



# SIMULTANEOUSLY DETERMINATION OF BISPHENOL A AND URIC ACID BY ZINC/ALUMINUM-LAYERED DOUBLE HYDROXIDE 2(2,4-DICHLOROPHENOXY) PROPIONATE PASTE ELECTRODE



pustaka.upsi.edu.my

Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shal PustakaTBainu



NURUL SYAHIDA BINTI MAT RAIS

# UNIVERSITI PENDIDIKAN SULTAN IDRIS

2020











### SIMULTANEOUSLY DETERMINATION OF BISPHENOL A AND URIC ACID BY ZINC/ALUMINUM-LAYERED DOUBLE HYDROXIDE 2(2,4-DICHLOROPHENOXY)PROPIONATE PASTE ELECTRODE

### NURUL SYAHIDA BINTI MAT RAIS





DISSERTATION SUBMITTED IN FULFILMENT OF THE REQUIREMENT FOR THE DEGREE OF MASTER OF SCIENCE (MASTER BY RESEARCH)

### FACULTY OF SCIENCE AND MATHEMATICS UNIVERSITI PENDIDIKAN SULTAN IDRIS

2020











UPSI/IPS-3/BO 32 Pind : 00 m/s: 1/1



Please tick (√) Project Paper Masters by Research Master by Mixed Mode PhD

ĺ		
l	$\checkmark$	
l		
ſ		

### INSTITUTE OF GRADUATE STUDIES DECLARATION OF ORIGINAL WORK

This declaration is made on the 14 day of 3000 day of 3000

i. Student's Declaration:

I. NURUL SYAHIDA BINTI MAT RAIS (M20171000193) FSM (PLEASE INDICATE STUDENT'S NAME, MATRIC NO. AND FACULTY) hereby declare SIMULTANEOUSLY DETERMINATION OF that the work entitled BISPHENOL AND URIC ACID BY ZINC/ALUMINUM-LAYERED Α 2(2,4-DICHLOROPHENOXY) **HYDROXIDE** DOUBLE PROPIONATE **PASTE ELECTRODE** is my original work. I have not copied from any other students' work or from any other sources except where due reference or acknowledgement is made explicitly in the text, nor has any part been written for me by another person.

Signature of the student

ii. Supervisor's Declaration:

I <u>ILLYAS MD ISA</u> (SUPERVISOR'S NAME) hereby certifies that the work entitled <u>SIMULTANEOUSLY DETERMINATION OF BISPHENOL A AND</u> <u>URIC ACID BY ZINC/ALUMINUM-LAYERED DOUBLE HYDROXIDE 2-</u> (2,4-DICHLOROPHENOXY) PROPIONATE PASTE ELECTRODE (TITLE) was prepared by the above named student, and was submitted to the Institute of Graduate Studies as a \* partial/full fulfillment for the conferment

of <u>MASTER OF SCIENCE (CHEMISTRY)</u> (PLEASE INDICATE THE DEGREE), and the aforementioned work, to the best of my knowledge, is the said student's work.

Date: 21/8/2020

Signature of the Supervisor







📢 pustaka.upsi.edu.i

Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah





iii



UPSI/IPS-3/BO 31 Pind.: 01 m/s:1/1

### INSTITUT PENGAJIAN SISWAZAH / INSTITUTE OF GRADUATE STUDIES

#### BORANG PENGESAHAN PENYERAHAN TESIS/DISERTASI/LAPORAN KERTAS PROJEK DECLARATION OF THESIS/DISSERTATION/PROJECT PAPER FORM

Tajuk / Title:

#### SIMULTANEOUSLY DETERMINATION OF BISPHENOL A AND URIC ACID BY ZINC/ALUMINUM-LAYERED DOUBLE HYDROXIDE 2(2,4-DICHLOROPHENOXY) PROPIONATE PASTE ELECTRODE

No. Matrik /Matric No.: M2017100

Saya / I:

M20171000193

NURUL SYAHIDA BINTI MAT RAIS (Nama pelajar / Student's Name)

mengaku membenarkan Tesis/Disertasi/Laporan Kertas Projek (Kedoktoran/Sarjana)\* ini disimpan di Universiti Pendidikan Sultan Idris (Perpustakaan Tuanku Bainun) dengan syarat-syarat kegunaan seperti berikut:-

acknowledged that Universiti Pendidikan Sultan Idris (Tuanku Bainun Library) reserves the right as follows:-

- 1. Tesis/Disertasi/Laporan Kertas Projek ini adalah hak milik UPSI. The thesis is the property of Universiti Pendidikan Sultan Idris
- 2. Perpustakaan Tuanku Bainun dibenarkan membuat salinan untuk tujuan rujukan dan penyelidikan. Tuanku Bainun Library has the right to make copies for the purpose of reference and research.
  - 3. Perpustakaan dibenarkan membuat salinan Tesis/Disertasi ini sebagai bahan pertukaran antara Institusi Pengajian Tinggi. The Library has the right to make copies of the thesis for academic exchange.
  - 4. Sila tandakan ( $\sqrt{}$ ) bagi pilihan kategori di bawah / Please tick ( $\sqrt{}$ ) from the categories below:-



SULIT/CONFIDENTIAL



TERHAD/RESTRICTED

Mengandungi maklumat terhad yang telah ditentukan oleh organisasi/badan di mana penyelidikan ini dijalankan. / *Contains* 

Mengandungi maklumat yang berdarjah keselamatan

atau kepentingan Malaysia seperti yang termaktub dalam Akta Rahsia Rasmi 1972. / Contains confidential

information under the Official Secret Act 1972



TIDAK TERHAD / OPEN ACCESS

(Tandatangan Pelajar/ Signature)

Tarikh: <u>21/8/2020</u>

(Tandatangan Penyelia / Signature of Supervisor

Catatan: Jika Tesis/Disertasi ini **SULIT** @ **TERHAD**, sila lampirkan surat daripada pihak berkuasa/organisasi berkenaan dengan menyatakan sekali sebab dan tempoh laporan ini perlu dikelaskan sebagai **SULIT** dan **TERHAD**.

