

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

**THANALECHUMI A/P PARAMALINGGAM**

**UNIVERSITI TEKNOLOGI MALAYSIA**

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

THANALECHUMI A/P PARAMALINGGAM

A thesis submitted in fulfilment of the  
requirements for the award of the degree of  
Doctor of Philosophy (Chemistry)

Faculty of Science  
Universiti Teknologi Malaysia

JULY 2018

*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*

*Mr. Gunalan & Mrs. Kalimah*

*Mr. Partiban & Mrs. Visalatshi*

*Sharenya*

*Reshikha*

*Thiran*

*Thebaan*

*Devesht*

*Shashinie*

*Tanisha & Taniskha*

*Grace Niresha*

## ACKNOWLEDGEMENT

First of all, I wish to give my highest praise to God “*ellam pugallum iraiwaneke*” for showering me with love, blessings and strength to complete this Ph.D study.

My deepest gratitude goes to my supervisor Prof. Dr. Abdull Rahim Mohd. Yusoff for the continuous support of my Ph.D study and related research, for his patience, motivation and immense knowledge. His guidance assisted me in all the time of research and writing of this thesis. I could not imagine having such a great supervisor for my Ph.D study.

I am also very thankful to all lecturers and lab assistants of the Department of Chemistry, Faculty of Science and Centre for Environmental Sustainability and Water Security (IPASA), Universiti Teknologi Malaysia, for their assistance and who gave access to the laboratory and research facilities. Without their precious support it would not be possible to conduct this research.

I also wish to thank Ministry of Higher Education Malaysia and Universiti Teknologi Malaysia for providing LRGS grant (R.J130000. 7809. 4L810) on Water Security entitled Protection of Drinking Water: Source Abstraction and Treatment (203/PKT/6720006) as financial support of this project. I am grateful for the UTM Zamalah scholarship and this support is greatly appreciated.

Finally, my sincere appreciation goes to my fellow labmates for the stimulating discussions, for the sleepless nights we were working together before deadlines, and for all the fun we had in the last four years.

To my beloved parents and all my family members, I would like to express my heartfelt gratitude for their love, motivation and supporting me spiritually in completing this overwhelming task.

Thanks for all your encouragement.

## 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  $3.66 \times 10^{-8}$  M and  $8.86 \times 10^{-8}$  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  $2.75 \times 10^{-8}$  M (GCE),  $6.42 \times 10^{-9}$  M (Nyl-MGCE),  $2.37 \times 10^{-8}$  M (HBPE),  $1.33 \times 10^{-8}$  M (Nyl-MHBPE),  $2.52 \times 10^{-8}$  M (SPE),  $1.05 \times 10^{-8}$  M (Nyl-MSPE),  $2.86 \times 10^{-8}$  M (BDDE), and  $1.54 \times 10^{-8}$  M (Nyl-MBDDE). The novel sensors, Nyl-MSPE and Nyl-MHBPE were utilized for lindane and chlorothalonil analysis, and the LODs obtained were  $4.26 \times 10^{-8}$  M and  $2.13 \times 10^{-8}$  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  $3.66 \times 10^{-8}$  M dan  $8.86 \times 10^{-8}$  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  $2.75 \times 10^{-8}$  M (GCE),  $6.42 \times 10^{-9}$  M (Nyl-MGCE),  $2.37 \times 10^{-8}$  M (HBPE),  $1.33 \times 10^{-8}$  M (Nyl-MHBPE),  $2.52 \times 10^{-8}$  M (SPE),  $1.05 \times 10^{-8}$  M (Nyl-MSPE),  $2.86 \times 10^{-8}$  M (BDDE) dan  $1.54 \times 10^{-8}$  M (Nyl-MBDDE). Sensor baharu Nyl-MSPE dan Nyl-MHBPE telah digunakan untuk menganalisis lindane dan klorotalonil dengan LOD yang diperoleh masing-masing ialah  $4.26 \times 10^{-8}$  M dan  $2.13 \times 10^{-8}$  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 ( $R^2 = 0.995$ ).

## TABLE OF CONTENTS

CHAPTER	TITLE	PAGE
	<b>DECLARATION</b>	ii
	<b>DEDICATION</b>	iii
	<b>ACKNOWLEDGEMENT</b>	iv
	<b>ABSTRACT</b>	v
	<b>ABSTRAK</b>	vi
	<b>TABLE OF CONTENTS</b>	vii
	<b>LIST OF TABLES</b>	xvi
	<b>LIST OF FIGURES</b>	xx
	<b>LIST OF ABBREVIATIONS</b>	xxxiv
	<b>LIST OF SYMBOLS</b>	xxxviii
	<b>LIST OF APPENDICES</b>	xl
<b>1</b>	<b>INTRODUCTION</b>	<b>1</b>
	1.1 Background of Study	1
	1.2 Problem Statement	4
	1.3 Objectives of Study	5
	1.4 Scope of the Study	6
	1.5 Significance of Study	7
	1.6 Thesis Outline	8
<b>2</b>	<b>LITERATURE REVIEW</b>	<b>10</b>
	2.1 Agriculture in Malaysia	10
	2.2 Pesticides and Their Importance	11
	2.3 Impacts of Pesticides on Ecosystem	14
	2.3.1 Effects of Pesticides on Health	15

2.3.2	Reports Based on Regulation and Guidelines	16
2.4	Analytical Methods for Pesticide Determination	20
2.5	Electrochemical Techniques	21
2.5.1	Types of Voltammetric Techniques	23
2.5.1.1	Differential Pulse Voltammetry (DPV)	23
2.5.1.2	Cyclic Voltammetry (CV)	23
2.5.1.3	Square-Wave Voltammetry (SWV)	24
2.5.1.4	Anodic Stripping Voltammetry (ASV)	24
2.5.1.5	Cathodic Stripping Voltammetry (CSV)	25
2.5.1.6	Adsorptive Stripping Voltammetry (AdSV)	25
2.5.1.7	Linear Sweep Voltammetry (LSV)	26
2.6	Application of Voltammetry for Pesticide Analysis	27
2.7	Criteria for Selection of the Working Electrode Material	30
2.8	Polymeric Modification on Working Electrode	32
2.8.1	Types of Surface Modification	34
<b>3</b>	<b>EXPERIMENTAL</b>	<b>37</b>
3.1	Chemicals and Reagents	37
3.2	Voltammetry Instrumentation	38
3.2.1	Working Electrodes	39
3.3	Preparation of Nylon 6,6 Solution	40
3.4	Preparation of Stock Solutions	41
3.4.1	Paraquat Dichloride Standard Solution	41
3.4.2	Metsulfuron-Methyl Standard Solution	41
3.4.3	Lindane Standard Solution	42
3.4.4	Chlorothalonil Standard Solution	42
3.4.5	Glyphosate Standard Solution	42
3.4.6	Britton-Robinson Buffer	42
3.4.7	Sodium Hydroxide Solution	43



3.4.8	Hydrochloric Acid Solution	43
3.5	Preparation of Metal Solutions	43
3.5.1	Cadmium Standard Solution	44
3.5.2	Copper Standard Solution	44
3.5.3	Iron Standard Solution	44
3.5.4	Lead Standard Solution	44
3.5.5	Zinc Standard Solution	45
3.6	Voltammetry Procedures	45
3.6.1	Optimization of Voltammetric Operating Parameters	45
3.6.1.1	Effect of pH of BRB	45
3.6.1.2	Effect of Initial Potential	46
3.6.1.3	Effect of Accumulation Potential	46
3.6.1.4	Effect of Accumulation Time	46
3.7	Calibration Curve	46
3.8	Interference Study	47
3.9	Pesticides Analysis in Water Samples	48
3.10	River Water Sampling	48
3.11	Characterization of Electrodes and Modifier	50
3.11.1	Morphological Analysis	50
3.12	Analytical Technique for UV-Vis Spectrophotometry Analysis	51
3.12.1	Analysis of Pesticides in Water Samples	51
<b>4</b>	<b>DIFFERENTIAL PULSE CATHODIC STRIPPING VOLTAMMETRIC DETERMINATION OF PARAQUAT DICHLORIDE AND METSULFURON-METHYL IN AQUEOUS SAMPLES USING HANGING MERCURY DROP ELECTRODE</b>	<b>52</b>
4.1	Introduction	52
4.2	Voltammetric Determination of Paraquat Dichloride on Hanging Mercury Drop Electrode Using Differential Pulse Cathodic Stripping Voltammetry	53

4.2.1	Effect of Operating Parameter on Peak Current	53
4.2.1.1	Effect of pH for Paraquat Dichloride Determination	53
4.2.1.2	Effects of Initial Potential, Accumulation Potential, Time Accumulation for Paraquat Dichloride Analysis	57
4.2.2	Analytical Characteristics of Paraquat Dichloride Using DPCSV Technique	59
4.2.3	Interference Study	60
4.2.4	Validation of the Proposed Method in Determination of Paraquat Dichloride in the Commercial Paraquat	62
4.3	Voltammetric Determination of Metsulfuron-Methyl in Water Samples Using DPCSV Technique	63
4.3.1	Effect of pH	64
4.3.2	Effects of Initial Potential, Accumulation Potential, Accumulation Time on Metsulfuron-Methyl Analysis	65
4.3.3	Analytical Characteristics of Metsulfuron-Methyl Using DPCSV Technique	67
4.3.4	Interference Study	69
4.3.5	Application of Proposed Method in Real Samples Analysis	71
4.4	Summary	72

<b>5</b>	<b>SENSITIVE VOLTAMMETRIC METHODS FOR THE DETERMINATION OF PARAQUAT DIHCHLORIDE USING NYLON 6,6 MODIFIED BORON-DOPED DIAMOND AND GLASSY CARBON ELECTRODES</b>	<b>73</b>
5.1	Introduction	73
5.2	Effect of Voltammetric Parameters on the Determination of Paraquat at Bare and Nylon 6,6-	

Modified Boron-Doped Diamond Electrode	73
5.2.1 Effect of Modifier Dosage	74
5.2.1 Effect of pH	75
5.2.3 Optimization of Voltammetric Operating Variables	78
5.2.4 Calibration Curve	80
5.2.5 Repeatability and Interference Study	82
5.2.6 Analysis on Real Samples	83
5.2.7 Morphological Studies	85
5.3 Effect of Voltammetric Parameters on the Determination of Paraquat at Bare and Nylon 6,6-Modified Glassy Carbon Electrode	86
5.3.1 Effect of Modifier Dosage	86
5.3.2 Effect of pH	87
5.3.3 Optimization of Voltammetric Operating Variables	90
5.3.4 Analytical Procedure for Paraquat Dichloride Quantification	93
5.3.5 Repeatability and Interference Study	95
5.3.6 Analysis on Real Samples	97
5.4 Comparison of Developed Sensors to UV-Vis Spectrophotometry	98
5.5 Summary	101

<b>6</b>	<b>ELECTROCHEMICAL BEHAVIOUR AND QUANTIFICATION OF THE PARAQUAT DICHLORIDE USING MODIFIED PENCIL LEAD AND SCREEN PRINTED ELECTRODES AS POTENTIAL SENSORS</b>	<b>102</b>
6.1	Introduction	102
6.2	Screen Printed Electrode Modified With Nylon 6,6 As A Sensitive Voltammetric Sensor for Determination of Paraquat Dichloride	102
6.2.1	Effect of Experimental Parameters	103
6.2.1.1	Effect of Modifier Dosage	103
6.2.1.2	Effect of pH	103
6.2.1.3	Optimization of Voltammetric Operating Variables	106
6.2.2	Calibration Curve	108
6.2.3	Repeatability and Interference Study	110
6.2.4	Analysis on Real Samples	112
6.2.5	Morphological Studies	115
6.3	Effect of Voltammetric Parameters on Paraquat Dichloride Analysis using Bare and Nylon 6,6 Modified HB Pencil Lead	116
6.3.1	Effect of Modifier Dosage	116
6.3.2	pH Optimization	117
6.3.3	Optimization of Voltammetric Operating Variables	118
6.3.4	Analytical Procedure for Paraquat Dichloride Quantification	121
6.3.5	Interference Study	122
6.3.6	Analysis on Real Samples	123
6.4	Comparison of Developed Sensors to UV-Vis Spectrophotometry	124
6.5	Summary	126

<b>7</b>	<b>VOLTAMMETRIC DETERMINATION OF CHLOROTHALONIL AND LINDANE USING GREEN SENSORS: GRAPHITE HB PENCIL AND SCREEN PRINTED ELECTRODES MODIFIED WITH NYLON 6,6</b>	<b>127</b>
	7.1 Introduction	127
	7.2 Differential Pulse Cathodic Stripping Voltammetry of Lindane on Bare and Nylon 6,6 Modified Graphite HB Pencil Electrode	128
	7.2.1 Effect of Experimental Parameters	129
	7.2.1.1 Effect of Modifier Dosage	129
	7.2.1.2 Effect of pH	129
	7.2.1.3 Effect of Initial Potential, Accumulation Potential and Accumulation Time	132
	7.2.2 Calibration Curve	135
	7.2.3 Interference Study	137
	7.2.4 Analysis on Real Samples	139
	7.3 Differential Pulse Cathodic Stripping Voltammetry of Chlorothalonil on Bare and Nylon 6,6 Modified Graphite HB Pencil Electrode	141
	7.3.1 Effects of Experimental Parameters	141
	7.3.1.1 Effect of Modifier Dosage	141
	7.3.1.2 Effect of pH	142
	7.3.1.3 Effect of Initial Potential, Accumulation Potential and Accumulation Time	145
	7.3.2 Calibration Curve	147
	7.3.3 Interference Study	149
	7.3.4 Real Samples Analysis	150
	7.3.5 Comparison with Mercury Electrode	151
	7.4 Voltammetric Determination of Lindane on Bare and Modified Screen Printed Electrode (SPE) Using Differential Pulse Cathodic Stripping Voltammetry (DPCSV)	153
	7.4.1 Effects of Experimental Parameters	154

7.4.1.1	Effect of Modifier Dosage	154
7.4.1.2	Effect of pH of Supporting Electrolyte	154
7.4.1.3	Effect of Initial Potential, Accumulation Potential and Accumulation Time	157
7.4.2	Analytical Calibration Curve	159
7.4.3	Interference Study	161
7.4.4	Real Samples Analysis	163
7.5	Determination of Chlorothalonil on Bare and Modified Screen Printed Electrode (SPE) Using Differential Pulse Cathodic Stripping Voltammetry (DPCSV)	165
7.5.1	Effect of Experimental Parameters	165
7.5.1.1	Effect of Modifier Dosage	166
7.5.1.2	Effect of pH	166
7.5.1.3	Effect of Initial Potential, Accumulation Potential and Accumulation Time	169
7.5.2	Analytical Calibration Curve	172
7.5.3	Interference Study	173
7.5.4	Application of Developed SPE for the Determination of Chlorothalonil in Water Samples	175
7.6	Comparison of Developed Sensors to UV-Vis Spectrophotometry	177
7.7	Summary	179
<b>8</b>	<b>CONCLUSIONS AND RECOMMENDATIONS</b>	<b>181</b>
8.1	Conclusions	181
8.2	Recommendations	184
	<b>REFERENCES</b>	<b>185</b>
	Appendices A-C	209-211

**LIST OF TABLES**

<b>TABLE NO.</b>	<b>TITLE</b>	<b>PAGE</b>
2.1	Pesticides and its functions	11
2.2	Common pesticides used in agriculture	12
2.3	World pesticide usage at the producer level by pesticide type, 2011 and 2012 estimates	12
2.4	Classification of pesticides according to toxicity, expressed as LD <sub>50</sub> (mg/kg)	14
2.5	Long-term effects of pesticides on human health	16
2.6	Interim national water quality standard (INWQS) of pesticides	17
2.7	Physical properties of the selected pesticides	19
2.8	Pesticides determination using different analytical techniques	20
2.9	Voltammetric techniques applied for environmental applications	27
2.10	Studies on pesticides using voltammetric techniques	28
2.11	A list of common conductive polymers	33
2.12	Conductivity values of some conductive polymers	33
2.13	Polymeric modification of working electrode for pesticides analysis	35
3.1	Concentrations of nylon 6,6 solution	41
3.2	Concentrations of metal standard solutions	43
4.1	Parameters of the DPCSV calibration plot for paraquat dichloride	60

