC), gas chromatography (GC), capillary electrophoresis (CE) and colorimetry are commonly used for the determination of pesticides. However, owing to the high maintenance cost, requires more time and complex analysis, these methods are fairly difficult for measurement. On the contrary, the electrochemical techniques have attracted increasing levels of interest. This is due to the fact that electrochemical methods possess relatively low detection limit and it emerged as a better technique in analysing the pesticides or other organic compounds.

For this study, the DPCSV with working electrode modifications using nylon 6,6 were applied for measuring the trace level of pesticides. The development of these modified solid electrodes were examined to be more detective for the

determination of pesticides. In addition, potential of using nylon 6,6 as modifier on the surface of solid electrodes also enhanced the detectivity of DPCSV technique in the current pesticides study. Besides that, the results of this research gave an account on the application of new electrochemical methods for pesticides study in water samples. The developed modified working electrode were presumed more simple and safe as compared to mercury electrode. The novelty of this research includes:

- i. A novel and detective method for the determination of paraquat dichloride, lindane and chlorothalonil on simple and safe “green sensors” compared to mercury based electrode (HMDE).
- ii. Development of new modified electrodes using nylon 6,6 as modifier with better detection performance than the unmodified electrode for determination of pesticides in environmental aqueous samples.

1.6 Thesis Outline

This thesis contains of eight chapters. The first chapter of this thesis elaborates comprehensively the basic introduction, problem statement, objectives, scope including significance of the study. Chapter 2 compiles the literature review on the importance and effect of pesticides, analytical methods for pesticides determinations, voltammetry and its application for pesticides analyses. The details on conductive polymers and polymeric modification on working electrodes has been explained in brief. Chapter 3 explains in details the experimental works of this voltammetric studies of selected pesticides, electrodes modification, application of newly developed sensors in real water samples, UV-vis analyses as well as morphological studies on surface of the developed sensor using SEM.

The results of this study is discussed in four main chapters. Chapter 4 reports on the differential pulse cathodic stripping voltammetric determination of paraquat dichloride and metsulfuron-methyl in aqueous samples using hanging mercury drop electrode. The obtained optimum voltammetric operating parameters using HMDE

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