Notes: If the thesis is CONFIDENTAL or RESTRICTED, please attach with the letter from the related authority/organization mentioning the period of confidentiality and reasons for the said confidentiality or restriction.



) 05-45068

### **ACKNOWLEDGEMENTS**

First and foremost, I would like to express my deep and sincere gratitude to my supervisor, Prof. Dr. Illyas bin Md Isa, professor of analytical chemistry and chemical sensor from Chemistry Department, Faculty of Science and Mathematics, University Pendidikan Sultan Idris in particular has been a constant source of support and encouragement throughout my time in University Pendidikan Sultan Idris and me deeply indebted to him for his guidance, understanding, patience and boundless knowledge.

My acknowledgement goes to Ministry of Education Malaysia and Universiti Pendidikan Sultan Idris, Malaysia for their financial supported that I received from Funding Research Grant Scheme (FRGS), under grant number: 2017-0075-101-02 that funds me in apparatus and chemicals in the laboratory.

In the elaboration of this paper, I am thankful for the collaboration of specialists, professional, and human qualities. I would like to express my gratitude, respect and thanks to Assoc. Prof. Dr. Norhayati binti Hashim, Dr. Siti Nur Akmar binti Mohd Yazid, Dr. Mohamad Idris bin Saidin, and Dr. Mohamad Syahrizal bin Ahmad for their great efforts to explain things clearly and simply. Their discussions around my work and constructive comments have been very helpful for this research.

I especially thank to all staff and laboratory technicians, Mr. Farhan, Mr. Hashimi, Mr. Isa and Mr. Supian with their help and guidance for the use of advanced equipments such as potentiostat, SEM and TEM, as well as HPLC instrument. Regarding my time at laboratory, I owe big thank to my colleague from the electrochemistry group, Nurashikin binti Abd Azis. Also, I wish to extend my warmest thanks to my friends and to all those who have helped me with my work, Nurul Husna binti Othman from Physic Department, Nurul Amira binti Jamaluddin and Fadhlin Sakina binti Rajidi from Chemistry department.

Finally, I would like to express my deepest gratitude to my father, Mat Rais bin Ismail who is fully financially supported me throughout my entire study at this university, my mother, Azimah binti Ibrahim, and all my families for their constant support, understanding and love that I received.



### ABSTRACT

The purpose of this study was to determine simultaneously of bisphenol A and uric acid by zinc/aluminium-layered double hydroxide 2(2,4-dichlorophenoxy)propionate paste electrode. The morphology of the electrode materials was performed by using electron microscopy and transmission electron microscopy. scanning The electrochemical performance of modified paste electrode was studied by using cyclic voltammetry, square wave voltammetry, electrochemical impedance spectroscopy and chronocoulometry. Special importance effecting sensitivity and selectivity of the modified electrode must evaluated via optimization conditions which include effect of modifier composition percentage (15%), types of supporting electrolyte (PBS), pH of electrolyte (6.0) and square wave voltammetry parameters that encompassed of frequency (180Hz), pulse size (80mV) and step increment (7mV). The square wave voltammetry studies at an applied potential of -0.30 V to +1.0V, showed fast response within 1 second and detected at high sensitivity. The modified sensor had showed a linear range from 5.0 µM to 0.7 mM with detection limit of 0.871 µM and 0.795 µM for bisphenol A and uric acid, respectively. The modified sensors also exhibited good anti-interferences towards nitrate, chloride, sulphate, captopril, phthaldialdehyde, aspartic acid, glycine and fructose. In conclusion, the modified electrodes have been developed are able to detect bisphenol A and uric acid. By implication, the electrodes have been developed can be used as a suitable alternative for the determination of bisphenol A and uric acid because it has characteristics such as high sensitivity, reproducibility, repeatability and stability.







#### PENENTUAN SERENTAK BISFENOL A DAN ASID URIK OLEH ELEKTROD PASTE ZINK/ALUMINIUM-BERLAPIS HIDROKSIDA 2(2,4-DIKLOROFENOKSI) PROPIONAT

#### ABSTRAK

Tujuan kajian ini adalah untuk menentukan bisfenol A dan asid urik oleh elekrod paste zink/aluminium-berlapis hidroksida 2(2,4-diklorofenoksi)propionat. Morfologi bahan elektrod dilakukan dengan menggunakan mikroskop pengimbas elektron dan mikroskop transmisi elektron. Prestasi elektrokimia elektrod paste terubah suai telah dikaji dengan menggunakan voltammetri kitaran, voltammetri gelombang persegi, spektroskopi impedans elektrokimia dan khronokoulometri. Kepentingan khusus yang mempengaruhi kepekaan dan kepilihan elektrod terubah suai dinilai melalui keadaan pengoptimuman yang merangkumi kesan peratusan komposisi pengubah suai (15%), jenis elektrolit penyokong (PBS), pH elektrolit (6.0) dan parameter voltammetri gelombang persegi yang merangkumi kekerapan (180Hz), saiz nadi (80mV) dan kenaikan langkah (7mV). Kajian voltammetri gelombang persegi pada keupayaan -0.30 V hingga + 1.0V yang digunakan, menunjukkan gerak balas yang cepat dalam masa 1 saat dan dikesan pada kepekaan yang tinggi. Penderia terubah suai telah menunjukkan julat linear bisfenol A dan asid urik dari 5.0 µM hingga 0.7 mM dengan masing-masing had pengesanan 0.871 µM dan 0.795 µM untuk bisfenol A dan asid urik. Penderia terubah suai juga menunjukkan anti-gangguan baik terhadap nitrat, klorida, sulfat, kaptopril, phthaldialdehida, asid aspartik, glisin dan fruktosa. Kesimpulannya, elektrod-elektrod terubah suai yang telah dibangunkan ini mampu mengesan bisfenol A dan asid urik. Implikasinya, elektrod-elektrod yang telah dibangunkan boleh digunakan sebagai alternatif yang sesuai bagi penentuan bisfenol A dan asid urik kerana mempunyai ciri-ciri seperti kepekaan, kebolehasilan, keboleh ulangan dan kestabilan yang tinggi.