4.2	Recovery values of standard paraquat and commercial paraquat dichloride	62
4.3	Recovery values for paraquat dichloride in spiked water samples	63
4.4	Parameters of DPCSV calibration plot for metsulfuron-methyl	68
4.5	Recovery values of metsulfuron-methyl in ultra-pure water (spiked) and in commercial product, Ally at different level of concentrations	71
4.6	Real water samples analysis for metsulfuron-methyl	72
5.1	Optimization of nylon 6,6 dosage for BDDE modification	74
5.2	Summary results of paraquat dichloride analysis using DPCSV technique	81
5.3	Recovery values of paraquat dichloride in commercial paraquat at different level of concentrations	84
5.4	Determination of paraquat dichloride in real water samples	84
5.5	Optimization of nylon 6,6 dosage for GCE modification	87
5.6	The optimum parameters of paraquat dichloride determination	91
5.7	Summary results of paraquat dichloride analysis at bare GCE and Nyl-MGCE using DPCSV technique	94
5.8	Recovery values of paraquat dichloride in commercial paraquat at different level of concentrations	97
5.9	Determination of paraquat dichloride in real water samples	98
5.10	Summary results of paraquat dichloride analysis at bare BDDE, Nyl-MBDDE, bare GCE and Nyl-MGCE using DPCSV technique	99
5.11	Comparison of various voltammetric studies for paraquat dichloride determination	100



5.12	Analysis on paraquat dichloride in tap and river water samples using DPCSV and UV-vis spectrophotometry	100
6.1	Optimization of Nylon 6,6 dosage for SPE modification	103
6.2	The optimum parameters of paraquat dichloride determination	108
6.3	Comparison of LOD value for paraquat dichloride determination	110
6.4	Recovery values of paraquat dichloride in commercial paraquat at different level of concentrations	113
6.5	Determination of paraquat dichloride in real water samples	113
6.6	Optimization of nylon 6,6 dosage for HBPE modification	117
6.7	Summary results of paraquat dichloride analysis at bare HBPE and Nyl-MHBPE using DPCSV technique	122
6.8	Determination of paraquat dichloride in real water samples	124
6.9	Comparison of LOD values for paraquat dichloride determination	125
6.10	Analysis on paraquat dichloride in tap and river water samples using DPCSV and UV-vis spectrophotometry	125
7.1	Optimization of nylon 6,6 dosage for HBPE modification	129
7.2	Summary on optimization results for lindane analysis	134
7.3	Summary results of lindane using DPCSV	136
7.4	Determination of lindane in water sample using bare HBPE	140
7.5	Determination of lindane in water samples using Nyl-MHBPE	140
7.6	Optimization of nylon 6,6 dosage for HBPE modification	142
7.7	Summary results of chlorothalonil using DPCSV	148

7.8	Comparison on LOD values of chlorothalonil with other published studies	149
7.9	Determination of chlorothalonil in real water samples using bare HBPE	151
7.10	Determination of chlorothalonil in water samples using Nyl- MHBPE	151
7.11	Optimization of nylon 6,6 dosage for SPE modification	154
7.12	Summary results of lindane at bare SPE and Nyl-MSPE using DPCSV	161
7.13	Determination of lindane at bare SPE in real water samples using DPCSV method	164
7.14	Determination of lindane at Nyl-MSPE in real water samples using DPCSV method	164
7.15	Optimization of nylon 6,6 dosage for SPE modification	166
7.16	Summary on optimization results for chlorothalonil analysis	171
7.17	Summary results of chlorothalonil at bare SPE and Nyl-MSPE using DPCSV	173
7.18	Determination of chlorothalonil at bare SPE in real water samples using DPCSV method	176
7.19	Determination of chlorothalonil at Nyl-MSPE in real water samples using DPCSV method	176
7.20	Summary results of lindane analysis using DPCSV and UV-vis spectrophotometry	177
7.21	Summary results of chlorothalonil analysis using DPCSV and UV-vis spectrophotometry	178
7.22	Water samples analysis of lindane using UV-vis spectrophotometry	179
7.23	Water samples analysis of chlorothalonil using UV-vis spectrophotometry	179

## LIST OF FIGURES

<b>FIGURE NO.</b>	<b>TITLE</b>	<b>PAGE</b>
1.1	Water treatment processes	1
2.1	Classification of pesticides by chemical structure	13
2.2	Effects of pesticides on ecosystem	15
2.3	Chemical structures of the selected pesticides	18
2.4	Voltammetry electrodes system	22
2.5	Electrodes used in voltammetry analysis	22
2.6	Potential window range for some common working electrodes	31
2.7	Dip-coating process	36
3.1	Voltammetry PGSTAT 30 Autolab Metrohm Model and VA 663 stand	38
3.2	Voltammetric cell with three electrodes system	39
3.3	Working electrodes (a) HMDE, (b) SPE, (c) HBPE, (d) BDDE and (e) GCE	40
3.4	HB pencil lead modification	40
3.5	Photographic view of the river water sampling location	49
3.6	Location of water sampling point (red spot): From (A) (UTM) to (B) Kampung Jaya Sepakat (nearer to sampling point)	49
3.7	The surrounding areas near to the sampling point	50

- 4.1 Effect of pH on DPCSV peak current of  $1.5 \times 10^{-6}$  M paraquat dichloride. The experimental conditions were as follows:  $E_i = 0$  V,  $E_f = -1.2$  V,  $t_{acc} = 30$  s,  $v = 20$  mV s<sup>-1</sup> and pulse amplitude = -50 mV 54
- 4.2 (A) Plot peak potential vs. pH and (B) DPCS voltammogram of  $1.5 \times 10^{-6}$  M paraquat dichloride at different pH BRB. The experimental conditions were as follows:  $E_i = 0$  V,  $E_f = -1.2$  V,  $t_{acc} = 30$  s,  $v = 20$  mV s<sup>-1</sup> and pulse amplitude = -50 mV 55
- 4.3 DPCS voltammogram of paraquat dichloride at pH 2.0 of 0.04 M BRB. Concentration of analyte: (a) 0, (b)  $0.5 \times 10^{-6}$  M, (c)  $1.5 \times 10^{-6}$  M, and (d)  $2.5 \times 10^{-6}$  M. The experimental conditions were as follows:  $E_i = 0$  V,  $E_f = -1.2$  V,  $t_{acc} = 30$  s,  $v = 20$  mV s<sup>-1</sup> and pulse amplitude = -50 mV 56
- 4.4 Optimization of operating parameters for  $1.5 \times 10^{-6}$  M paraquat dichloride determination using HMDE: (A)  $E_i$ , (B)  $E_{acc}$  and (C)  $t_{acc}$ . The experimental conditions were as follows: pH 2.0 of 0.04 M BRB,  $v = 20$  mV s<sup>-1</sup> and pulse amplitude = -50 mV 58
- 4.5 (A) DPCS voltammogram corresponding to the calibration curve of paraquat dichloride with concentrations: (a) 0, (b)  $2.5 \times 10^{-7}$  M, (c)  $5.0 \times 10^{-7}$  M, (d)  $7.5 \times 10^{-7}$  M, (e)  $1.0 \times 10^{-6}$  M, (f)  $1.25 \times 10^{-6}$  M, (g)  $1.5 \times 10^{-6}$  M, and (h)  $1.75 \times 10^{-6}$  M and (B) Calibration plot for DPCSV of paraquat dichloride. The experimental conditions were as follows: pH 2.0 of 0.04 M BRB,  $E_i = -0.6$  V,  $E_f = -0.7$  V,  $t_{acc} = 30$  s,  $v = 20$  mV s<sup>-1</sup> and pulse amplitude = -50 mV 59
- 4.6 DPCS voltammogram of paraquat dichloride with increasing concentration: (a) 0, (b)  $0.5 \times 10^{-6}$  M, (c)  $1.5 \times 10^{-6}$  M, and (d)  $2.5 \times 10^{-6}$  M at pH 2.0 of 0.04 M BRB. The experimental conditions were as follows:  $E_i = -0.6$  V,  $E_f = -0.7$  V,  $t_{acc} = 30$  s,  $v = 20$  mV s<sup>-1</sup> and pulse amplitude = -50 mV 60
- 4.7 (A) DPCS voltammogram of paraquat dichloride after the addition of Cd<sup>2+</sup> ion (B) Effect of Cd<sup>2+</sup> ion on peak current and (C) The effects of metal ion concentrations on  $I_p$  of paraquat dichloride. The experimental conditions were as follows: pH 2.0 of 0.04 M BRB,  $E_i = -0.6$  V,  $E_f = -0.7$  V,  $t_{acc} = 30$  s,  $v = 20$  mV s<sup>-1</sup> and pulse amplitude = -50 mV 61

- 4.8 DPCS voltammogram of  $2.5 \times 10^{-6}$  M of metsulfuron-methyl in 0.04 M BRB at pH (a) pH 2.0, (b) pH 3.0 and (c) pH 4.0. The experimental conditions were as follows:  $E_i = 0$  V,  $E_f = -1.2$  V,  $t_{acc} = 30$  s,  $v = 20$  mV s<sup>-1</sup>, pulse amplitude = -50 mV 64
- 4.9 DPCS voltammogram of metsulfuron-methyl as a function of concentration in pH 2.0 of 0.04 M BRB. Concentration of analyte: (a) 0, (b)  $0.5 \times 10^{-6}$  M, (c)  $1.5 \times 10^{-6}$  M, and (d)  $2.5 \times 10^{-6}$  M. The experimental conditions were as follows:  $E_i = 0$  V,  $E_f = -1.2$  V,  $t_{acc} = 30$  s,  $v = 20$  mV s<sup>-1</sup> and pulse amplitude = -50 mV 65
- 4.10 Optimization of operating parameters for  $1.5 \times 10^{-6}$  M metsulfuron-methyl determination using HMDE: (A)  $E_i$ , (B)  $E_{acc}$  and (C)  $t_{acc}$ . The experimental conditions were as follows: pH 2.0 of 0.04 M BRB,  $v = 20$  mV s<sup>-1</sup> and pulse amplitude = -50 mV 67
- 4.11 (A) DPCS voltammogram corresponding to the calibration curve of metsulfuron-methyl with concentrations: (a) 0, (b)  $2.5 \times 10^{-7}$  M, (c)  $5.0 \times 10^{-7}$  M, (d)  $7.5 \times 10^{-7}$  M, (e)  $1.0 \times 10^{-6}$  M, (f)  $1.25 \times 10^{-6}$  M, (g)  $1.5 \times 10^{-6}$  M, (h)  $1.75 \times 10^{-6}$  M, and (i)  $2.00 \times 10^{-6}$  and (B) Calibration plot for DPCSV of metsulfuron-methyl. The experimental conditions were as follows: pH 2.0 of 0.04 M BRB,  $E_i = -0.5$  V,  $E_f = -0.5$  V,  $t_{acc} = 60$  s,  $v = 20$  mV s<sup>-1</sup> and pulse amplitude = -50 mV 68
- 4.12 DPCSV voltammogram of metsulfuron-methyl with increasing concentration: (a) 0, (b)  $0.5 \times 10^{-6}$  M, (c)  $1.5 \times 10^{-6}$  M, and (d)  $2.5 \times 10^{-6}$  M in pH 2.0 of 0.04 M BRB. The experimental conditions were as follows:  $E_i = -0.5$  V,  $E_f = -0.5$  V,  $t_{acc} = 60$  s,  $v = 20$  mV s<sup>-1</sup> and pulse amplitude = -50 mV 69
- 4.13 (A) DPCS voltammogram of metsulfuron-methyl with increasing concentration of Pb<sup>2+</sup> ion (B) Effect of Pb<sup>2+</sup> ion on  $I_p$  and (C) The effects of metal ion concentrations on  $I_p$  of metsulfuron-methyl. The experimental conditions were as follows: pH 2.0 of 0.04 M BRB,  $E_i = -0.5$  V,  $E_f = -0.5$  V,  $t_{acc} = 60$  s,  $v = 20$  mV s<sup>-1</sup> and pulse amplitude = -50 mV 70

- 5.1 DPCS voltammogram of  $2.5 \times 10^{-5}$  M paraquat dichloride at different pH of 0.04 M BRB: (A) bare BDDE and (B) Nyl-MBDDE. The experimental conditions were as follows:  $E_i = 0$  V,  $E_f = -1.4$  V,  $E_{acc} = 0$  V,  $t_{acc} = 30$  s,  $v = 20$  mV s<sup>-1</sup> and pulse amplitude = -50 mV 76
- 5.2 Plot of peak current vs. pH for  $2.5 \times 10^{-5}$  M paraquat dichloride at bare and Nyl-MBDDE. The experimental conditions were as follows:  $E_i = 0$  V,  $E_f = -1.4$  V,  $E_{acc} = 0$  V,  $t_{acc} = 30$  s,  $v = 20$  mV s<sup>-1</sup> and pulse amplitude = -50 mV 77
- 5.3 DPCS voltammogram of paraquat dichloride at optimum pH 10.0 of 0.04 M BRB: (A) bare BDDE and (B) Nyl-MBDDE: (a) 0, (b)  $0.5 \times 10^{-5}$  M, (c)  $1.5 \times 10^{-5}$  M, (d)  $2.5 \times 10^{-5}$  M. The experimental conditions were as follows:  $E_i = 0$  V,  $E_f = -1.4$  V,  $E_{acc} = 0$  V,  $t_{acc} = 30$  s,  $v = 20$  mV s<sup>-1</sup> and pulse amplitude = -50 mV 77
- 5.4 Effect of voltammetric operating variables on peak current at  $2.5 \times 10^{-6}$  M of paraquat dichloride at optimum pH 10.0 of BRB. (A)  $E_i$ , (B)  $E_{acc}$ , and (C)  $t_{acc}$ . The experimental conditions were as follows:  $E_f = -1.4$  V,  $v = 20$  mV s<sup>-1</sup> and pulse amplitude = -50 mV 79
- 5.5 DPCS voltammogram of  $2.5 \times 10^{-6}$  M paraquat dichloride at optimum pH 10.0 of BRB: (A) Nyl-MBDDE and (B) bare BDDE: The experimental conditions were as follows:  $E_i = -0.3$  V,  $E_f = -1.4$  V,  $E_{acc} = -0.4$  V,  $t_{acc} = 30$  s,  $v = 20$  mV s<sup>-1</sup> and pulse amplitude = -50 mV 80
- 5.6 Calibration curves and calibration plots for DPCSV of (A) bare BDDE and (B) Nyl-MBDDE: (a) 0 (b)  $2.0 \times 10^{-7}$  M, (c)  $3.0 \times 10^{-7}$  M, (d)  $4.0 \times 10^{-7}$  M, (e)  $5.0 \times 10^{-7}$  M, (f)  $6.0 \times 10^{-7}$  M and (g)  $7.0 \times 10^{-7}$  M. The experimental conditions were as follows:  $E_i = -0.3$  V,  $E_f = -1.4$  V,  $E_{acc} = -0.4$  V,  $t_{acc} = 30$  s,  $v = 20$  mV s<sup>-1</sup> and pulse amplitude = -50 mV 81
- 5.7 Graph peak current of paraquat dichloride vs. added concentration of metal ions. (A) bare BDDE and (B) Nyl-MBDDE. The experimental conditions were as follows:  $E_i = -0.3$  V,  $E_f = -1.4$  V,  $E_{acc} = -0.4$  V,  $t_{acc} = 30$  s,  $v = 20$  mV s<sup>-1</sup> and pulse amplitude = -50 mV 82