### TABLE OF CONTENTS

		Page		
DECLARATIO	ON OF ORIGINAL WORK	ii		
DECLARATIO	DECLARATION OF DISSERTATION FORM			
ACKNOWLEI	DGEMENTS	iv		
ABSTRACT		V		
ABSTRAK		vi		
TABLE OF CO	DNTENTS	vii		
LIST OF TAB	LES	xii		
LIST OF FIGU	JRES a.upsi.edu.my f Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun REVIATIONS	xv ptbups xviii		
LIST OF APPI	ENDIXES	xxi		
CHAPTER 1	INTRODUCTION	1		
1.1	Voltammetry Sensors	1		
1.2	Electrochemical Detection Techniques	8		
	1.2.1 CyclicVoltammetry	8		
	1.2.2 Chronocoulometry	13		
	1.2.3 Electrochemical impedance spectroscopy (EIS)	15		
	1.2.4 Square wave voltammetry (SWV)	18		
	1.3 Carbon Paste Electrode (CPE)	21		

05-4



	1.4 Multi-walled Carbon Nanotubes	24
	1.5 Layered Double Hydroxide	27
	1.6 Introduction To Bisphenol A and Uric Acid	29
	1.7 Problem Statement	35
	1.8 Significant Study	39
	1.9 Objectives Of The Study	40
CHAPTER 2	LITERATURE REVIEW	41
2.1	Introduction	41
2.2	Modified Carbon Nanotubes (CNT) paste electrode for Determination of Uric Acid and Bisphenol A	42
06832 😯 2.3	Electrochemical Sensor modified With Layered Double Hydro	oxide 47 <sup>toupsi</sup>
2.4	Performances of Modified Layered Double Hydroxides with Anionic Herbicides Electrodes	50
2.5	Conventional Techniques	53
CHADTED 2	METHODOLOCY	55
		55
3.1	Chemical and Reagents	55
3.2	Instrumentations	56
3.3	Fabrication of the Zn/Al-LDH-DPPA modified MWCNT and Unmodified MWCNT Paste Electrodes	l the 58
3.4	Analytical Procedure	60
3.5	Characterization of Zn/Al-LDH-DPPA and MWCNT nanocomposite	63







	3.5.1 SI	EM analysis of the Zn/Al-LDH-DPPA modified MWCN	T
			63
	3.5.2 T	EM analysis of the Zn/Al-LDH-DPPA modified MWC	NT
			63
3.6	Optimizat	ion of the Experimental Variables	64
	3.6.1 Ef	fect of modifier composition percentages	64
	3.6.2 Ef	fect of supporting electrolyte	65
	3.6.3 Ef	fect of pH	65
	3.6.4 Ef	fect of Square Wave Voltammetry Parameters	68
3.7	Linearity	range and the limit of detection	69
3.8	Reproduc	ibility, repeatability and stability	71
3.9 pustaka	Interferen	Ces Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah	72 ptbup
3.10	Chronoco	oulometry	74
3.11	Analysis	of real samples	75
	3.11.1	Determination of Uric Acid and Bisphenol A in Human Urine	n 76
	3.11.2	Determination of Uric Acid and Bisphenol A in Water Samples	77
3.12	Validat	ion data by using HPLC technique for determination of	uric
2.22	acid an	d bisphenol A	77





81

## CHAPTER 4 RESULT AND DISCUSSION

4.1	Electroana Zn/Al-LD	ulytical de H-DPPA	termination of uric acid and bisphenol a by us modified MWCNT paste electrode	sing 81
	4.1.1	Character MWCN7	ization of the Zn/Al-LDH-DPPA modified [ paste electrode	82
	4.1.2	Electroch DPPA m	nemical characterization of the Zn/Al-LDH- odified MWCNT paste electrode	84
	4.1.3	SWV res the Zn/A	ponses of 0.1 mM Uric Acid and Bisphenol A l-LDH-DPPA modified MWCNT paste electr	4 on rode 89
	4.1.4	Optimiza determin Zn/Al-LI	ation of experimental variables for the ation of uric acid and bisphenol A by using DH-DPPA modified MWCNT paste electrode	291
		4.1.4.1	The effect of Zn/Al-LDH-DPPA composition percentages	on 92
		4.1.4.2	The effect of type supporting electrolyte for determination of uric acid and bisphenol A	94
		4.1.4.3	The effect of pH of electrolyte	96
		4.1.4.4	The Effect of Square Wave Voltammetry Parameters for Determination of Uric Acid Bisphenol A	and 98
	4.1.5	Calibrati LDH-DP	on Curve and Limit of Detection of the Zn/Al PA modified MWCNT paste electrode	l- 102
	4.1.6	Chronoco modified	oulometry study of the Zn/Al-LDH-DPPA MWCNT paste electrode	104
	4.1.7	Reproduce LDH-DP	cibility, repeatability and stability of the Zn/A PA modified MWCNT paste electrode	.l- 108
	4.1.8	Interferen bispheno	nces study for determination of uric acid and l A	112









4.1.9 Analysis for determination of uric acid and bisphenol A 113

CHAPTER 5	CONCLUSION	115
5.1	Conclusion	115
5.2	Recommendation for Future Prospect	119
REFERENCE	S	121
APPENDIXES	5	137



















### LIST OF TABLES

Ta	ble No.		Page
	2.1	Electrochemical performance of modified electrodes with various types of modifiers	46
	2.2	The performance of layered double hydroxide as an electrochemical sensor in the determination of various analytes	49
	2.3	Summarize of electrochemical performance of modified electrodes with various types of modifiers	52
	3.1	The list of chemicals and reagents used in this study	57
	3.2	The list of instrumentations used in the study	58
	3.3 pus	The mass required to prepare 0.01 M of analytes in the 50.00 mL of volumetric flask	66 -
	3.4	The modifier composition percentages of the MWCNT and Zn/Al- LDH-DPPA used for preparing paste electrode	67
	3.5	Different weight of salts required for the preparation of 0.1 M concentration of each supporting electrolytes in 50.0 mL Volumetric flasks.	67
	3.6	Admeasurement of the experimental conditions and ranges of pH of the solutions studied for Zn/Al-LDH-DPPA modified MWCNT paste electrode	68
	3.7	The parameters ranges of square wave voltammetry (SWV) studied for Zn/Al-LDH-DPPA modified MWCNT paste electrode	70
	3.8	The different volume of stock solution added for the preparation of series concentrations of UA and BPA in 25.00 mL volumetric flasks	71

05-4506









3.9	The mass required to prepare stock solution of interfering ions in 25.00 mL volumetric acid	73
3.10	The summary of HPLC setting	79
3.11	The mobile phase system of HPLC	79
3.12	Summary of experimental conditions study for SWV measurements of analyte on Zn/Al-LDH-DPPA modified MWCNT paste electrode	80
4.1	Main parameters of Randle's equivalent circuit obtained from EIS analysis	89
4.2	Peak currents obtained for different 0.1 M supporting electrolytes on the determination of 0.1 mM UA and BPA at pH 6.0	94
4.3 pus	Reproducibility of the Zn/Al-LDH-DPPA modified MWCNT paste electrode for determination of 0.1 mM UA in the presence of 0.1 M PBS at pH 6.0 ( $n = 3$ )	109 ptbup
4.4	Reproducibility of the Zn/Al-LDH-DPPA modified MWCNT paste electrode for determination of 0.1 mM BPA in the presence of 0.1 M PBS at pH 6.0 ( $n = 3$ )	109
4.5	Repeatability of the Zn/Al-LDH-DPPA modified MWCNT paste electrode for determination of 0.1 mM UA in the presence of 0.1 M PBS at pH 6.0 ( $n = 3$ )	110
4.6	Repeatability of the Zn/Al-LDH-DPPA modified MWCNT paste electrode for determination of 0.1 mM BPA in the presence of 0.1 M PBS at pH 6.0 ( $n = 3$ )	110
4.7	Stability of the Zn/Al-LDH-DPPA modified MWCNT paste electrode for determination of 0.1 mM UA in the presence of 0.1 M PBS at pH 6.0 ( $n = 3$ )	111









4.8	Stability of the Zn/Al-LDH-DPPA modified MWCNT paste electrode for determination of $0.1$ mM BPA in the presence of $0.1$ M PBS at pH 6.0 (n = 3)	111
4.9	Recoveries of Zn/Al-LDH-DPPA modified MWCNT paste electrode in real samples applications ( $n = 3$ )	114
4.10	Comparison of UA and BPA determination by SWV and HPLC techniques $(n=5)$	115



😭 pustaka.upsi.edu



Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah

PustakaTBai

ptbupsi





Figures No.		Page
1.1	A typical experimental set-up showing of (RE = reference electrode, WE = working electrode and the CE = counter electrode that immersed into an electrolyte solution (adapted from Brownson & Banks, 2014)	6
1.2	General three-electrode electrochemical cells. A: working electrode (WE), reference electrode (RE), and counter electrode (CE) in solution, set-up to a potentiostat. At the WE, species are converted from their reduced (red) to their oxidized form (ox), and vice-versa at the CE. B: Three-electrode system in a thin-layer configuration (adapted from Van Den Brink, 2016)	7
1.3 4506832 💽 pus	Typical cyclic voltammogram produce by application of the potential waveform (adapted from Compton, Eduardo, and Ward, 2013) Taka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah	11 ptbup
1.4	Cyclic voltammograms for reversible (a); quasi-reversible (b); and irreversible (c) electron transfer (adapted from Brownson and Banks, 2014).	12
1.5	EIS Nyquist plot (Zimag against Zreal) and Randles circuit (W is a so-called Warburg element, which accounts for diffusion processes (adapted from Estrela, Hammond, Carrara, Tkac, and Formisano, 2016)	17
1.6	Example of carbon nanotube shape of single-walled carbon nanotube (SWCNT), double-walled carbon nanotube (DWCNT) and multi-walled carbon nanotube (MWCNT) (adapted from Nakashima & Shiraki, 2016)	25
1.7	Schematic structure of layered double hydroxide	27
1.8	The structure of bisphenol A	29
1.9	The structure of uric acid	32



O 05-4506832 O pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun

LIST OF FIGURES



ge





2.1	The structure of 2-(2, 4-dichlorophenoxy) propionate layered double hydroxide (DPPA-LDH)	50
3.1	Illustration fabrication of the modified MWCNT paste electrode	59
3.2	The diagram of the basic components cell for electrochemical measurements (WE: working electrode, RE: reference electrode and CE: counter electrode)	62
4.1	The SEM image of (a) Zn/Al-LDH-DPPA nanocomposite, the TEM image of (b) Zn/Al-LDH-DPPA modified MWCNT nanocomposite	83
4.2	CV curve of the bare MWCNT (curve a) and modified Zn/Al-LDH-DPPA modified MWCNT paste electrode (curve b) in 4.0 mM $K_3$ [Fe(CN) <sub>6</sub> ] containing 0.1M KCl at scan rate of 100 mV s <sup>-1</sup>	85
4.3	(a) CV curve of modified Zn/Al-LDH-DPPA modified MWCNT paste electrode in 4.0 mM at $K_3$ [Fe(CN) <sub>6</sub> ] containing 0.1M KCl at different scan rate from 50 to 300 mVs <sup>-1</sup> and (b) the plot of peak current vs. square root of scan rate from 50 to 300 mVs <sup>-1</sup> and (b) the plot of peak current vs. square root of scan rate from 50 to 300 mVs <sup>-1</sup> and (b) the plot of peak current vs. square root of scan rate from 50 to 300 mVs <sup>-1</sup> and (b) the plot of peak current vs.	86 ptbuj
4.4	Electrochemical impedance spectroscopic (EIS) pattern of Nyquist plot of the (a) bare MWCNT (b) Zn/Al-LDH-DPPA modified MWCNT in a solution of 4.0 mM $K_3$ [Fe (CN <sub>6</sub> )] containing 0.1M KCl. Inset: Randle's equivalent electrical circuit system	90
4.5	SW voltammogram of 0.1 mM UA and BPA in the presence of 0.1 M PBS (pH 6.0) at the (a) unmodified MWCNT of UA and BPA and (b) modified Zn/Al-LDH-DPPA/MWCNT paste electrode of UA and BPA	91
4.6	The effect of (a) 0%, (b) 5%, (c) 10%, (d) 15%, (e) 20% composition of Zn/Al-LDH-DPPA modified MWCNT paste electrode towards determination of 0.1 mM UA and BPA in the presence of 0.1 M PBS at pH 6.0 (pulse size = 80 mV; step size = 7 mV; frequency ( $f$ ) = 180 Hz)	93
4.7	The whole possible reaction mechanism of UA and BPA solution on the surface of Zn/Al-LDH-DPPA/ MWCNT paste electrode	95