- 5.8 DPCSV voltammogram of paraquat dichloride (A) bare BDDE and (B) Nyl-MBDDE with increasing concentration of  $\text{Cu}^{2+}$  ion (a) pH 10.0 of 0.04 M BRB (b)  $2.5 \times 10^{-6}$  M paraquat dichloride (c) 0.1 ppm  $\text{Cu}^{2+}$  ion, (d) 0.3 ppm  $\text{Cu}^{2+}$  ion and (e) 0.5 ppm  $\text{Cu}^{2+}$  ion. The experimental conditions were as follows:  $E_i = -0.3$  V,  $E_f = -1.4$  V,  $E_{acc} = -0.4$  V,  $t_{acc} = 30$  s,  $v = 20$  mV  $\text{s}^{-1}$  and pulse amplitude =  $-50$  mV 83
- 5.9 SEM micrographs of (A) bare BDDE and (B) Nyl-MBDDE 85
- 5.10 DPCS voltammograms of  $2.5 \times 10^{-5}$  M of paraquat dichloride at different pH BRB: (A) GCE and (B) Nyl-MGCE. The experimental conditions were as follows:  $E_i = 0$  V,  $E_f = -1.4$  V,  $E_{acc} = 0$  V,  $t_{acc} = 30$  s,  $v = 20$  mV  $\text{s}^{-1}$  and pulse amplitude =  $-50$  mV 88
- 5.11 Plot of peak current vs. pH for  $2.5 \times 10^{-5}$  M paraquat dichloride at bare GCE and Nyl-MGCE. The experimental conditions were as follows:  $E_i = 0$  V,  $E_f = -1.4$  V,  $E_{acc} = 0$  V,  $t_{acc} = 30$  s,  $v = 20$  mV  $\text{s}^{-1}$  and pulse amplitude =  $-50$  mV 89
- 5.12 DPCS voltammograms of paraquat dichloride at (A) bare GCE (at pH 11.0 BRB) and (B) Nyl-MGCE (at pH 10.0 BRB) with the increasing concentrations (a) 0, (b)  $0.5 \times 10^{-5}$  M, (c)  $1.5 \times 10^{-5}$  M, (d)  $2.5 \times 10^{-5}$  M. The experimental conditions were as follows: pH BRB 11.0,  $E_i = 0$  V,  $E_f = -1.4$  V,  $E_{acc} = 0$  V,  $t_{acc} = 30$  s,  $v = 20$  mV  $\text{s}^{-1}$  and pulse amplitude =  $-50$  mV 90
- 5.13 Optimization of operating parameters for  $2.5 \times 10^{-6}$  M paraquat dichloride determination using bare GCE (pH 11.0 of 0.04 M BRB) and Nyl-MGCE (pH 10.0 of 0.04 M BRB): (A)  $E_i$ , (B)  $E_{acc}$ , and (C)  $t_{acc}$ . The experimental conditions were as follows:  $E_f = -1.4$  V,  $v = 20$  mV  $\text{s}^{-1}$  and pulse amplitude =  $-50$  mV 92
- 5.14 DPCS voltammogram for  $2.5 \times 10^{-6}$  M paraquat dichloride at (a) bare GCE and (b) Nyl-MGCE at optimum conditions as listed in Table 5.6 93
- 5.15 Calibration curves and calibration plots for  $2.5 \times 10^{-6}$  M paraquat dichloride using (A) bare GCE and (B) Nyl-MGCE. The experimental conditions were as in Table 5.6 94

5.16	Effects of metal ions on the peak current of $2.5 \times 10^{-5}$ M paraquat dichloride at bare GCE in BRB 0.04 M at pH 11.0. The experimental conditions were as in Table 5.6	95
5.17	Effects of metal ions on the peak current of $2.5 \times 10^{-5}$ M paraquat dichloride at Nyl-MGCE in BRB 0.04 M at pH 10.0. The experimental conditions were as in Table 5.6	96
5.18	Calibration plots for paraquat dichloride using UV-vis spectrophotometry	99
6.1	Effects of pH on $2.5 \times 10^{-5}$ M paraquat dichloride analysis at Nyl-MSPE: (A) DPCS voltammogram, (B) Peak current vs. pH and (C) Peak potential vs. pH. The experimental conditions were as follows: $E_i = 0$ V, $E_f = -1.2$ V, $E_{acc} = 0$ V, $t_{acc} = 30$ s, $v = 20$ mV $s^{-1}$ and pulse amplitude = $-50$ mV	105
6.2	DPCS voltammogram of paraquat dichloride: (A) bare SPE (optimal pH 10.0) and (B) Nyl-MSPE (optimal pH 9.0): (a) 0, (b) $0.5 \times 10^{-5}$ M, (c) $1.5 \times 10^{-5}$ M, (d) $2.5 \times 10^{-5}$ M. The experimental conditions were as follows: $E_i = 0$ V, $E_f = -1.4$ V, $E_{acc} = 0$ V, $t_{acc} = 30$ s, $v = 20$ mV $s^{-1}$ and pulse amplitude = $-50$ mV	106
6.3	Effect of optimization parameters: (A) $E_i$ , (B) $E_{acc}$ and (C) $t_{acc}$ at bare and modified SPE. The experimental conditions were as follows: $E_f = -1.4$ V, $v = 20$ mV $s^{-1}$ and pulse amplitude = $-50$ mV	107
6.4	DPCS voltammogram for $2.5 \times 10^{-6}$ M paraquat dichloride at (a) bare SPE and (b) Nyl-MSPE at optimum conditions as listed in Table 6.2	108
6.5	Calibration curves and calibration plots for DPCSV of (A) bare SPE and (B) Nyl-MSPE at optimum conditions (a) 0, (b) $1 \times 10^{-7}$ M (c) $2 \times 10^{-7}$ M, (d) $3 \times 10^{-7}$ M, (e) $4 \times 10^{-7}$ M, (f) $5 \times 10^{-7}$ M and (g) $6 \times 10^{-7}$ M. The experimental conditions were as in Table 6.2	109
6.6	(A) DPCS voltammogram of $2.5 \times 10^{-6}$ M paraquat dichloride analysis using bare SPE with the addition of $Pb^{2+}$ ion, (B) Graph peak current of paraquat dichloride vs. added concentration of $Pb^{2+}$ ion and (C) Interference studies of other metal ions. The experimental conditions were as in Table 6.2	111



- 6.7 (A) DPCS voltammogram of  $2.5 \times 10^{-6}$  M paraquat dichloride analysis using Nyl-SPE with the addition of  $\text{Fe}^{3+}$  ion, (B) Graph peak current of paraquat dichloride vs. added concentration of  $\text{Fe}^{3+}$  ion and (C) Interference studies of other metal ions. The experimental conditions were as in Table 6.2 112
- 6.8 DPCS voltammogram of  $3 \times 10^{-7}$  M paraquat dichloride for water samples analysis at bare SPE and Nyl-MSPE: (A) drinking water taken from water dispenser, (B) tap water and (C) river water. The experimental conditions were as in Table 6.2 115
- 6.9 SEM micrographs of (A) bare SPE and (B) Nyl-MSPE 116
- 6.10 Effects of pH on  $2.5 \times 10^{-5}$  M paraquat dichloride analysis at Nyl-HBPE: (A) DPCS voltammogram, (B) peak current vs. pH and (C) DPCS voltammogram at optimal pH 10.0: (a) 0, (b)  $0.5 \times 10^{-5}$  M, (c)  $1.5 \times 10^{-5}$  M, (d)  $2.5 \times 10^{-5}$  M. The experimental conditions were as follows:  $E_i = 0$  V,  $E_f = -1.2$  V,  $E_{acc} = 0$  V,  $t_{acc} = 30$  s,  $v = 20$  mV s<sup>-1</sup> and pulse amplitude = -50 mV 118
- 6.11 Optimization of operating parameters for  $2.5 \times 10^{-6}$  M paraquat dichloride determination using bare HBPE (pH 8.0 of 0.04 M BRB) and Nyl-MHBPE (pH 10.0 of 0.04 M BRB): (A)  $E_i$ , (B)  $E_{acc}$ , and (C)  $t_{acc}$ . Experimental conditions were as follows:  $E_f = -1.4$  V,  $v = 20$  mV s<sup>-1</sup> and pulse amplitude = -50 mV 120
- 6.12 DPCS voltammogram for  $2.5 \times 10^{-6}$  M paraquat dichloride at bare HBPE and Nyl-HBPE at optimum conditions. The experimental conditions were as follows:  $E_i = -0.2$  V,  $E_f = -1.4$  V,  $E_{acc} = -0.4$  V,  $t_{acc} = 60$  s,  $v = 20$  mV s<sup>-1</sup> and pulse amplitude = -50 mV 121
- 6.13 Calibration curve and calibration plot for paraquat dichloride using Nyl-MHBPE at pH 10.0 of 0.04 M BRB. The experimental conditions were as follows:  $E_i = -0.2$  V,  $E_f = -1.4$  V,  $E_{acc} = -0.4$  V,  $t_{acc} = 60$  s,  $v = 20$  mV s<sup>-1</sup> and pulse amplitude = -50 mV 122
- 6.14 Effects of metal ions on the peak current of paraquat dichloride at (A) bare HBPE and (B) Nyl-MHBPE. The experimental conditions were as follows:  $E_i = -0.3$  V,  $E_f = -1.4$  V,  $E_{acc} = -0.4$  V,  $t_{acc} = 60$  s,  $v = 20$  mV s<sup>-1</sup> and pulse amplitude = -50 mV 123

- 7.1 DPCS voltammogram of  $2.5 \times 10^{-5}$  M lindane at different pH of 0.04 M BRB: (A) bare HBPE: (b) pH 6.0, (c) pH 7.0, (d) pH 8.0, (e) pH 9.0, (f) pH 10.0, (g) pH 11.0 and (B) Nyl-HBPE: (a) pH 5.0, (b) pH 6.0, (c) pH 7.0, (d) pH 8.0, (e) pH 9.0. The experimental conditions were as follows:  $E_i = 0$  V,  $E_f = -1.4$  V,  $E_{acc} = 0$  V,  $t_{acc} = 30$  s,  $v = 20$  mV s<sup>-1</sup> and pulse amplitude = -50 mV 130
- 7.2 Plot of peak current vs. pH for  $2.5 \times 10^{-5}$  M lindane at bare HBPE and Nyl-MHBPE. The experimental conditions were as follows:  $E_i = 0$  V,  $E_f = -1.4$  V,  $E_{acc} = 0$  V,  $t_{acc} = 30$  s,  $v = 20$  mV s<sup>-1</sup> and pulse amplitude = -50 mV 131
- 7.3 Plot of peak potential vs. pH for  $2.5 \times 10^{-5}$  M lindane at bare HBPE and Nyl-MHBPE. The experimental conditions were as follows:  $E_i = 0$  V,  $E_f = -1.4$  V,  $E_{acc} = 0$  V,  $t_{acc} = 30$  s,  $v = 20$  mV s<sup>-1</sup> and pulse amplitude = -50 mV 131
- 7.4 DPCS voltammogram of lindane at optimum pH of 0.04 M BRB: (A) bare HBPE (at pH 8.0) and (B) Nyl-MHBPE (at pH 7.0): (a) 0, (b)  $0.5 \times 10^{-5}$  M, (c)  $1.5 \times 10^{-5}$  M, (d)  $2.5 \times 10^{-5}$  M. The experimental conditions were as follows:  $E_i = 0$  V,  $E_f = -1.4$  V,  $E_{acc} = 0$  V,  $t_{acc} = 30$  s,  $v = 20$  mV s<sup>-1</sup> and pulse amplitude = -50 mV 132
- 7.5 Effect of  $E_{acc}$  on peak current of  $2.5 \times 10^{-6}$  M lindane at bare HBPE and Nyl-MHBPE. The experimental conditions were as follows:  $E_i = -0.1$  V,  $E_f = -1.2$  V,  $t_{acc} = 30$  s,  $v = 20$  mV s<sup>-1</sup> and pulse amplitude = -50 mV 134
- 7.6 Effect of  $t_{acc}$  on peak current of  $2.5 \times 10^{-6}$  M of lindane at bare HBPE and Nyl-MHBPE. The experimental conditions were as follows:  $E_i = -0.1$  V,  $E_f = -1.2$  V,  $E_{acc} = -0.1$ ,  $v = 20$  mV s<sup>-1</sup> and pulse amplitude = -50 mV 134
- 7.7 DPCS voltammogram of lindane at optimum condition: (A) bare HBPE and (B) Nyl-MHBPE: (a) 0, (b)  $0.5 \times 10^{-6}$  M, (c)  $1.5 \times 10^{-6}$  M, (d)  $2.5 \times 10^{-6}$  M. The experimental conditions were as in Table 7.2 135

- 7.8 Calibration curves and calibration plots for DPCSV of (A) bare HBPE and (B) Nyl-MHBPE: (a) 0, (b)  $1 \times 10^{-7}$  M, (c)  $2 \times 10^{-7}$  M, (d)  $3 \times 10^{-7}$  M, (e)  $4 \times 10^{-7}$  M, (f)  $5 \times 10^{-7}$  M, (g)  $6 \times 10^{-7}$  M and (h)  $7 \times 10^{-7}$  M. The experimental conditions were as in Table 7.2 136
- 7.9 (A) DPCSV voltammogram of lindane with increasing concentration of  $\text{Fe}^{3+}$  ion (a) BRB pH 8.0 (b)  $2.5 \times 10^{-6}$  M lindane (c) 0.1 ppm  $\text{Fe}^{3+}$  ion, (d) 0.3 ppm  $\text{Fe}^{3+}$  ion and (e) 0.5 ppm  $\text{Fe}^{3+}$  ion under optimum operating parameters with scan rate  $20 \text{ mV s}^{-1}$ , (B) Effect of  $\text{Fe}^{3+}$  on peak current of lindane and (C) Effect of other interfering metal ions on peak current of lindane 138
- 7.10 (A) DPCSV voltammogram of lindane with increasing concentration of  $\text{Cd}^{2+}$  ion (a) BRB pH 7.0 (b)  $2.5 \times 10^{-6}$  M lindane (c) 0.1 ppm  $\text{Cd}^{2+}$  ion, (d) 0.3 ppm  $\text{Cd}^{2+}$  ion and (e) 0.5 ppm  $\text{Cd}^{2+}$  ion under optimum operating parameters with scan rate  $20 \text{ mV s}^{-1}$  (B) Effect of  $\text{Cd}^{2+}$  on peak current of lindane and (C) Effect of other interfering metal ions on peak current of lindane 139
- 7.11 DPCSV voltammogram of  $2.5 \times 10^{-5}$  M chlorothalonil at different pH of 0.04 M BRB: (A) bare HBPE: (a) pH 6.0, (b) pH 7.0, (c) pH 8.0, (d) pH 9.0, (e) pH 10.0, (f) pH 11.0, (g) pH 12.0 and (B) Nyl-MHBPE: (a) pH 4.0, (b) pH 5.0, (c) pH 6.0, (d) pH 7.0, (e) pH 8.0, (f) pH 9.0, (g) pH 10.0. The experimental conditions were as follows:  $E_i = 0 \text{ V}$ ,  $E_f = -1.4 \text{ V}$ ,  $E_{\text{acc}} = 0 \text{ V}$ ,  $t_{\text{acc}} = 30 \text{ s}$ ,  $v = 20 \text{ mV s}^{-1}$  and pulse amplitude =  $-50 \text{ mV}$  143
- 7.12 Plot of peak current vs. pH for  $2.5 \times 10^{-5}$  M chlorothalonil. (A) bare HBPE and (B) Nyl-MHBPE. The experimental conditions were as follows:  $E_i = 0 \text{ V}$ ,  $E_f = -1.4 \text{ V}$ ,  $E_{\text{acc}} = 0 \text{ V}$ ,  $t_{\text{acc}} = 30 \text{ s}$ ,  $v = 20 \text{ mV s}^{-1}$  and pulse amplitude =  $-50 \text{ mV}$  143
- 7.13 Plot of peak potential vs. pH for  $2.5 \times 10^{-5}$  M chlorothalonil at bare HBPE and Nyl-MHBPE. The experimental conditions were as follows:  $E_i = 0 \text{ V}$ ,  $E_f = -1.4 \text{ V}$ ,  $E_{\text{acc}} = 0 \text{ V}$ ,  $t_{\text{acc}} = 30 \text{ s}$ ,  $v = 20 \text{ mV s}^{-1}$  and pulse amplitude =  $-50 \text{ mV}$  144