05-4506



to ptbupsi xvii

4.8	Plot of peak current and peak potential vs. pH (5.0 to 8.0) of 0.1 mM (a) UA and (b) BPA in 0.1 M PBS ( $a = 40 \text{ mV}, \Delta E_s = 6 \text{mV}, f = 120 \text{ Hz}$ )	97
4.9	The effect of frequency of 0.1 mM UA and BPA in the presence of 0.1 M PBS at pH 6.0. Plot of peak current <i>vs</i> . peak potential ( $\Delta E_s = 4 \text{ mV}$ , $a = 40 \text{ mV}$ )	100
4.10	The effect of pulse size of 0.1 mM UA and BPA in the presence of 0.1 M PBS at pH 6.0. Plot of peak current <i>vs</i> . peak potential ( $\Delta E_s = 4 \text{ mV}, f = 180 \text{ Hz}$ )	100
4.11	The effect of step size of 0.1 mM UA and BPA in the presence of 0.1 M PBS at pH 6.0. Plot of peak current <i>vs</i> . peak potential ( $a = 80 \text{ mV}, f = 180 \text{ Hz}$ )	101
4.12	SWV curve of different concentration at 5 $\mu$ M to 700 $\mu$ M of BPA and UA in the presence of 0.1 M PBS (pH 6.0) at optimum experimental condition	101
4.13	Calibration plot of (a) BPA and (b) UA having a concentration of 5 $\mu$ M to 700 $\mu$ M in the presence of 0.1 M PBS at pH 6.0 and at optimum conditions	103
4.14	Plot of Q vs t and plot Q vs $t^{1/2}$ of (a) modified Zn/Al-LDH- DPPA/MWCNT, and (b) unmodified MWCNT in 4.0 mM $K_3$ Fe(CN) <sub>6</sub> containing 0.1 M KCl	106
4.15	Plot Q vs t and Q vs $t^{1/2}$ of the Zn/Al-LDH-DPPA/MWCNT in 0.1 M PBS at pH 6.0 (a) in the presence and (b) absence of 0.1 mM UA and BPA	107
4.16	The effect of interfering ions in 0.1 mM UA and BPA containing 0.1 M PBS (pH 6) at modified Zn/Al-LDH-DPPA/MWCNT paste electrode ( $a = 80 \text{ mV}$ , $\Delta E_s = 7 \text{mV}$ , $f = 180 \text{ Hz}$ )	112







### LIST OF ABBREVIATIONS

	AGR	Activated graphene
	BPA	Bisphenol A
	CE	Counter electrode
	CNT	Carbon nanotube
	CPE	Carbon paste electrode
	СРРА	2(3-chlorophenoxy) propionate
	CV	Cyclic voltammetry
	DAD	Diode array detector
	DIC	Diclofenac
05-45068	DME 832 pustaka.upsi.edu.my	Dropping mercury electrode
	DPPA	2-(2, 4-dichlorophenoxy) propionate
	DPV	Differential pulse voltammetry
	DWCNT	Double-walled carbon nanotube
	EEC	Electrical equivalent circuit
	EIS	Electrochemical impedance spectroscopy
	ELISA	Enzyme-linked immunoassay
	EP	Epinephrine
	EPA	Environmental Protection Agency
	EU	European Union
	FESEM	Field emission scanning electron microscopy
	FL	Fluorescent
	GC-MS	Gas chromatography couple with mass spectrometry



05-45





HPLC	High performance liquid chromatography
LC-MS	Liquid chromatography-tandeem mass spectrometry
LDH	Layered double hydroxide
LOD	Limit of detection
MIP	Molecularly imprinted polymer
MPP	3(4-methoxyphenyl) propionate
MSU	Monosodium urate
MWCNT	Multi-walled carbon nanotube
NHANES	National Health and Nutrition Examination Survey
NPV	Normal pulse voltammetry
PBS	Phosphate buffer saline
PEI	Polyethylenimine
PGA pustaka.upsi.edu.my	Perpustakaan Tuanku Bainun Polyglutamate acid ul Jalil Shah
RE	Reference electrode
RMM	Relative molecular mass
RSD	Relative standard deviation
SDS	Sodium dodecyl sulfate
SEM	Scanning electron microscope
SMT	Specific migration limit
SWCNT	Single-walled carbon nanotube
SWV	Square wave voltammetry
TDI	Tolerable daily intake
TEM	Transmission electron microscope
UA	Uric acid



Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah



UVUltravioletWEWorking electrode



pustaka.upsi.e



Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah

PustakaTE

ptbups











## LIST OF APPENDIXES

А	Knowledge and dissemination		
B1	Cyclic voltammetry (CV) behavior		
B2	Limit of detection (LOD) study		
B3	Electrochemical impedance spectroscopy (EIS) in Ferrocynide		
B4	Chronocoulometry study		
B5	Real sample study		
C1 4506832	The independent sample t-test result comparison method of SWV and HPLC validation for determination of urine sample		
C2	The independent sample t-test result comparison method of SWV and HPLC validation for determination of river sample		
C3	The independent sample t-test result comparison method of SWV and HPLC validation for determination of lake sample		
D1	HPLC chromatogram of lake sample		
D2	HPLC chromatogram of river sample		
D3	HPLC chromatogram of urine sample		









### **CHAPTER 1**

### INTRODUCTION



### 1.1 Voltammetry Sensors

Voltammetry is the study of current as a function of applied potential and a category of electroanalytical methods in analytical chemistry and various industrial processes. Voltammetric have been used since many years ago to study the thermodynamics and kinetics of heterogeneous reactions involving organic compounds. Hence, the appearance of new voltammetric techniques have encouraged the development of electroanalytical methods for the determination of analytes in a wide range of concentrations (up to traces) in real samples from different areas of great importance for human being and animal's health. The first discovery of first voltammetric technique was polarography which was developed by Jaroslav Heyrovsky in 1922 (Heyrovský, 1924). Significantly advances were





ptbups 2

made in all areas of voltammetry including theory, methodology and instrumentation, making them less than ideal for routine analytical use (Saito & Takumi Kikuchi, 2013).

In voltammetry, the common characteristics of all voltammetric techniques are involving the application of a potential (E) to an electrode and monitoring of the resulting current (i) flows through electrochemical cell is which measures over a period of time (t). Thus, voltammetric techniques can be described as some function of E, i and t. respectively (Kounaves, 1997). The measured signal obtained through the resulting current versus the potential plot will be showed in the form of voltammogram, whereby current signal (vertical axis) versus the excitation potential (horizontal axis). The exact shape and magnitude of the voltammetric response was driven by the process involved in the electrode reaction (Wang, 2000). The response current is the result of the electrochemical reaction that occurs at the electrode surface and the electrode/electrolyte interface layer. By controlling the applied potential, the electrode can be used as a variable free energy source (or sink) of electrons. Thus, electrons crossing the electrode-solution interface can be determined with great sensitivity by measuring current (Murray, Ewing, Durst, 1987).

Electron transfer in the voltammetry electrochemical cell causes the reaction possess oxidation or reduction to occur on the redox species (analyte). The redox reactions involve Faradaic or non-Faradaic processes. Theoretically, Faradaic process distinguished by charge transfer flows through the redox electrode and obeys Faraday's law. In contrast, non-Faradaic can be determined if there is no charge transfer or reaction at the electrode occur and do not obey Faraday's law. In this way,





electronic charge injected into an electrode is truly transferred out of it and not being stored (Bard & Faulkner, 2000; Biesheuvel & Dykstra, 2018). In this case, the mobility of ions to reach the electrode surface can be accomplished via three possible mechanisms which can transport through diffusion in concentration region, migration of ions in a potential systems and convection, respectively (Scholz, 2015).

The basic component of a modern electroanalytical system for voltammetry is a potentiostat, computer and electrochemical cell. The role of potentiostat is to apply a known potential and monitor the current falls. There are several different modes of voltammetry such as cyclic voltammetry (CV), square wave voltammetry (SWV), stripping voltammetry, pulse voltammetry and chronocoulometry. Each mode will classify their typical current-potential and distinguished by a different form of voltammogram. The typical electrochemical cell that commonly used in a modern electroanalytical system is known as three - electrode cells which consist of working electrode that is made of platinum, gold, and/or carbon, a reference electrode that is usually a silver-silver chloride electrode (Ag/AgCl), and a platinum wire or foil is used as a counter or auxiliary electrode. The working, reference and auxiliary electrodes are immersed in the sample solution containing a supporting electrolyte and the analyte (Naveen, Gurudatt, & Shim, 2017). The typical instrumentation setup and schematic illustration of a basic voltammetric system is shown in Figure 1.1 and Figure 1.2.

Any electrochemical cell needs electrodes to extract analytical information determine from the flowing current as a function of potential applied. An electrode is a conductor, which directly contacts an electrolyte solution. The common working





electrode is made of platinum, gold, and/or various kinds of carbon materials. Since the electron transfer rate between analyte and electrode surfaces is usually slow, electrode materials with small dimension up to nanometer level may greatly enhance the electron transfer rate. Therefore, the materials that used as a working electrode is highly influenced the selectivity and sensitivity of the voltammetric sensor which passes the current to other species without being affected by that current (Li & Miao, 2013).

Counter electrode also known as auxiliary electrode. The auxiliary electrode usually conducts the current flow during the redox reaction at working electrode. It must provide a surface area equal or larger than that of the working electrode. Most often the counter electrode is an inert conducting materials such as thin Pt wire, Au and sometimes (carbon) graphite (Braungardt, 2015).

The third electrode is reference electrode. This electrode has a fixed and wellknown electrode potential. No current should ever pass this electrode, as a current would change its potential, and possibly damage this electrode. Reference electrode is used to control the potential of the working electrode by measuring the voltage between two electrodes. Therefore, reference electrode is used to control potential of the working electrode in the electrochemical cell by measuring the voltage between two electrodes. Silver-silver chloride electrode (Ag/AgCl) reference electrode is commonly used reference electrode that commercially available in a variety of sizes and shapes (Ag/AgCl) electrode (Scholz, 2015).





Supporting electrolyte is essential in electrochemical experiments. Addition of supporting electrolyte in electrochemical cell provides less error conductivity and minimizes the significant potential loss in solution, respectively. Additionally, supporting electrolyte acts as pathway for mobility of ions and established chemical equilibrium amongst of reacting species. The usual supporting electrolyte concentration ranges from 0.1 M to 1.0 M. There are several categories of supporting electrolytes from inorganic salt, a mineral acid, or a buffer. The common supporting electrolytes use that are inert salt in electrochemical cell such as potassium chloride (KCl), sodium chloride (NaCl), potassium nitrate (KNO<sub>3</sub>) and sodium sulphate  $(Na_2SO_4)$ . While buffer systems such as acetate, phosphate or citrate and commonly use buffer is phosphate (PBS). Supporting electrolyte is required in controlledpotential experiments in order to decrease the resistance of the solution, and subsequently reduce Ohmic drop effect that probably coming from voltage which causes over-potential of electron flows to the interface of electrode and solution. If there is high Ohmic drop effect obtained from voltage consequences will creating errors in data analysis. The important of supporting electrode also can smoother the migration of electroactive species toward electrodes through electrostatic attraction thus achieve diffusion-controlled currents, maintain ionic strength and constant pH (Wang, 2006; Tsierkezos & Ritter, 2012; Tsirlina, 2017).