- 7.14 DPCS voltammogram of chlorothalonil at optimum pH of 0.04 M BRB: (A) bare HBPE (at pH 9.0) and (B) Nyl-MHBPE (at pH 8.0): (a) 0, (b)  $0.5 \times 10^{-5}$  M, (c)  $1.5 \times 10^{-5}$  M, (d)  $2.5 \times 10^{-5}$  M. The experimental conditions were as follows:  $E_i = 0$  V,  $E_f = -1.4$  V,  $E_{acc} = 0$  V,  $t_{acc} = 30$  s,  $v = 20$  mV s<sup>-1</sup> and pulse amplitude = -50 mV 144
- 7.15 Effect of  $E_{acc}$  for  $2.5 \times 10^{-6}$  M chlorothalonil analysis at both electrodes. The experimental conditions were as follows:  $E_i = -0.1$  V,  $E_f = -1.2$  V,  $t_{acc} = 30$  s,  $v = 20$  mV s<sup>-1</sup> and pulse amplitude = -50 mV 146
- 7.16 Effect of  $t_{acc}$  for  $2.5 \times 10^{-6}$  M chlorothalonil analysis at both electrodes. The experimental conditions were as follows:  $E_i = -0.1$  V,  $E_f = -1.2$  V,  $E_{acc} = -0.1$  V,  $v = 20$  mV s<sup>-1</sup> and pulse amplitude = -50 mV 146
- 7.17 DPCS voltammogram of chlorothalonil at optimum condition: (A) bare HBPE (at pH 9.0) and (B) Nyl-MHBPE (at pH 8.0): (a) 0, (b)  $0.5 \times 10^{-6}$  M, (c)  $1.5 \times 10^{-6}$  M, (d)  $2.5 \times 10^{-6}$  M. The experimental conditions were as follows:  $E_i = -0.1$  V,  $E_f = -1.4$  V,  $E_{acc} = -0.1$  V,  $t_{acc} = 30$  s,  $v = 20$  mV s<sup>-1</sup> and pulse amplitude = -50 mV 147
- 7.18 Calibration curves and calibration plots for DPCSV of (A) bare HBPE and (B) Nyl-MHBPE: (a) 0, (b)  $1 \times 10^{-7}$  M, (c)  $2 \times 10^{-7}$  M, (d)  $3 \times 10^{-7}$  M, (e)  $4 \times 10^{-7}$  M, (f)  $5 \times 10^{-7}$  M, (g)  $6 \times 10^{-7}$  M and (h)  $7 \times 10^{-7}$  M. The experimental conditions were as follows:  $E_i = -0.1$  V,  $E_f = -1.4$  V,  $E_{acc} = -0.1$  V,  $t_{acc} = 30$  s,  $v = 20$  mV s<sup>-1</sup> and pulse amplitude = -50 mV 148
- 7.19 DPCSV voltammogram of chlorothalonil (A) bare HBPE (at pH 9.0) and (B) Nyl-MHBPE (at pH 8.0) with increasing concentration of Cd<sup>2+</sup> ion (a) 0 (b)  $2.5 \times 10^{-6}$  M chlorothalonil (c) 0.1 ppm Cd<sup>2+</sup> ion, (d) 0.3 ppm Cd<sup>2+</sup> ion and (e) 0.5 ppm Cd<sup>2+</sup> ion. The experimental conditions were as follows:  $E_i = -0.1$  V,  $E_f = -1.4$  V,  $E_{acc} = -0.1$  V,  $t_{acc} = 30$  s,  $v = 20$  mV s<sup>-1</sup> and pulse amplitude = -50 mV 150
- 7.20 (A) Plot of peak current vs. pH for  $2.5 \times 10^{-5}$  M chlorothalonil at HMDE and (B) DPCS voltammogram of chlorothalonil at optimum pH 8.0 of 0.04 M BRB: (a) 0, (b)  $0.5 \times 10^{-5}$  M, (c)  $1.5 \times 10^{-5}$  M, (d)  $2.5 \times 10^{-5}$  M. The experimental conditions were as follows:  $E_i = 0$  V,  $E_f = -1.4$  V,  $E_{acc} = 0$  V,  $t_{acc} = 30$  s,  $v = 20$  mV s<sup>-1</sup> and pulse amplitude = -50 mV 152

- 7.21 Comparison on electrode performance for  $2.5 \times 10^{-5}$  M chlorothalonil analysis at pH 8.0 of 0.04 M BRB. The experimental conditions were as follows:  $E_i = 0$  V,  $E_f = -1.4$  V,  $E_{acc} = 0$  V,  $t_{acc} = 30$  s,  $v = 20$  mV  $s^{-1}$  and pulse amplitude =  $-50$  mV 153
- 7.22 DPCS voltammogram of  $2.5 \times 10^{-5}$  M lindane at different pH of 0.04 M BRB: (A) bare SPE and (B) Nyl-MSPE. The experimental conditions were as follows:  $E_i = 0$  V,  $E_f = -1.4$  V,  $E_{acc} = 0$  V,  $t_{acc} = 30$  s,  $v = 20$  mV  $s^{-1}$  and pulse amplitude =  $-50$  mV 155
- 7.23 Plot of peak current vs. pH for  $2.5 \times 10^{-5}$  M lindane at both bare SPE and Nyl-MSPE. The experimental conditions were as follows:  $E_i = 0$  V,  $E_f = -1.4$  V,  $E_{acc} = 0$  V,  $t_{acc} = 30$  s,  $v = 20$  mV  $s^{-1}$  and pulse amplitude =  $-50$  mV 155
- 7.24 Plot of peak current vs. pH for  $2.5 \times 10^{-5}$  M lindane at both bare SPE and Nyl-MSPE. The experimental conditions were as follows:  $E_i = 0$  V,  $E_f = -1.4$  V,  $E_{acc} = 0$  V,  $t_{acc} = 30$  s,  $v = 20$  mV  $s^{-1}$  and pulse amplitude =  $-50$  mV 156
- 7.25 DPCS voltammogram of lindane at optimum pH 5.0 of 0.04 M BRB: (A) bare SPE and (B) Nyl-MSPE: (a) 0, (b)  $0.5 \times 10^{-5}$  M, (c)  $1.5 \times 10^{-5}$  M, (d)  $2.5 \times 10^{-5}$  M. The experimental conditions were as follows:  $E_i = 0$  V,  $E_f = -1.4$  V,  $E_{acc} = 0$  V,  $t_{acc} = 30$  s,  $v = 20$  mV  $s^{-1}$  and pulse amplitude =  $-50$  mV 156
- 7.26 Effect of  $E_i$  for  $2.5 \times 10^{-6}$  M lindane analysis at both bare SPE and Nyl-MSPE. The experimental conditions were as follows: pH 5.0 of 0.04 M BRB,  $E_f = -1.2$  V,  $t_{acc} = 30$  s,  $v = 20$  mV  $s^{-1}$  and pulse amplitude =  $-50$  mV 158
- 7.27 Effect of  $E_{acc}$  for  $2.5 \times 10^{-6}$  M lindane analysis at bare SPE and Nyl-MSPE. The experimental conditions were as follows: pH 5.0 of 0.04 M BRB,  $E_f = -1.2$  V,  $t_{acc} = 30$  s,  $v = 20$  mV  $s^{-1}$  and pulse amplitude =  $-50$  mV 158
- 7.28 Effect of  $t_{acc}$  on peak current for  $2.5 \times 10^{-6}$  M lindane analysis at both bare SPE and Nyl-MSPE. The experimental conditions were as follows: pH 5.0 of 0.04 M BRB,  $E_i = -0.3$  V,  $E_f = -1.2$  V,  $E_{acc} = -0.3$ ,  $v = 20$  mV  $s^{-1}$  and pulse amplitude =  $-50$  mV 159

- 7.29 DPCS voltammogram of lindane at optimum conditions: (A) bare SPE and (B) Nyl-MSPE: (a) 0, (b)  $0.5 \times 10^{-6}$  M, (c)  $1.5 \times 10^{-6}$  M, (d)  $2.5 \times 10^{-6}$  M. The experimental conditions were as follows: pH 5.0 of 0.04 M BRB,  $E_i = -0.3$  V,  $E_f = -1.4$  V,  $E_{acc} = -0.3$  V,  $t_{acc} = 30$  s,  $v = 20$  mV s<sup>-1</sup> and pulse amplitude = -50 mV 159
- 7.30 Calibration curves and calibration plots for DPCSV of lindane (A) bare SPE and (B) Nyl-MSPE: (a) 0, (b)  $1 \times 10^{-7}$  M, (c)  $2 \times 10^{-7}$  M, (d)  $3 \times 10^{-7}$  M, (e)  $4 \times 10^{-7}$  M, (f)  $5 \times 10^{-7}$  M, (g)  $6 \times 10^{-7}$  M and (h)  $7 \times 10^{-7}$  M. The experimental conditions were as follows: pH 5.0 of 0.04 M BRB,  $E_i = -0.3$  V,  $E_f = -1.4$  V,  $E_{acc} = -0.3$  V,  $t_{acc} = 30$  s,  $v = 20$  mV s<sup>-1</sup> and pulse amplitude = -50 mV 160
- 7.31 (A) DPCS voltammogram of lindane with increasing concentration of Cd<sup>2+</sup> ion (a) 0, (b)  $2.5 \times 10^{-6}$  M lindane (c) 0.1 ppm Cd<sup>2+</sup> ion, (d) 0.3 ppm Cd<sup>2+</sup> ion and (e) 0.5 ppm Cd<sup>2+</sup> ion under optimum operating parameters with scan rate 20 mV s<sup>-1</sup>, (B) Graph peak current of lindane vs. added concentration of Cd<sup>2+</sup> ion and (C) Effect of metal ions on peak current of lindane 162
- 7.32 (A) DPCS voltammogram of lindane with increasing concentration of Cd<sup>2+</sup> ion (a) 0, (b)  $2.5 \times 10^{-6}$  M lindane (c) 0.1 ppm Cd<sup>2+</sup> ion, (d) 0.3 ppm Cd<sup>2+</sup> ion and (e) 0.5 ppm Cd<sup>2+</sup> ion under optimum operating parameters with  $v = 20$  mV s<sup>-1</sup>, (B) Graph peak current of lindane vs. added concentration of Cd<sup>2+</sup> ion and (C) Effect of metal ions concentration on peak current of lindane 163
- 7.33 DPCS voltammogram of  $2.5 \times 10^{-5}$  M chlorothalonil at different pH of 0.04 M BRB: (A) bare SPE and (B) Nyl-MSPE. The experimental conditions were as follows:  $E_i = 0$  V,  $E_f = -1.4$  V,  $E_{acc} = 0$  V,  $t_{acc} = 30$  s,  $v = 20$  mV s<sup>-1</sup> and pulse amplitude = -50 mV 167
- 7.34 Plot of peak current vs. pH for  $2.5 \times 10^{-5}$  M chlorothalonil at bare SPE and Nyl-MSPE. The experimental conditions were as follows:  $E_i = 0$  V,  $E_f = -1.4$  V,  $E_{acc} = 0$  V,  $t_{acc} = 30$  s,  $v = 20$  mV s<sup>-1</sup> and pulse amplitude = -50 mV 167

- 7.35 Plot of peak potential vs. pH for  $2.5 \times 10^{-5}$  M chlorothalonil at bare SPE and Nyl-MSPE. The experimental conditions were as follows:  $E_i = 0$  V,  $E_f = -1.4$  V,  $E_{acc} = 0$  V,  $t_{acc} = 30$  s,  $v = 20$  mV s<sup>-1</sup> and pulse amplitude = -50 mV 168
- 7.36 DPCS voltammogram of chlorothalonil at optimum pH 6.0 of 0.04 M BRB: (A) bare SPE and (B) Nyl-MSPE: (a) 0, (b)  $0.5 \times 10^{-5}$  M, (c)  $1.5 \times 10^{-5}$  M, (d)  $2.5 \times 10^{-5}$  M. The experimental conditions were as follows:  $E_i = 0$  V,  $E_f = -1.4$  V,  $E_{acc} = 0$  V,  $t_{acc} = 30$  s,  $v = 20$  mV s<sup>-1</sup> and pulse amplitude = -50 mV 168
- 7.37 Effect of  $E_i$  for  $2.5 \times 10^{-6}$  M chlorothalonil analysis at bare SPE and Nyl-MSPE. The experimental conditions were as follows: pH 6.0 of 0.04 M BRB,  $E_f = -1.2$  V,  $t_{acc} = 30$  s,  $v = 20$  mV s<sup>-1</sup> and pulse amplitude = -50 mV 169
- 7.38 Effect of  $E_{acc}$  for  $2.5 \times 10^{-6}$  M chlorothalonil analysis at bare SPE and Nyl-MSPE. The experimental conditions were as follows: pH 6.0 of 0.04 M BRB,  $E_i = -0.5$  V (bare SPE),  $E_i = -0.6$  V (Nyl-MSPE),  $t_{acc} = 30$  s,  $E_f = -1.2$  V,  $v = 20$  mV s<sup>-1</sup> and pulse amplitude = -50 mV 170
- 7.39 Effect of accumulation time for  $2.5 \times 10^{-6}$  M chlorothalonil analysis at optimal pH 6.0 of 0.04 M BRB: (A) bare SPE and (B) Nyl-MSPE. The experimental conditions were as follows:  $E_i = -0.5$  V (bare SPE),  $E_i = -0.6$  V (Nyl-MSPE),  $E_{acc} = -0.4$  V,  $E_f = -1.2$  V,  $v = 20$  mV s<sup>-1</sup> and pulse amplitude = -50 mV 171
- 7.40 DPCS voltammograms for  $2.5 \times 10^{-6}$  M chlorothalonil analysis at optimal pH 6.0 of 0.04 M BRB: (A) bare SPE and (B) Nyl-MSPE. The experimental conditions were as in Table 7.16 171
- 7.41 Calibration curves and calibration plots for DPCSV of chlorothalonil (A) bare SPE and (B) Nyl-MSPE: (a) 0 (b)  $1 \times 10^{-7}$  M, (c)  $2 \times 10^{-7}$  M, (d)  $3 \times 10^{-7}$  M, (e)  $4 \times 10^{-7}$  M, (f)  $5 \times 10^{-7}$  M, (g)  $6 \times 10^{-7}$  M and (h)  $7 \times 10^{-7}$  M. The experimental conditions were as in Table 7.16 172

- 7.42 (A) DPCS voltammogram of chlorothalonil with increasing concentration of  $\text{Cd}^{2+}$  ion (a) BRB pH 6.0 (b)  $2.5 \times 10^{-6}$  M chlorothalonil (c) 0.1 ppm  $\text{Cd}^{2+}$  ion, (d) 0.3 ppm  $\text{Cd}^{2+}$  ion and (e) 0.5 ppm  $\text{Cd}^{2+}$  ion under optimum operating parameters with scan rate  $20 \text{ mV s}^{-1}$ , (B) Graph peak current of chlorothalonil vs. added concentration of  $\text{Cd}^{2+}$  ion and (C) Effect of metal ions on peak current of chlorothalonil 174
- 7.43 (A) DPCS voltammogram of chlorothalonil with increasing concentration of  $\text{Cd}^{2+}$  ion (a) BRB pH 6.0 (b)  $2.5 \times 10^{-6}$  M chlorothalonil (c) 0.1 ppm  $\text{Cd}^{2+}$  ion, (d) 0.3 ppm  $\text{Cd}^{2+}$  ion and (e) 0.5 ppm  $\text{Cd}^{2+}$  ion under optimum operating parameters with scan rate  $20 \text{ mV s}^{-1}$ , (B) Graph peak current of chlorothalonil vs. added concentration of  $\text{Cd}^{2+}$  ion and (C) Effect of metal ions on peak current of chlorothalonil 175
- 7.44 Calibration plots for lindane using UV-vis spectrophotometry 177
- 7.45 Calibration plots for chlorothalonil using UV-vis spectrophotometry 178