05-450





*Figure 1. 1.* A typical experimental set-up showing of (RE = reference electrode, WE = working electrode and the CE = counter electrode that immersed into an electrolyte solution (adapted from Brownson & Banks, 2014)





*Figure 1. 2.* The general three-electrode electrochemical cells. A: working electrode (WE), reference electrode (RE), and counter electrode (CE) in solution, set-up to a potentiostat. At the WE, species are converted from their reduced (red) to their oxidized form (ox), and vice-versa at the CE. B: Three-electrode system in a thin-layer configuration (adapted from Van Den Brink, 2016)

05-4506

### **1.2** Electrochemical detection techniques

Electrochemical detection techniques provided robust analytical techniques with advantages of instrumental simplicity, low cost, profitability. There are many electrochemical techniques encompassed of cyclic voltammetry (CV), square wave voltammetry (SWV), electrochemical impedance spectroscopy (EIS) and chronocoulometry are used in the determine redox species (analytes). The chosen electrochemical technique will be used in the subsequent subsections as this technique could be used as promising effective technique that can obtain the best electrochemical response in an analysis data.

### 1.2.1 Cyclic Voltammetry

Wang (2000) described an essential use of CV is to study electrode reactions or mechanism in the medium of electrode-electrolyte system with the presence or absence of modifier. Besides that, CV also can be used to study the adsorption processes, quantitative applications, stability of reaction products, determining the presence of intermediates in redox reactions, reaction kinetics, reversibility of a reaction and electron transfer kinetics. These reactions also can be demonstrated in the form of anodic where oxidation occur and cathodic where the reduction occur and displayed as "duck"- shaped voltammograms. The potential waveform input to the electrochemical cell in the form of cyclic as show in the Figure 1.3 (Rusling & Suib, 1994; Kissinger & Heineman, 1983).





The fact that CV is powerful and popular member of voltammetry technique in electrochemistry, CV is obtained by measuring the current at the working electrode during the potential scan. Current can be considered as the response signal to the potential excitation signal. CV is distributed as current (*i*) at the vertical axis *versus* potential (*E*) at the horizontal axis. The important parameters in CV are anodic and cathodic peak potentials ( $E_{pa}$  and  $E_{pc}$ ), anodic and cathodic peak currents ( $i_{pa}$  and  $i_{pc}$ ) and half-peak potential ( $E_{1/2}$ ) at which half of peak current is observed (Brownson & Banks, 2014).

The main application of cyclic voltammetry is in the preliminary electrochemical characterization of a system. Therefore, cyclic voltammetry is often chosen in studying a particular system for the first time. Its main advantage is cyclic voltammogram will provides instant information on the reversibility of a system. In cyclic voltammetry, mass transport of the reducible or oxidizable electroactive species occurs only by diffusion. Therefore, to avoid migration currents and ensure conductivity, supporting electrolyte is added to the solution (Heinze, 1984).

The shape of the CV voltammogram indicated that system criteria of CV, for example if an electrode reactions are reversible, quasi-reversible, and irreversible. For reversible voltammogram (Figure 1.4, curve a), reversible system can be indicated via fast electron transfer. Peak-to-peak separation ( $\Delta E_p$ ) should be very close to the theoretical value of Nernstian electrode process which is 59 mV per one electron (*n*) at 25°C, where *n* is equal to the number of proton and electron transferred. Varying the scan rate has no effect on the peak potential for reversible system, but does cause a change in the peak current. Randles and Sevcik developed the following equation to





10 ptbups

relate peak current to scan rate for a reduction process at 25°C (Rusling & Suib, 1994);

$$i_p = 2.69 \text{ x } 10^5 \text{ n}^{3/2} \text{A } \text{D}^{1/2} \text{C}_o v^{1/2}$$
 (1.1)

where;  $i_p$  = Peak current (in Ampere)

- n = Number of electron transferred
- A = Electrode area (in  $cm^2$ )
- D = Diffusion coefficient (in  $\text{cm}^2 \text{ s}^{-1}$ )
- v =Scan rate (in V s<sup>-1</sup>)
- $C_o$  = Concentration of analyte (in moles cm<sup>-3</sup>)

As the rate of electron transfer lowers, the electrochemistry is said to be quasireversible. For a quasi-reversible system, the peak to peak separation is larger than reversible system and it will increases by increasing the scan rate. Otherwise if slower kinetic occur, it might also effects slow rate of change in concentration at the electrode surface and this occurrence to a somewhat broader peak in the cyclic voltammogram can be seen.

The absence of a reverse peak suggests the system irreversible. In irreversible system, peaks are reduced in size and widely separated. Only one peak current observed since reverse reaction is not significant. In completely irreversible systems, the peaks are characterized by a shift in the peak potential with the scan rate. This may due to a purely irreversible mechanism, or as a result of the product undergoing a







further chemical reaction. When electron transfer at the electrode surface is slow compared to mass transport, the process the called as an electrochemically irreversible (Elgrishi et al., 2018).



*Figure 1. 3.* Typical cyclic voltammogram produce by application of the potential waveform (adapted from Compton, Eduardo, and Ward, 2013).









### 1.2.2 Chronocoulometry

In chronocoulometry system, usually an interesting action takes place at the interface between the conducting (usually solid) electrode and an electrolyte solution (usually liquid). This condition is where ionic current is converted into electronic current by an electrode reaction. The electrode-electrolyte interface in any electrochemical cell often exhibits chemical properties that differ substantially from those observed in the bulk of the electrode and in the electrolyte solution far from the interface. In one predominantly interesting property of many electrode electrolyte interfaces is their tendency to attract and retain reactants. The phenomenon is often described as the "adsorption" of the reactants at surface of electrode (Anson & Osteryoung, 1983).