## 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	-	Dichlorodiphenyltrichloroethane
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 <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	-	Iron (III) nitrate
Fe <sup>3+</sup>	-	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 <sub>3</sub> BO <sub>3</sub>	-	Boric acid
H <sub>3</sub> PO <sub>4</sub>	-	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 <sub>2</sub>	-	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 <sup>2+</sup>	-	Lead ion
Pb <sub>3</sub> (NO <sub>3</sub> ) <sub>2</sub>	-	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 <sup>2+</sup>	-	Paraquat dication
Pt	-	Platinum
PTh	-	Polythiophene
PTh-V	-	Polythiophene-vinylene
PTV	-	Poly(2,5-thienylenevinylene)
PVP	-	Polyvinylpyrrolidone
r <sup>2</sup>	-	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 <sub>2</sub>	-	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 <sub>3</sub> ) <sub>2</sub> .6H <sub>2</sub> O	-	Zinc nitrate
Zn <sup>2+</sup>	-	Zinc ion
ZnO	-	Zinc oxide
ZrO <sub>2</sub>	-	Zirconium Oxide

## LIST OF SYMBOLS

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

$\text{mg L}^{-1}$	-	Milligrams per litre
mg	-	Milligram
min	-	Minute
mL	-	Millilitre
mM	-	Millimolar
$\text{mV s}^{-1}$	-	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
$t_{\text{acc}}$	-	Accumulation time
$\nu$	-	Scan rate
V	-	Volt
vs	-	Versus
w/v	-	Weight to volume
$\lambda$	-	Wavelength
$\mu\text{g L}^{-1}$	-	Microgram per litre

**LIST OF APPENDICES**

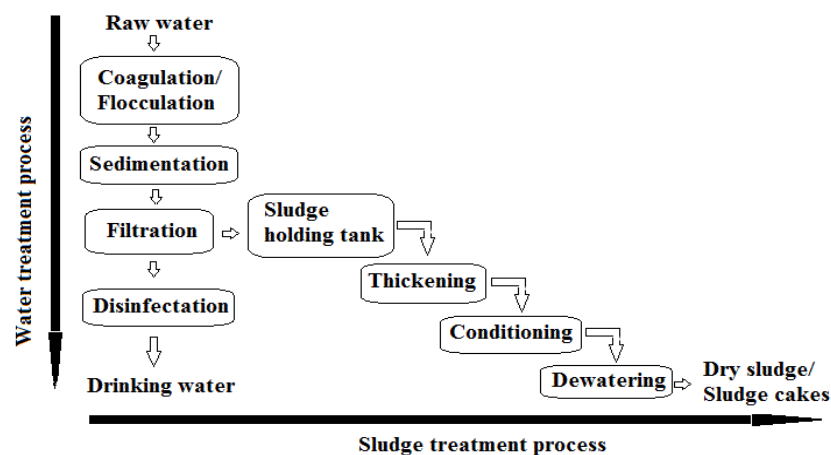
<b>APPENDIX</b>	<b>TITLE</b>	<b>PAGE</b>
A	Cyclic Voltammogram for Glyphosate Analysis	209
B	Publications	210
C	Presentations	211

## 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; Gavrilescu *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  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Pb}^{2+}$  and  $\text{Zn}^{2+}$  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

## REFERENCES

- Abdullah. A. R. (2003). Pesticide use in Malaysia: Trends and impacts. In Taylor, M. D., Klaine, S. J., Carvalho, F. P., Barcelo, D. and Everaarts, J. (Eds.) *Pesticide Residues in Coastal Tropical Ecosystems Distribution, Fate and Effects*. (pp. 159-179). New York: CRC Press.
- Afful, S., Dogbe, S. A., Ahmad, K. and Ewusie, A. T. (2008). Thin Layer Chromatographic Analyses of Pesticides in a Soil Ecosystem. *West African Journal of Applied Ecology*. 14(1), 1-7.
- Agarwal, A., Prajapati, R., Singh, O., Raza, S. K. and Thakur, L. K. (2015). Pesticide Residue in Water-A Challenging Task in India. *Environmental Monitoring and Assessment*. 187(2), 54-75.
- Ahmad, T., Rafatullah, M., Ghazali, A., Sulaiman, O., Hashim, R. and Ahmad, A. (2010). Removal of Pesticides from Water and Wastewater by Different Adsorbents: A Review. *Journal of Environmental Science and Health C*. 28(4), 231–271.
- Al-Badaii, F., Shuhaimi-Othman, M. and Gasim, M. B. (2013). Water Quality Assessment of the Semenyih River, Selangor, Malaysia. *Journal of Chemistry*. 2013, 1-10.
- Alfonso, L. F., German, G. V., del Carmen, P. C. M. and Hossein, G. (2017). Adsorption of Organophosphorus Pesticides in Tropical Soils: The Case of Karst Landscape of Northwestern Yucatan. *Chemosphere*. 166, 292-299.
- Ali, U., Syed, J., Malik, R., Katsoyiannis, A., Li, J., Zhang, G. and Jones, K. (2014). Organochlorine Pesticides (OCPs) in South Asian Region: A Review. *Science of the Total Environment*. 476–477, 705–717.
- Alvarez, E., Sevilla, M. T., Pinilla, J. M. and Hernandez, J. M. (1992). Cathodic Stripping Voltammetry of Paraquat on a Carbon Paste Electrode Modified with Amberlite XAD Resin. *Analytica Chimica Acta*. 260(1), 19-23.



- Amorello, D. and Orecchio, S. (2013). Micro-Determination of Dithiocarbamates in Pesticide Formulations using Voltammetry. *Microchemical Journal*. 110, 334–339.
- Asadpour-Zeynali, K. and Mollarasouli, F. (2017). Novel Electrochemical Biosensor Based on PVP Capped CoFe<sub>2</sub>O<sub>4</sub>@ CdSe Core-shell Nanoparticles Modified Electrode for Ultra-trace Level Determination of Rifampicin by Square Wave Adsorptive Stripping Voltammetry. *Biosensors and Bioelectronics*, 92, 509–516.
- Atwood, D. and Paisley-Jones, C. (2017). Pesticides Industry Sales and Usage 2008–2012 Market Estimates: U.S. Environmental Protection Agency, Washington.
- Babu, T., Reddy, S. and Sujana, P. (2014). Comparative Voltammetric Study and Determination of Carbamate Pesticide Residues in Soil at Carbon Nanotubes Paste Electrodes. *Journal of Electrochemical Science and Engineering*. 4(1), 19–26.
- Bagheri, H., Pajoohepour, N., Afkhami, A. and Khoshsafar, H. (2016). Fabrication of a Novel Electrochemical Sensing Platform Based on A Core–Shell Nano-Structured/Molecularly Imprinted Polymer For Sensitive and Selective Determination of Ephedrine. *RSC Advances*. 6(56), 51135–51145.
- Bagotsky, V. S. (2005). *Fundamentals of Electrochemistry*. (2<sup>nd</sup> Ed.) New York: Wiley.
- Bai, W., Zhu, C., Liu, J., Yan, M., Yang, S. and Chen, A. (2015). Gold Nanoparticle–based Colorimetric Aptasensor for Rapid Detection of Six Organophosphorous Pesticides. *Environmental Chemistry*. 34 (10), 2244–2249.
- Bakouri, H. E., Morillo, J., Usero, J. and Ouassini, A. (2009). Natural Attenuation of Pesticide Water Contamination by Using Ecological Adsorbents: Application for Chlorinated Pesticides Included in European Water Framework Directive. *Journal of Hydrology*. 364, 175–181.
- Balaji, K., Sridevi, C., Ananda Kumar Reddy, N., Reedy, K. M. M. S. and Suresh Reddy, C. (2010a). Voltammetric Behaviour and Analysis of Fluchloralin. *Journal of Chemistry*. 7(4), 1605–1611.
- Balaji, K., Sridevi, C., Reddy, N. A. K., Reddy, K. M. M. S. and Reddy, C. S. (2010b). Electrochemical Reduction Behavior and Analysis of Fluazinam. *International Journal of Pharmacology and Biosciences*. 1(2), BS61.

- Baldissera, A. F., Miranda, K. L. D., Bressy, C., Martin, C., Margailan, A. and Ferreira, C. A. (2015). Using Conducting Polymers as Active Agents for Marine Antifouling Paints. *Materials Research*. 18(6), 1129-1139.
- Balint, R., Cassidy, N. J. and Cartmell, S. H. (2014). Conductive Polymers: Towards a Smart Biomaterial for Tissue Engineering. *Acta Biomaterialia*. 10(6), 2341–2353.
- Bandzuchova, L., Selesovska, R., Navratil, T. and Chylkova, J. (2013). Sensitive Voltammetric Method for Determination of Herbicide Triasulfuron Using Silver Solid Amalgam Electrode. *Electrochimica Acta*. 113, 1-8.
- Bard, A. J. and Faulkner, L. R. (2001). *Electrochemical Methods: Fundamentals and Applications*. (2<sup>nd</sup> Ed.) New York: Wiley.
- Barek, J. (2013). Possibilities and Limitations of Mercury and Mercury-based Electrodes in Practical Electroanalysis of Biologically Active Organic Compounds. *Portugaliae Electrochimica Acta*. 31(6), 291-295.
- Baron-Jaimez, J., Joya, M. R. and Barba-Ortega, J. (2013). Anodic Stripping Voltammetry–ASV for Determination of Heavy Metals. In *Journal of Physics: Conference Series*. 466 (1), 012023.
- Batchelor-McAuley, C., Katelhon, E., Barnes, E. O., Compton, R. G., Laborda, E. and Molina, A. (2015). Recent advances in voltammetry. *Chemistry Open*. 4(3), 224-260.
- Benner, J., Helbling, D. E., Kohler, H-P, E., Wittebol, J., Kaiser, E., Prasse, C., Ternes, T. A., Alber, C. A., Aamand, J., Horemans, B., Springael, D., Walravens, E. and Boon, N. (2013). Review: Is Biological Treatment a Viable Alternative for Micropollutants Removal in Drinking Water Treatment Processes? *Water Research*. 47(16), 5955-5976.
- Berger, P. S., Clark, R. M., Reasoner, D. J., Rice, E. W. and Domingo, J. W. S. (2009). *Water, Drinking. Applied Microbiology: Agro/ Food/ Water, Drinking in Encyclopedia of Microbiology*. Academic Press.
- Bist, R. and Bhatt, D. K. (2009). The Evaluation of Effect of Alpha-lipoic Acid and Vitamin E on the Lipid Peroxidation, Gamma-Amino Butyric Acid and Serotonin Level in the Brain of Mice (*Mus musculus*) Acutely Intoxicated with Lindane. *Journal of the Neurological Sciences*. 276(1), 99-102.
- Blair, A., Ritz, B., Wesseling, C. and Freeman, L. B. (2015). Pesticides and Human Health. *Occupational and Environmental Medicine*. 72(2), 81-82.

- Boxall, A. B. A. (2012). *New and Emerging Water Pollutants Arising from Agriculture*. OECD Publishing.
- Buffle, J. and Tercier-Waeber, M. L. (2005). Voltammetric Environmental Trace-Metal Analysis and Speciation: From Laboratory to In Situ Measurements. *TrAC Trends in Analytical Chemistry*. 24(3), 172-191.
- Caldas, S. S., Rombaldi, C., de Oliveira Arias, J. L., Marube, L. C., Primel, E. G. (2016). Multi-residue Method for Determination of 58 Pesticides, Pharmaceuticals and Personal Care Products in Water using Solvent Demulsification Dispersive Liquid-liquid Microextraction Combined with Liquid Chromatography-tandem Mass Spectrometry. *Talanta*. 146, 676-688.
- Carmona, E., Andreu, V. and Pico, Y. (2014). Occurrence of Acidic Pharmaceuticals and Personal Care Products in Turia River Basin: From Waste to Drinking Water. *Science of the Total Environment*. 484 (1), 53-63.
- Cesarino, I, Moraes, F. C., Lanza, M. R. and Machado, S. A. (2012). Electrochemical Detection of Carbamate Pesticides in Fruit and Vegetables with a Biosensor Based on Acetylcholinesterase Immobilised on a Composite of Polyaniline-Carbon Nanotubes. *Food Chemistry*. 135(3), 873-879.
- Chang, P-L., Hsieh, M-M. and Chiu, T. C. (2016). Recent Advances in the Determination of Pesticides in Environmental Samples by Capillary Electrophoresis. *International Journal of Environmental Research and Public Health*. 13(4), 409-429.
- Chen, J. and Chen, C. (2013). A New Data Analysis Method to Determine Pesticide Concentrations by Cyclic Voltammetry. *Measurement*. 46, 1828-1833.
- Chen, L., Li, Z., Meng, Y., Zhang, P., Su, Z., Liu, Y., Huang, Y., Zhou, Y., Xie, Q. and Yao, S. (2014). Sensitive Square Wave Anodic Stripping Voltammetric Determination of Cd<sup>2+</sup> and Pb<sup>2+</sup> Ions at Bi/Nafion/overoxidized 2-Mercaptoethanesulfonate-Tethered Polypyrrole/Glassy Carbon Electrode. *Sensors and Actuators B: Chemical*. 191, 94-101.
- Chen, M., Zhao, Z., Lan, X., Chen, Y., Zhang, L., Ji, R. and Wang, L. (2015). Determination of Carbendazim and Metiram Pesticides Residues in Reapeseed and Peanut Oils by Fluorescence Spectrophotometry. *Measurement*. 73, 313-317.

- Cheng, Z., Dong, F., Xu, J., Liu, X., Wu, X., Chen, Z., Pan, X. and Zheng, Y. (2016). Atmospheric Pressure Gas Chromatography Quadrupole-Time-of-Flight Mass Spectrometry for Simultaneous Determination of Fifteen Organochlorine Pesticides in Soil and Water. *Journal of Chromatography A*, 1435, 115-124.
- Chidya, R. C. G., Sajidu, S. M. I., Mwatseteza, J. F. and Masamba, W. R. L. (2012). Evaluation and Assessment of Water Quality in Likangala River and Its Catchment Area. *Physics and Chemistry of the Earth*. 36(14-14), 865-871.
- Chorti, P., Fischer, J., Vyskocil, V., Economou, A. and Barek, J. (2014). Voltammetric Determination of Insecticide Thiamethoxam on Silver Solid Amalgam Electrode. *Electrochimica Acta*. 140, 5-10.
- Chui, M. Q., Thang, L. Y. and See, H. H. (2017). Integration of the Free Liquid Membrane into Electrokinetic Supercharging–Capillary Electrophoresis for the Determination of Cationic Herbicides in Environmental Water Samples. *Journal of Chromatography A*. 1481, 145-151.
- Ciucu, A. A., Negulescu, C. and Baldwin, R. P. (2003). Detection of Pesticides Using an Amperometric Biosensor Based on Ferophthalocyanine Chemically Modified Carbon Paste Electrode and Immobilized Bienzymatic System. *Biosensors and Bioelectronics*. 18(2-3), 303-310.
- Cohn, B. A., Wolff, M. S., Cirillo, P. M. and Sholtz, R. I. (2007). DDT and Breast Cancer Inyoung Women: New Data on the Significance of Age at Exposure. *Environmental Health Perspectives*. 115(10), 1406–1414.
- Dabrowski, J. M., Shadung, J. M. and Wepener, V. (2014). Prioritizing Agricultural Pesticides Used in South Africa Based on Their Environmental Mobility and Potential Human Health Effects. *Environment International*. 62, 31–40.
- De Figueiredo-Filho, L. C. S., dos Santos, V.B., Janegitz, B. C., Guerreiro, T. B., Fatibello-Filho, O. and Faria, R. C. and Marcolino-Junior, L. H. (2010). Differential Pulse Voltammetric Determination of Paraquat Using a Bismuth-film Electrode. *Electroanalysis*. 22(11), 1260–1266.
- De Souza, D., Codognoto, L., Machado, S. A. S. and Avaca. L. A. (2005). Electroanalytical Determination of the Herbicide Paraquat in Natural Water and Commercial Tea Samples with Gold Electrodes Obtained from Recordable Compact Disc. *Analytical Letters*. 38(2), 331–341.

- De Souza, D., de Toledo, R. A., Suffredini, H. B., Mazo, L. H. and Machado, S. A. (2006a). Characterization and Use of Copper Solid Amalgam Electrode for Electroanalytical Determination of Triazines- Based Herbicides. *Electroanalysis*. 18(6), 605 – 612.
- De Souza, D., Machado, S. A. and Pires, R. C. (2006b). Multiple Square Wave Voltammetry for Analytical Determination of Paraquat in Natural Water, Food, and Beverages using Microelectrodes. *Talanta*. 69(5), 1200–1207.
- Desai, K. R., Moid, N., Patel, P. B. and Highland, H. N. (2016). Evaluation of Deltamethrin Induced Reproductive Toxicity in Male Swiss Albino Mice. *Asian Pacific Journal of Reproduction*. 5(1), 24-30.
- Deylova, D., Yosypchuk, B., Vyskocil, V. and Barek, J. (2011). Voltammetric Determination of 4-Nitrophenol and 5-Nitrobenzimidazole Using Different Types of Silver Solid Amalgam Electrodes – A Comparative Study. *Electroanalysis*. 23(7), 1548–1555.
- Dordevic, J., Papp, Z., Guzsivany, V., Svancara, I., Trtic-Petrovic, T., Purenovic, M. and Vytras, K. (2012). Voltammetric Determination of the Herbicide Linuron using a Tricresyl Phosphate-Based Carbon Paste Electrode. *Sensor*. 12, 148-161.
- Dornellasa, R. M., Franchini, R. A. and Aucelio, R. Q. (2013). Determination of the Fungicide Picoxystrobin using Anodic Stripping Voltammetry on a Metal Film Modified Glassy Carbon Electrode. *Electrochimica Acta*. 97, 202-209.
- Dos Santos, L. B. O., Silva, M. S. P. and Masini, J. C. (2005). Developing a Sequential Injection-Square Wave Voltammetry (SI-SWV) Method for Determination of Atrazine Using a Hanging Mercury Drop Electrode. *Analytica Chimica Acta*. 528(1), 21-27.
- El Harmoudi, H., Achak, M., Farahi, A., Lahrich, S., El Gaini, L., Abdennouri, M., Bouzidi. A, Bakasse, M. and El Mhammedi, M. A. (2013). Sensitive Determination of Paraquat by Square Wave Anodic Stripping Voltammetry with Chitin Modified Carbon Paste Electrode. *Talanta*. 115, 172-177.
- El Mhammedi, M.A. Bakasse, M., Bachirat, R. and Chtaini, A. (2008). Square Wave Voltammetry for Analytical Determination of Paraquat at Carbon Paste Electrode Modified with Fluoroapatite. *Food Chemistry*. 110(4), 1001–1006.

- El Mhammedi, M.A., Bakasse, M. and Chtaini. A. (2007). Square-wave Voltammetric Determination of Paraquat at Carbon Paste Electrode Modified with Hydroxyapatite. *Electroanalysis*. 19(16), 1727–1733.
- Elbashir A. A. and Aboul- Enein H. Y. (2015). Separation and Analysis of Triazine Herbicide Residues by Capillary Electrophoresis. *Biomedical Chromatography*. 29(6), 835–842.
- Erdogdu, G. and Titretir, S. (2007). Voltammetric Determination of Mesotrione at Hanging Mercury Drop Electrode. *Journal of Analytical Chemistry*. 62(8), 777-780.
- Fantke, P., Friedrich, R. and Jolliet, O. (2012). Health Impact and Damage Cost Assessment of Pesticides in Europe. *Environment International*. 49, 9–17.
- Farahi, A., Lahrich, S., Achak, M., El Gaini, L., Bakasse, M. and El Mhammedi, M. A. (2014). Parameters Affecting the Determination of Paraquat at Silver Rotating Electrodes using Differential Pulse Voltammetry. *Analytical Chemistry Research*. 1, 16–21.
- Farghaly, O. A., Hameed, R. A. and Abu-Nawwas, A. A. H. (2014). Analytical Application using Modern Electrochemical Techniques. *International Journal of Electrochemical Science*. 9(1), 3287 – 3318.
- Fayemi, O. E., Adekunle, A. S. and Ebenso, E. E. (2016). A Sensor for the Determination of Lindane Using PANI/Zn, Fe(III) Oxides and Nylon 6, 6/MWCNT/Zn, Fe(III) Oxides Nanofibers Modified Glassy Carbon Electrode. *Journal of Nanomaterials*. 2016, 78, Article ID 4049730.
- Fera @ Nony Cleophas, Isidore, F., Han, L. K. and Bidin, K. (2013). Water Quality Status of Liwagu River, Tambunan, Sabah, Malaysia. *Journal of Tropical Biology and Conservation*. 10, 67-73.
- Fischer, J., Barek, J. and Wang, J. (2012). New Methods for Electrochemical Determination of Pesticides (A Review). Kalcher, K., Metelka, R., Svancara, I. and Vytras, K. (Eds.) *Sensing in Electroanalysis* (pp. 79–86). Czech Republic: University Press Centre, Pardubice.
- Fotouhi, L., Farzinnegad, N., Heravi, M. M. and Khaleghi, S. (2003). Study the Electrochemical Reduction of Some Triazines in N, N-dimethylformamide at Glassy Carbon Electrode. *Bulletin of the Korean Chemical Society*. 24(12), 1751-1756.

- Fuad, M. M., Junaidi, A. B., Habibah, A., Hamzah, J., Toriman, M. E., Lyndon, N. and Azima, A. M. (2012). The impact of pesticides on paddy farmers and ecosystem. *Advances in Natural and Applied Sciences*. 6(1), 65-70.
- Gaal, F. F., Guzsivany, V. J. and Bjelica, L. J. (2007). Determination of Various Insecticides and Pharmaceuticals using Differently Modified Glassy Carbon Electrodes. *Journal of the Serbian Chemical Society*. 72(12), 1465-1475.
- Garcia, L. L. C., Filho, L. C. S. F., Oliveira, G. G., Fatibello-Filho, O. F. and Banks, C. E. (2013). Square-Wave Voltammetric Determination of Paraquat using a Glassy Carbon Electrode Modified with Multiwalled Carbon Nanotubes within a Dihexadecylhydrogenphosphate (DHP) Film. *Sensors and Actuators B*. 181, 306-311.
- Gavrilescu, M., Demnerova, K., Aamand, J., Agathos, S. and Fava, F. (2015). Emerging Pollutants in the Environment: Present and Future Challenges in Biomonitoring, Ecological Risks and Bioremediation. *New Biotechnology*. 32(1), 147-156.
- Geremedhin, W., Amare, M. and Admassie, S. (2013). Electrochemically Pretreated Glassy Carbon Electrode for Electrochemical Detection of Fenitrothion in Tap Water and Human Urine. *Electrochimica Acta*. 87, 749-755.
- Gill, H. K and Garg, H. (2014). Chapter 8: Pesticides: Environmental Impacts and Management Strategies. In Soloneski, S. (Ed.) *Pesticides - Toxic Aspects* (pp. 187-229). Vienna: InTech.
- Grube, A., Donaldson, D., Kiely, T. and Wu, L. (2011). Report on Pesticides Industry Sales and Usage 2006/ 2007 Market Estimates: U.S. Environmental Protection Agency, Washington.
- Gui, W., Tian, C., Sun, Q., Li, S., Zhang, W., Tang, J. and Zhu, G. (2016). Simultaneous Determination of Organotin Pesticides by HPLC-ICP-MS and Their Sorption, Desorption and Transformation in Freshwater Sediments. *Water Research*. 95, 185-194.
- Guimard, N. K., Gomez, N., Schmidt, C. E. (2007). Conducting Polymers in Biomedical Engineering. *Progress in Polymer Science*. 32(8-9), 876-921.
- Gulaboski, R. and Pereira, C. M. (2008). Electroanalytical Techniques and Instrumentation in Food Analysis. In Ottles, S. (Ed.) *Handbook of Food Analysis Instruments* (pp. 379-402). United States: Taylor & Francis.

- Guler, M., Turkoglu, V. and Kivrak, A. (2016). Electrochemical Detection of Malathion Pesticide Using Acetylcholinesterase Biosensor Based on Glassy Carbon Electrode Modified with Conducting Polymer Film. *Environmental Science and Pollution Research*. 23(12), 12343-12351.
- Guo, H., Riter, L.S., Wujcik, C.E. and Armstrong, D.W., 2016. Direct and Sensitive Determination of Glyphosate and Aminomethylphosphonic Acid in Environmental Water Samples by High Performance Liquid Chromatography Coupled to Electrospray Tandem Mass Spectrometry. *Journal of Chromatography A*. 1443, 93-100.
- Gupta, R.C., Melatovic, D., Marrs, T.C. (Ed.) (2012). *Mammalian Toxicology of Insecticides*. Cambridge: Royal Society of Chemistry.
- Gupta, V. K., Jain, R., Radhapyari, K., Jadon, N. and Agarwal, S. (2011). Voltammetric Techniques for the Assay of Pharmaceuticals—A Review. *Analytical Biochemistry*. 408(2), 179-196.
- Guziejewski, D., Skrzypek, S. and Ciesielski, W. (2012). Square Wave Adsorptive Stripping Voltammetric Determination of Diazinon in Its Insecticidal Formulations. *Environmental Monitoring Assessment*. 184(11), 6575–6582.
- Guzsvany, V. J. Gaal, F. F. Bjelica, L. J. and Okresz, S. N. (2005). Voltammetric Determination of Imidacloprid and Thiamethoxam. *Journal of the Serbian Chemical Society*. 70(5), 735-743.
- Guzsvany, V., Kadar, M., Gaal, F., Bjelica, L. and Toth, K. (2006). Bismuth Film Electrode for the Cathodic Electrochemical Determination of Thiamethoxam. *Electroanalysis*. 18(13-14), 1363-1371.
- Hao, C., Zhao, X., Morse, D., Yang, P., Taguchi, V. and Morra, F. (2013). Optimized Liquid Chromatography Tandem Mass Spectrometry Approach for the Determination of Diquat and Paraquat Herbicides. *Journal of Chromatography A*. 1304, 169-176.
- Hernandez, A. F., Gonzalez-Alzaga, B., Lopez-Flores, I. and Lacasana, M. (2016). Systematic Reviews on Neurodevelopmental and Neurodegenerative Disorders Linked to Pesticide Exposure: Methodological Features and Impact on Risk Assessment. *Environment International*. 92, 657-679.



- Hirakawa, Y., Yamasaki, T., Watanabe, E., Okazaki, F., Murakami-Yamaguchi, Y., Oda, M., Iwasa, S., Narita, H. and Miyake, S. (2015). Development of an Immunosensor for Determination of the Fungicide Chlorothalonil in Vegetables, Using Surface Plasmon Resonance. *Journal of Agricultural and Food Chemistry*. 63(28), 6325-6330.
- Hossain M. A., Sujaul I. M. and Nasly, M. A. (2013). Water Quality Index: An Indicator of Surface Water Pollution in Eastern Part of Peninsular Malaysia. *Research Journal of Recent Sciences*. 2(10), 10-17.
- Hossain, M. U., Rahman, M. T. and Ehsan, M. Q. (2015). Simultaneous Detection and Estimation of Catechol, Hydroquinone, and Resorcinol in Binary and Ternary Mixtures Using Electrochemical Techniques. *International Journal of Analytical Chemistry*. Article ID 862979.
- Houtman, C. J. (2010). Emerging Contaminants in Surface Waters and Their Relevance for the Production of Drinking Water in Europe. *Journal Integrative Environmental Sciences*. 7(4), 271-295.
- Hu, Y. (2015). Simultaneous Determination of Phenylurea Herbicides in Yam by Capillary Electrophoresis with Electrochemiluminescence Detection. *Journal of Chromatography B*. 986, 143-148.
- Inam, R., Can, E. and Demir, E. (2013). Electrooxidation and Determination of Methacetin (p-acetanisidide) by Square Wave Voltammetry using Multiwalled Carbon Nanotube Electrode. *Analytical Methods*. 5, 6338-6344.
- Irimia-Vladu, M. (2014). "Green" Electronics: Biodegradable and Biocompatible Materials and Devices for Sustainable Future. *Chemical Society Reviews*. 43(2), 588-610.
- Jamaludin, N., Sham, S. M. and Ismail, S. N. S. (2013). Health Risk Assessment of Nitrate Exposure in Well Water of Residents in Intensive Agriculture Area. *American Journal of Applied Sciences*. 10(5), 442-448.
- Jin, X. and Peldszus, S. (2011). Selection of Representative Emerging Micropollutants for Drinking Water Treatment Studies: A Systematic Approach. *Science of the Total Environment*. 414, 653-663.
- Jing, T., Xia, H., Niu, J., Zhou, Y., Dai, Q., Hao, Q., Zhou, Y. and Mei, S. (2011). Determination of Trace 2,4-dinitrophenol in Surface Water Samples Based on Hydrophilic Molecularly Imprinted Polymers/Nickel Fiber Electrode. *Biosensors and Bioelectronics*. 26(11), 4450-4456.

- Jouzi, Z., Azadi, H., Taheri, F., Zarafshani, K., Gebrehiwot, K., Van Passel, S. and Lebailly, P. (2017). Organic Farming and Small-Scale Farmers: Main Opportunities and Challenges. *Ecological Economics*. 132, 144-154.
- Jurate, V., Rajender, S. and Varma, J. (2010). *Treatment of Micropollutants in Water and Wastewater*, IWA Publishing.
- Kafilzadeh, F. (2015). Assessment of Organochlorine Pesticide Residues in Water, Sediments and Fish from Lake Tashk, Iran. *Achievements in the Life Sciences*. 9 (2), 107-111.
- Kaur, G., Adhikari, R., Cass, P., Bown, M. and Gunatillake, P. (2015). Electrically Conductive Polymers and Composites for Biomedical Applications. *RSC Advances*. 5(47), 37553-37567.
- Kegley, S. E., Hill, B. R., Orme S. and Choi A. H. (2016). *PAN Pesticide Database*, Pesticide Action Network, North America from <http://www.pesticideinfo.org>.
- Kesik, M., Kanik, F. E., Turan, J., Kolb, M., Timur, S., Bahadir, M. and Toppare, L. (2014). An Acetylcholinesterase Biosensor Based on a Conducting Polymer Using Multiwalled Carbon Nanotubes for Amperometric Detection of Organophosphorous Pesticides. *Sensors and Actuators B: Chemical*. 205, 39-49.
- Knopp, G., Prasse, C., Ternes, T.A. and Cornel, P. (2016). Elimination of Micropollutants and Transformation Products from a Wastewater Treatment Plant Effluent through Pilot Scale Ozonation Followed By Various Activated Carbon and Biological Filters. *Water Research*. 100, 580-592.
- Kounaves, S. P. (1997). *Chapter 37: Voltammetric Techniques*. In Settle, F. A. (Ed.) *Handbook of instrumental Techniques for Analytical Chemistry* (pp. 709-726). Virginia: Prentice Hall.
- Kumar, R., Singh, S. and Yadav, B. C. (2015). Conducting Polymers: Synthesis, Properties and Applications. *International Advanced Research Journal in Science, Engineering and Technology*. 2(11), 110-124.
- Kusvuran, E., Yildirim, D., Mavruk, F. and Ceyhan, M. (2012). Removal of Chloropyrifos Ethyl, Tetradifon and Chlorothalonil Pesticide Residues from Citrus by using Ozone. *Journal of Hazardous Materials*. 241, 287– 300.

- Lang, Q., Han, L., Hou, C., Wang, F. and Liu, A. (2016). A sensitive Acetylcholinesterase Biosensor Based on Gold Nanorods Modified Electrode for Detection of Organophosphate Pesticide. *Talanta*. 156-157, 34–41.
- Larson S. J., Capel, P. D. and Majewski, M. (2010). *Pesticides in Surface Waters: Distribution, Trends and Governing Factors*. Boca Raton: CRC Press.
- Lee, H. U., Shin, H. Y., Lee, J. Y., Song, Y. S., Park, C. and Kim, S. W. (2010). Quantitative Detection of Glyphosate by Simultaneous Analysis of UV Spectroscopy and Fluorescence Using DNA-Labeled Gold Nanoparticles. *Journal of Agricultural and Food Chemistry*. 58(23), 12096-12100.
- Lewis, K. A., Tzilivakis, J., Warner, D. J. and Green, A. (2016). An International Database for Pesticide Risk Assessments and Management. *Human and Ecological Risk Assessment: An International Journal*, 22(4), 1050-1064.
- Li, H., Xie, C. and Fu, X. (2013). Electrochemiluminescence Sensor for Sulfonylurea Herbicide with Molecular Imprinting Core–Shell Nanoparticles/Chitosan Composite Film Modified Glassy Carbon Electrode. *Sensors and Actuators B: Chemical*. 181, 858-866.
- Li, J., Lei, W., Xu, Y., Zhang, Y., Xia, M. and Wang, F. (2015a). Fabrication of Polypyrrole-Grafted Nitrogen-Doped Graphene and Its Application for Electrochemical Detection of Paraquat. *Electrochimica Acta*. 174, 464-471.
- Li, J., Yoon, S. J., Hsieh, B-Y., Tai, W., O'Donnell, M. and Gao, X. (2015b). Stably Doped Conducting Polymer Nanoshells by Surface Initiated Polymerization. *Nano Letters*. 15(12), 8217-8222.
- Liu, G. and Lin, Y. (2005). Electrochemical Stripping Analysis of Organophosphate Pesticides and Nerve Agents. *Electrochemistry Communications*. 7, 339-343.
- Liu, G., Guo, W. and Song, D. (2014). A Multianalyte Electrochemical Immunosensor Based on Patterned Carbon Nanotubes Modified Substrates for Detection of Pesticides. *Biosensors and Bioelectronics*. 52, 360-366.
- Lu, T. H. and Sun, I. W. (2000). Electrocatalytic Determination of Paraquat Using a Nafion Film Coated Glassy Carbon Electrode. *Talanta*. 53(2), 443–451.
- Luo, Y., Guo, W., Ngo, H. H., Nghiem, L. D., Hai, F. I., Zhang, J., Liang, S. and Wang, X. C. (2014). A Review on the Occurrence of Micropollutants in the Aquatic Environment and Their Fate and Removal during Wastewater Treatment. *Science of the Total Environment*. 473-474, 619-641.

- Lv, P., Zhang, J., Shi, T., Dai, L., Li, X., Wu, X., Li, X., Tang, J., Wang, Y., Li, Q.X. and Hua, R. (2017). Procyanidolic oligomers enhance photodegradation of chlorothalonil in water via reductive dechlorination. *Applied Catalysis B: Environmental*, 217, 137-143.
- Mahmood, A., Malik, R. N., Li, L. and Zhang, G. (2014). Human Health Risk Assessment and Dietary Intake of Organochlorine Pesticides through Air, Soil and Food Crops (Wheat and Rice) along Two Tributaries of River Chenab, Pakistan. *Food and Chemical Toxicology*. 71, 17–25.
- Majidi, M. R., Ghaderi, S., Asadpour-Zeynali, K. and Dastango, H. (2015). Synthesis of Dendritic Silver Nanostructures Supported by Graphene Nanosheets and Its Application for Highly Sensitive Detection of Diazepam. *Materials Science and Engineering C*. 57, 257-264.
- Malagoli, C., Costanzini, S., Heck, J. E., Malavolti, M., De Girolamo, G., Oleari, P., Palazzi, G., Teggi, S. and Vinceti, M. (2016). Passive Exposure to Agricultural Pesticides and Risk of Childhood Leukemia in an Italian Community. *International Journal of Hygiene and Environmental Health*. 219(8), 742-748.
- Manda, I. K. M., Chidya, R. C. G., Saka, J. D. K. and Biswick. T. T. (2016). Comparative Assessment of Water Treatment Using Polymeric and Inorganic Coagulants. *Physics and Chemistry of the Earth, Parts A/B/C*. 93, 119-129.
- Manisankar, P., Selvanathan, G. and Vedhi, C. (2005a). Utilization of Sodium Montmorillonite Clay-Modified Electrode for the Determination of Isoproturon and Carbendazim in Soil and Water Samples. *Applied Clay Science*, 29(3-4), 249-257.
- Manisankar, P., Selvanathan, G. and Vedhi, C. (2006). Determination of Pesticides using Heteropolyacid Montmorillonite Clay-Modified Electrode with Surfactant. *Talanta*. 68(3), 686–692.
- Manisankar, P., Sundari, P. A. and Sasikumar, R. (2009). Square-Wave Stripping Voltammetric Determination of Some Organic Pollutants Using Modified Electrodes. *International Journal of Environmental and Analytical Chemistry*. 89(4), 245-260.

- Manisankar, P., Sundari, P. L. A., Sasikumar, R. and Palaniappan, S. P. (2008). Electroanalysis of Some Common Pesticides using Conducting Polymer/Multiwalled Carbon Nanotubes Modified Glassy Carbon Electrode. *Talanta*. 76(5), 1022–1028.
- Manisankar, P., Viswanathan, S., Puspahalatha, A. M. and Rani, C. (2005b). Electrochemical Studies and Square Wave Stripping Voltammetry of Five Common Pesticides on Poly 3, 4-ethylenedioxythiophene Modified Wall-Jet Electrode. *Analytica Chimica Acta*. 528 (2), 157-163.
- March, G., Nguyen, T. D. and Piro, B. (2015). Review: Modified Electrodes Used for Electrochemical Detection of Metal Ions in Environmental Analysis. *Biosensors*. 5, 241-275.
- Marzari, G., Cappellari, M. V., Morales, G. M. and Fungo, F. (2017). Electro-Chemiluminescent Detection of Glyphosate Using Electrodes Modified with Self-Assembled Monolayers. *Analytical Methods*. 9(16), 2452-2457.
- McGlynn, K. A., Abnet, C. C., Zhang, M., Sun, X. D., Fan, J. H., O'Brien, T. R., Wei, W. Q., Ortiz-Conde, B. A., Dawsey, S. M., Weber, J. P., Taylor, P. R., Katki, H., Mark, S. D. and Qiao, Y. L. (2006). Serum concentrations of 1,1,1-trichloro-2,2-bis(pchlorophenyl)ethane (DDT) and 1,1-dichloro-2,2-bis (p-chlorophenyl)ethylene (DDE) and risk of primary liver cancer. *Journal of the National Cancer Institute*. 98(14), 1005-1010.
- McManus, S. L., Coxon, C. E., Richards, K. G. and Danaher, M. (2013). Quantitative Solid Phase Microextraction–Gas Chromatography Mass Spectrometry Analysis of the Pesticides Lindane, Heptachlor and Two Heptachlor Transformation Products in Groundwater. *Journal of Chromatography A*. 1284, 1-7.
- Merz, J. P., Gamoke, B. C., Foley, M. P., Raghavachari, K. and Peters, D. G. (2011). Electrochemical Reduction of (1R, 2r, 3S, 4R, 5r, 6S)-hexachlorocyclohexane (Lindane) at Carbon Cathodes in Dimethylformamide. *Journal of Electroanalytical Chemistry*. 660(1), 121-126.
- Montory, M., Ferrer, J., Rivera, D., Villouta, M. V. and Grimalt, J. O. (2017). First Report on Organochlorine Pesticides in Water in a Highly Productive Agro-Industrial Basin of the Central Valley, Chile. *Chemosphere*. 174, 148-156.

- Mremaa, E. J., Rubino, F. M., Brambilla, G., Morettoc, A., Tsatsakis, A. M. and Colosio, C. (2013). Persistent Organochlorinated Pesticides and Mechanisms of Their Toxicity. *Toxicology*. 307, 74–88.
- Nazarudin, M. F., Zainal, Z., Tan, W. T., Hamadneh, I. and Kadri, E. F. (2012). Abrasive Stripping Voltammetric (AbrSV) Studies of  $\text{ErBa}_2\text{Cu}_3\text{O}_{7-\delta}$  Superconductor Synthesised Via Co-precipitation and Solid State Methods. *International Journal of Electrochemical Science*. 7, 2965-2982.
- Ni, Y., Qiu, P. and Kokot, S. (2004). Simultaneous Determination of Three Organophosphorus Pesticides by Differential Pulse Stripping Voltammetry and Chemometrics. *Analytica Chimica Acta*. 516(1-2), 7–17.
- Nieto, L. M., Hodaifa, G. and Casanova, M. S. (2009). Elimination of Pesticide Residues from Virgin Olive Oil by Ultraviolet Light: Preliminary Results. *Journal of Hazardous Materials*. 168 (1), 555–559.
- Norouzi, P., Gupta, V. K., Asif, M., Rasoolipour, S., Faridbod, F. and Ganjali, M. R. (2014). Determination of Methyl Parathion in Liquid Phase by Nano-Composite Carbon Paste Surface Biosensor and Differential FFT Continuous Linear Sweep Voltammetry. *Journal of Molecular Liquids*. 198, 239-245.
- Novotny, V. and Barek, J. (2015). A Voltammetric Technique Using a Modified Carbon Paste Electrode for the Determination of Aclonifen. *Ecological Chemistry and Engineering S*. 22(3), 451-458.
- Oksel, O., Razali, N., Yusoff, M. K., Ismail, M. Z., Pa'ee, K. F. and Ibrahim, K. N. (2009). The Impacts of Integrated Farming to Water Quality: Case Study on Langgas River, Kunak, Sabah, Malaysia. *International Journal of Engineering and Technology IJET-IJENS*. 9(9), 55-58.
- Oudou, H. C., Alonso, R. M. and Hansen, H. C. B. (2004). Voltammetric Behaviour of the Synthetic Pyrethroid Lambda- Cyhalothrin and Its Determination in Soil and Well Water. *Analytica Chimica Acta*. 523(1), 69-74.
- Ozkan, D., Kerman, K., Meric, B., Kara, P., Demirkan, H., Polverejan, M., Pinnavaia, T. J. and Ozsoz, M. (2002). Heterostructured Fluorohectorite Clay as an Electrochemical Sensor for the Detection of 2,4-Dichlorophenol and the Herbicide 2,4-D. *Chemistry of Materials*. 14(4), 1755-1761.
- Ozkan, S. A. and Uslu, B. (2016). From Mercury to Nanosensors: Past, Present and the Future Perspective of Electrochemistry in Pharmaceutical and Biomedical Analysis. *Journal of Pharmaceutical and Biomedical Analysis*. 130, 126-140.

- Papp, Z. J., Guzsivany, V. J., Kubiak, S., Borowski, A. & Bjelica, L. J. (2010). Voltammetric Determination of the Neonicotinoid Insecticide Thiamethoxam Using a Tricresyl Phosphosphate-based Carbon Paste Electrode. *Journal of Serbian Chemical Society*. 75(5), 681-687.
- Parham, H. and Rahbar, N. (2010). Square Wave Voltammetric Determination of Methyl Parathion Using ZrO<sub>2</sub>-nanoparticles Modified Carbon Paste Electrode. *Journal of Hazardous Materials*. 177 (1–3), 1077-1084.
- Parron, P., Requena, M., Hernández, A. F. and Alarcon, R. (2014). Environmental Exposure to Pesticides and Cancer Risk in Multiple Human Organ Systems. *Toxicology Letters*. 230(2), 157–165.
- Peltola, A. (2009). Up-Scaling Plan for TiO<sub>2</sub> Coating Process. Bachelor Degree Thesis, Turku University of Applied Sciences, Finland.
- Pinter, J. S., Brown, K. L., De Young, P. A. and Peaslee, G. F. (2007). Amperometric Detection of Hydrazine by Cyclic Voltammetry and Flow Injection Analysis Using Ruthenium Modified Glassy Carbon Electrodes. *Talanta*. 71(3), 1219-1225.
- Postigo, C. and Barcelo, D. (2015). Synthetic Organic Compounds and Their Transformation Products in Groundwater: Occurrence, Fate and Mitigation. *Science of the Total Environment*. 503-504, 32–47.
- Prathap, M. A. and Srivastava, R. (2013). Electrochemical reduction of lindane ( $\gamma$ -HCH) at NiCo<sub>2</sub>O<sub>4</sub> modified electrode. *Electrochimica Acta*. 108, 145-152.
- Priyantha, N and Welivegamage, S. (2008). Interaction of Thiram with Glassy Carbon Electrode Surfaces under Applied Potentials Conditions. *International Journal of Electrochemical Science*. 3, 125-135.
- Puetz, J. and Aegerter, M. A. (2004). *Chapter 2: Dip Coating Technique*. Aegerter, M. A. and Mennig, M. (Eds.) *Sol-Gel Technologies for Glass Producers and Users* (pp. 37-48). New York: Springer.
- Pushpamalini, T., Umar, A. U., Arockia Selvi, J. and Aminu, K. S. (2015). A Study on Photocatalytic Activity on the Degradation of Metsulfuron Methyl. *International Journal of Advanced Chemical Science and Applications*. 3(3). 19-23.

- Qu, C., Albanese, S., Chen, W., Lima, A., Doherty, A. L., Piccolo, A., Arienzo, M., Qi, S. and De Vivo, B. (2016). The Status of Organochlorine Pesticide Contamination in the Soils of the Campanian Plain, Southern Italy, and Correlations with Soil Properties and Cancer Risk. *Environmental Pollution*. 216, 500-511.
- Raghu, P., Reddy, T. M., Swamy, B. E. K., Chandrashekar, B. N., Reddaiah, K. and Sreedhar, M. (2012). Development of AChE Biosensor for the Determination of Methyl Parathion and Monocrotophos in Water and Fruit Samples: A Cyclic Voltammteric Study. *Journal of Electroanalytical Chemistry*. 665 (15), 76-82.
- Ramachandran, R., Mani, V., Chen, S. M., Gnana-kumar, G. and Govindasamy, M. (2015). Recent Developments in Electrode Materials and Methods for Pesticide Analysis- An Overview. *International Journal of Electrochemical Science*. 10, 859-869.
- Raut-Jadhav, S., Saini, D., Sonawane, S. and Pandit, A. (2016). Effect of Process Intensifying Parameters on the Hydrodynamic Cavitation Based Degradation of Commercial Pesticide (Methomyl) in the Aqueous Solution. *Ultrasonics Sonochemistry*. 28, 283–293.
- Razzino, C. A., Sgobbi, L. F., Canevari, T. C., Cancino, J. and Machado, S. A. (2015). Sensitive Determination of Carbendazim in Orange Juice by Electrode Modified with Hybrid Material. *Food Chemistry*. 170, 360-365.
- Ribeiro, J. A., Carreira, C. A., Lee, H. J., Silva, F., Martins, A. and Pereira, C. M. (2010). Voltammetric Determination of Paraquat at DNA-Gold Nanoparticle Composite Electrodes. *Electrochimica Acta*. 55(27), 7892–7896.
- Richter, F., Gabby, L., McDowell, K. A., Mulligan, C. K., De La Rosa, K., Sioshansi, P. C., Mortazavi, F., Cely, I., Ackerson, L. C., Tsan, L., Murphy, N. P., Maidment, N. T. and Chesselet, M-F. (2017). Effects of Decreased Dopamine Transporter Levels on Nigrostriatal Neurons and Paraquat/ Maneb Toxicity in Mice. *Neurobiology of Aging*. 51, 54-66.
- Rodrigues, A. M., Ferreira, V., Cardoso, V. V., Ferreira, E. and Benoliel, M. J. (2007). Determination of Several Pesticides in Water by Solid-Phase Extraction, Liquid Chromatography and Electrospray Tandem Mass Spectrometry. *Journal of Chromatography A*. 1150, 267–278.



- Rojano-Delgado, A. M. and Luque de Castro, M. D. (2014). Capillary Electrophoresis and Herbicide Analysis: Present and Future Perspectives. *Electrophoresis*. 35(17), 2509–2519.
- Rosell G., Quero, C., Coll-Toledano, J. and Guerrero, A. (2008). Biorational Insecticides in Pest Management. *Journal of Pesticide Science*. 33(2), 103-121.
- Rozman, D., Hrkal, Z., Eckhardt, P., Novotna, E. and Boukalova, Z. (2015). Pharmaceuticals in Groundwaters: A Case Study of the Psychiatric Hospital at Horni Berkovice, Czech Republic. *Environmental Earth Sciences*. 73(7), 3775–3784.
- Sabin, G. P., Prestes, O. D., Adaime, M. B. and Zanella, R. (2009). Multiresidue Determination of Pesticides in Drinking Water by Gas Chromatography-Mass Spectrometry after Solid-Phase Extraction. *Journal of the Brazilian Chemical Society*. 20(5), 918-925
- Saleh, F. Y., Dickson, K. L. and Rodgers, J. H. (1982). Fate of Lindane in the Aquatic Environment: Rate Constants of Physical and Chemical Processes. *Environmental Toxicology and Chemistry*. 1(4), 289-297.
- Schaider, L. A., Rudel, R. A., Ackerman, J. M., Dunagan, S. C. and Brody, J. G. (2014). Pharmaceuticals, Perfluorosurfactants, and Other Organic Wastewater Compounds in Public Drinking Water Wells in a Shallow Sand and Gravel Aquifer. *Science of the Total Environment*. 468–469, 384–393.
- Sharma, D. K., Gupta, A., Kashyap, R. and Kumar, N. (2012). Spectrophotometric Method for the Determination of Glyphosate in Relation to Its Environmental and Toxicological Analysis. *Archives of Environmental Sciences*. 6, 42-49.
- Sharma, P. S., Pietrzyk-Le, A., D'souza, F. and Kutner, W. (2012b). Electrochemically Synthesized Polymers in Molecular Imprinting for Chemical Sensing. *Analytical and Bioanalytical Chemistry*. 402(10), 3177-3204.
- Sharma, P., Meher, P. K., Kumar, A., Gautam, Y. P. and Mishra, K. P. (2014). Changes in Water Quality Index of Ganges River at Different Locations in Allhabad. *Sustainability of Water Quality and Ecology*. 3, 67-76.
- Shi, H. J., Zhao, G. H., Liu, M. C., Fan, L. F. and Cao, T. C. (2013). Aptamer-based Colorimetric Sensing of Acetamiprid in Soil Samples: Sensitivity, Selectivity and Mechanism. *Journal Hazardous Materials*. 260, 754–761.

- Shrivastava, A., Sharma, J. and Soni, V. (2013). Various Electroanalytical Methods for the Determination of Uranium in Different Matrices. *Bulletin of Faculty of Pharmacy, Cairo University*. 51(1), 113–129.
- Singh, B. and Mandal, K. (2013). Environmental Impact of Pesticides Belonging to Newer Chemistry. In Dhawan, A. K, Singh, B., Brar-Bhullar, M. and Arora, R. (Eds.) *Integrated Pest Management* (pp. 152-190). India: Scientific Publishers.
- Singh, S. B. and Paul, R. (2011). Gas Chromatographic Method for Residue Analysis of Metsulfuron Methyl from Soil. *Bulletin of Environmental Contamination and Toxicology*. 86(2), 149-151.
- Skrzypczynska, K., Kusmierek, K. and Swiątkowski, A. (2016). Carbon Paste Electrodes Modified with Various Carbonaceous Materials for the Determination of 2, 4-dichlorophenoxyacetic Acid by Differential Pulse Voltammetry. *Journal of Electroanalytical Chemistry*. 766, 8-15.
- Solna, R., Sapelnikova, S., Skladal, P., Winther-Nielsen, M., Carlsson, C., Emmenus, J. and Ruzgas, T. (2005). Multienzyme Electrochemical Array Sensor for Determination of Phenols and Pesticides. *Talanta*. 65(2), 349-357.
- Songa, E. A. and Okonkwo, J. O. (2016). Recent Approaches to Improving Selectivity and Sensitivity of Enzyme-Based Biosensors for Organophosphorus Pesticides: A Review. *Talanta*. 155, 289–304.
- Springer, V.H. and Lista, A.G. (2010). A Simple and Fast Method for Chlorsulfuron and Metsulfuron Methyl Determination in Water Samples Using Multiwalled Carbon Nanotubes (MWCNTS) and Capillary Electrophoresis. *Talanta*. 83(1), 126–129.
- Sreedhar, M., Reddy, T. M., Sirisha, K. R. and Reddy, S. R. J. (2003). Differential Pulse Adsorptive Stripping Voltammetric Determination of Dinoseb and Dinoterb at a Modified Electrode. *Analytical Sciences*. 19(4), 511-516.
- Stavila, V., Volponi, J., Katzenmeyer, A. M., Dixon, M. C. and Allendorf, M. D. (2012). Kinetics and Mechanism of Metal–Organic Framework Thin Film Growth: Systematic Investigation of HKUST-1 Deposition on QCM Electrodes. *Chemical Science*. 3(5), 1531-1540.
- Sugeng, A. J., Beamer, P. I., Lutz, E. A. and Rosales, C. B. (2013). Hazard-Ranking of Agricultural Pesticides for Chronic Health Effects in Yuma County, Arizona. *Science of the Total Environment*. 463, 35-41.

- Sun, Z., Wei, X., Shen, H. and Hu, X. (2014). Preparation and Evaluation of Pd/Polymeric Pyrrole-Sodium Lauryl Sulfonate/Foam-Ni Electrode for 2, 4-dichlorophenol Dechlorination in Aqueous Solution. *Electrochimica Acta*. 129, 433-440.
- Sundaram, S., Kumar, A. S., Jagannathan, M. and Kadir, M. R. A. (2014). In Situ Stabilization of Hydroxylamine via Electrochemical Immobilization of 4-Nitrophenol on GCE/MWCNT Electrodes: NADH Electrocatalysis at Zero Potential. *Analytical Methods*. 6(22), 8894-8900.
- Svorc, L., Rievaj, M. and Bustin, D. (2013). Green Electrochemical Sensor for Environmental Monitoring of Pesticides: Determination of Atrazine in River Waters Using a Boron-Doped Diamond Electrode. *Sensors and Actuators B: Chemical*. 181, 294-300.
- Swarupa, C., Dhananjayulu, M. S. P. M. and Sreedhar, N. Y. (2013). Electrochemical Determination and Reduction Behaviour of Mancozeb at Glassy Carbon Electrode Modified with Polyaniline Based Nanosensors. *International Journal of Scientific and Engineering Research*. 4(7), 1234–1241.
- Syaza binti Azhari. (2017). Acetophenone - Benzaldehyde Ethylenediamine Modified Electrodes for the Determination of Metal Ions in Aqueous Solutions. PhD Thesis, Universiti Teknologi Malaysia, Skudai.
- Takegami, S., Kitamura, K., Ohsugi, M., Ito, A. and Kitade, T. (2015). Partitioning Of Organophosphorus Pesticides Into Phosphatidylcholine Small Unilamellar Vesicles Studied by Second-Derivative Spectrophotometry. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*. 145, 198-202.
- Tcheumi, H. L., Tonle, K. I., Ngameni, E. and Walcarius, A. (2010). Electrochemical Analysis of Methylparathion Pesticide by a Gemini Surfactant-intercalated Clay-modified Electrode. *Talanta*. 81(3), 972–979.
- Tonle, K. I. and Ngameni, E. (2011). Voltammetric Analysis of Pesticides. In Stoytcheva, M. (Ed.) *Pesticides in the Modern World - Trends in Pesticides Analysis* (pp. 465-488). Croatia: InTech.
- Toriman, M. E., Kamarudin, M. K. A., Gasim, M. B., Mokhtar, J., Nor Azlina, A. A. and Ia Lun, P. (2012). Water Quality Status and Hydrological Analysis in Upper Tropical River, Malaysia. *International Journal of Agriculture and Crop Science*. 4(2), 33-39.

- Tsaboula, A., Papadakis, E. N., Vryzas, Z., Kotopoulou, A., Kintzikoglou, K. and Papadopoulou-Mourkidou, E. (2016). Environmental and Human Risk Hierarchy of Pesticides: A Prioritization Method, Based on Monitoring, Hazard Assessment and Environmental Fate. *Environment International*. 91, 78-93.
- Tsiafoulis, C. G. and Nanos, C. G. (2010). Determination of Azinphos-Methyl and Parathion-Methyl in Honey by Stripping Voltammetry. *Electrochimica Acta*. 56(1), 566-574.
- Tufan, A. N., Baki, S., Guclu, K., Ozyurek, M. and Apak, R. (2014). A Novel Differential Pulse Voltammetric (DPV) Method for Measuring the Antioxidant Capacity of Polyphenols-Reducing Cupric Neocuproine Complex. *Journal of Agricultural and Food Chemistry*. 62(29), 7111-7117.
- Tyszczyk-Rotko, K., Bęczkowska, I. and Nosal-Wiercinska, A. (2014). Simple, Selective and Sensitive Voltammetric Method for the Determination of Herbicide (Paraquat) Using a Bare Boron-Doped Diamond Electrode. *Diamond and Related Materials*. 50, 86–90.
- Uygun, Z. O. and Dilgin, Y. (2013). A Novel Impedimetric Sensor Based on Molecularly Imprinted Polypyrrole Modified Pencil Graphite Electrode for Trace Level Determination of Chlorpyrifos. *Sensors and Actuators B: Chemical*. 188, 78-84.
- Van Scoy A. R. and Tjeerdema R. S. (2014) Environmental Fate and Toxicology of Chlorothalonil. In Whitacre, D. (Ed.) *Reviews of Environmental Contamination and Toxicology* (pp. 89-105). Cham: Springer.
- Verlicchi, P. and Masotti, L. (2001), Reuse of Drinking Water Treatment Plants Sludges in Agriculture: Problems, Perspectives and Limitations, Technology transfer. *Proceedings of the 9th International Conference on the FAO ESCORENA Network on Recycling of Agricultural, Municipal and Industrial Residues in Agriculture*. September 6-9, 2000, Gargano, Italy, 67-73.
- Vieno, N., Tuhkanen, T. and Kronberg, L. (2006). Removal of Pharmaceuticals In Drinking Water Treatment: Effect Of Chemical Coagulation. *Environmental Technology*. 27(2), 183-192.
- Vorkamp, K., Bossi, R., Bester, K., Bollmann, U. E. and Boutrup, S. (2014). New Priority Substances of the European Water Framework Directive: Biocides, Pesticides and Brominated Flame Retardants in the Aquatic Environment of Denmark. *Science of the Total Environment*. 470, 459-468.

- Wahizatul, A. A., Long, S. H. and Ahmad, A. (2011). Composition and Distribution of Aquatic Insect Communities in Relation to Water Quality in Two Freshwater Streams of Hulu Terengganu, Terengganu. *Journal of Sustainability Science and Management*. 6(1), 148-155.
- Wang, H., Qu, B., Liu, H., Ding, J. and Ren, N. (2018). Analysis of Organochlorine Pesticides in Surface Water of the Songhua River using Magnetoliposomes as Adsorbents Coupled with GC-MS/MS Detection. *Science of the Total Environment*. 618, 70-79.
- Wang, J. (1994). Chapter 6: Voltammetry: *Techniques and Instrumentation in Analytical Chemistry*. 15 (pp. 129-145). United States: Wiley
- Wang, J. (2004). *Analytical Electrochemistry*. (2<sup>nd</sup> Ed.) New Jersey: Wiley.
- Wen, D., Yang, Y., Xiang, P., Yu, F., Zheng, F., Liu, T., Shi, Y., Zhang, X., Dong, M., Cong, B. and Ma, C. (2018). A Novel Approach for Determination of Paraquat Based on Dried Blood Spot (DBS) Extraction and UHPLC-HRMS Analysis. *Journal of Pharmaceutical and Biomedical Analysis*. 159, 11-17.
- Wei, T., Huang, X., Zeng, Q. and Wang, L. (2015). Simultaneous Electrochemical Determination of Nitrophenol Isomers with the Polyfurfural Film Modified Glassy Carbon Electrode. *Journal of Electroanalytical Chemistry*. 743, 105–111.
- Wen, Z-H., Chen, L., Meng, X-Z., Duan, Y-P., Zhang, Z-S. and Zeng, E. Y. (2014). Occurrence and Human Health Risk of Wastewater-Derived Pharmaceuticals in a Drinking Water Source for Shanghai East China. *Science of the Total Environment*. 490, 987–993.
- World Health Organization. (2009). The WHO Recommended Classification of Pesticides by Hazard and Guidelines to Classification 2009. ISBN 978 92 4 154796 3 ISSN 1684-1042.
- Writer, J. H., Ferrer, I., Barber, L. B. and Thurman, E. M. (2013). Widespread Occurrence of Neuro-Active Pharmaceuticals and Metabolites in 24 Minnesota Rivers and Wastewaters. *Science of the Total Environment*. 461–462, 519–527.
- Wu, L., Lei, W., Han, Z., Zhang, Y., Xia, M. and Hao, Q. (2015a). A Novel Non-Enzyme Amperometric Platform Based on Poly (3-Methylthiophene)/ Nitrogen Doped Graphene Modified Electrode for Determination of Trace Amounts of Pesticide Phoxim. *Sensors and Actuators B: Chemical*. 206, 495-501.

- Wu, S., Li, D., Wang, J., Zhao, Y., Dong, S. and Wang, X. (2017). Gold Nanoparticles Dissolution Based Colorimetric Method for Highly Sensitive Detection of Organophosphate Pesticides. *Sensors and Actuators B: Chemical*. 238, 427-433.
- Yamamoto, A., Miyamoto, I., Kitagawa, M., Moriwaki, H., Miyakoda, H., Kawasaki, H. and Arakawa, R. (2009). Analysis of Chlorothalonil by Liquid Chromatography/Mass Spectrometry Using Negative-Ion Atmospheric Pressure Photoionization. *Analytical Sciences*. 25(5), 693-697.
- Yan, W., Li, J. and Bai, X. (2016). Comprehensive Assessment and Visualized Monitoring of Urban Drinking Water Quality. *Chemometrics and Intelligent Laboratory Systems*. 155, 26-35.
- Yang, X., Zhang, G., Wang, F., Wang, Y., Hu, X., Li, Q., Jia, G., Liu, Z., Wang, Y., Deng, R. and Zeng, X. (2015). Development of a colloidal gold-based strip test for the detection of chlorothalonil residues in cucumber. *Food and Agricultural Immunology*. 26(5), 729-737.
- Yatmaz, H. C. and Uzman, Y. (2009). Degradation of Pesticide Monochrotophos from Aqueous Solutions by Electrochemical Methods. *International Journal Electrochemical Science*. 4, 614-626.
- Ye, X., Gu, Y. and Wang, C. (2012). Fabrication of Modified Glassy Carbon-Rotating Disk Electrodes Based on Graphene Composites and Their Applications for Electrochemical Sensor Research. *Sensors and Actuators B*. 173, 530– 539.
- Zhang, H., Zhao, J., Liu, H., Wang, H., Liu, R. and Liu, J. (2010). Application of Poly (3-methylthiophene) Modified Glassy Carbon Electrode as Riboflavin Sensor. *International Journal of Electrochemical Science*. 5, 295-301.
- Zhang, S., Gitungo, S., Axe, L., Dyksen, J. E. and Raczko, R. F. (2016). A Pilot Plant Study Using Conventional and Advanced Water Treatment Processes: Evaluating Removal Efficiency of Indicator Compounds Representative of Pharmaceuticals and Personal Care Products. *Water Research*. 105, 85-96.
- Zhang, Y., Arugula, M. A., Wales, M., Wild, J. and Simonian, A. L. (2015). A Novel Layer-By-Layer Assembled Multi-Enzyme/CNT Biosensor for Discriminative Detection between Organophosphorus and Non-organophosphorus Pesticides. *Biosensors and Bioelectronics*. 67, 287-295.

- Zhou, Y. F. and Haynes, R. J. (2010). Removal of Pb (II), Cr(II) and Cr(VI) from Aqueous Solutions using Alum-Derived Water Treatment Sludge. *Water Air Soil Pollution*. 215(1-4), 631-643.
- Zolgharnein, J., Shahmoradi, A. and Ghasemi, J. (2011). Pesticides Removal using Conventional and Low-Cost Adsorbents: A Review. *Clean–Soil, Air, Water*. 39(12), 1105–1119.
- Zunic, M. J., Milutinovic-Nikolic, A. D., Stankovic, D. M., Manojlovic, D. D., Jovic-Jovicic, N. P., Bankovic, P. T., Mojovic, Z. D. and Jovanovic, D. M. (2014). Electrooxidation of *p*-Nitrophenol using a Composite Organo-smectite Clay Glassy Carbon Electrode. *Applied Surface Science*. 313, 440-448.