As describe by Srivastav and Kant (2015), chronocoulometry is used to measure charge (Coulombs) as a function of time. Chronocoulometry can be used to determine the real electrochemical active at electrode area, as well as diffusion coefficient, adsorption of electroactive species and rate constants for chemical reactions coupled to electron transfer reactions (Bard & Faulkner, 2000). The effort to measure the quantity of the reactant that is absorbed at the electrode-electrolyte interface is greatly evaluated. Hence, chronocoulometry is right method in electrochemistry that readily determines the real electrochemical active electrode area, as well as their respective diffusion coefficients, and adsorption capacity of electroactive species.

Anson equation a stated in Equation 1.2 was mentioned by Anson in chronocoulometry is used to determine quantities of adsorbed reactants as well as to







14

determine real effective surface area of the electrode. The charged measured during this step is plotted in a charge *versus* square root of time graph (Q *vs.*  $t^{1/2}$ ), this plot is often referred as the Anson plot ad-hoc, from the slope of the linear plot of obtained Q *vs.*  $t^{1/2}$ , the diffusion coefficient can be determined.

$$Q(t) = \frac{2nFAcD^{1/2}t^{1/2}}{\pi^{1/2}} + Q_{dl} + Q_{ads}$$
(1.2)

where;	Q(t)	= Charge (Coulombs)
	n	= Number of electron transfer
	F	= Faraday constant (96, 485 Coulombs/mole)
🔾 05-4506832 🔮 pus	A staka.upsi.	= Effective electrochemical surface area of the working electrode (cm <sup>2</sup> )
	c	= Concentration of substrate (mole/cm <sup>3</sup> )
	D	= Standard diffusion coefficient of $K_3[Fe(CN)_6]$ is 7.6 x10 <sup>-6</sup> cm <sup>2</sup> s <sup>-1</sup> at 25°C (act as model complex)
	t	= Time (second)
	$Q_{dl}$	= Double layer charge (Coulombs)
	Q <sub>ads</sub>	= Faradaic charge (Coulombs)

05-450

### **1.2.3** Electrochemical impedance spectroscopy (EIS)

An important role of the electrochemical impedance spectroscopy (EIS) is the characterization of electrical charge at the electrode/electrolyte interfaces. Complex electrical resistance encountered when current flow through the circuit was analyzed by EIS. EIS is powerful technique that is sensitive to surface phenomena and changes of bulk properties. EIS is a concept branch of ac theory whereby described the response of circuit to an alternating current or voltage as a function of frequency. Current flowing in an electrical equivalent circuit represents as electrified interface that include generates both faradaic and non-faradaic components. More than one semicircle could be observed in Nyquist plot when the interface is complex due to the adsorption or chemical reactions (Lisdat & Schäfer, 2008; Bansod, Kumar, Thakur, Rana, & Singh, 2017; Park & Yoo, 2003). In Turnet Barron Media Lett Sheh

An electrochemical reaction that takes place in an electrolytic cell is called as an electrical equivalent circuit (EEC). The simplest and the most common used EEC cell model in EIS known as Randles circuit as shown in Figure 1.5. Randles who was the first candidate that introduced EEC in EIS to prescribed the responses in the EIS system. Using Randles circuit as a model could be used to describe electrochemical reaction that take place at the electrode/electrolyte interface. Randles circuit includes a solution resistance ( $R_s$  or  $R_{\Omega}$ ), a double layer capacitor ( $C_{dl}$ ), a charge transfer resistance ( $R_{ct}$ ) and Warburg impedance (Lu et al., 2015) that connected in series with a resistor to measures the resistance of the electrolyte solution. According to the Randles, there are three conditions operate in controlling the speed of the electrode reaction where it is be affected by the rate of the electrode itself, the rate of diffusion

05-45068





of the reactant and product and the ohmic resistance of the electrolyte (Randles, 1947).

A complicated and wonderful shape of Nyquist plots of impedance spectra (Z) in EIS have been predicted and found for multistep mechanisms. The spectra of Nyquist plot is displayed as imaginary part  $Z_I$  (vertical axis) *versus* real part  $Z_R$  (horizontal axis). Warburg was the first researcher who is idealized an extension of the concept impedance to electrochemical systems and interpreted the ionic species diffusion from and to an electrode-electrolyte interface as a charge transport process and represented this process as electrical diffusional impedance. Thus, Nyquist plot gives all the necessary information about the electrode-electrolyte interface and the reaction. (Harrington, 2015; Lisdat & Schäfer, 2008; Warburg, 1899)

The magnitudes of the fitted Randles circuit elements may be used to calculate an electron-transfer rate constant by noting the relationship between circuit elements and the parameters characterizing the redox-active electrode-electrolyte. The apparent electron transfer rate constant is a measure of the electron transfer kinetics across interface. The apparent electron transfer rate constant ( $k_{app}$ ) of the electrode can be determined from Equation 1.3 (Nkosi, Pillay, Ozoemena, Nouneh, & Oyama, 2010);

$$k_{app} = RT/n^2 F^2 A R_{ct} C$$
(1.3)

where;

n = Number of electrons transferred (1 mol) F = Faraday constant (96, 485 C mol<sup>-1</sup>)

- R = Ideal gas constant (8.314 J mol<sup>-1</sup>K<sup>-1</sup>)
- T = Kelvin temperature (298 K)
- A = Experimentally-determined area of the electrode  $(0.0314 \text{ cm}^2)$
- $R_{ct}$ = value is obtained from the fitted Nyquist plots
- $C = Concentration of the [Fe(CN)_6]^{3-}$  (in mol cm<sup>3,</sup> the concentration of

 $[Fe(CN)_6]^{3-}$  and  $[Fe(CN)_6]^{4-}$  are equal) (4.0 x 10<sup>-6</sup> mol cm<sup>-6</sup>)



*Figure 1. 5.* EIS Nyquist plot (Zimag against Zreal) and Randles circuit (W is a socalled Warburg element, which accounts for diffusion processes (adapted from Estrela, Hammond, Carrara, Tkac, and Formisano, 2016)

### 1.2.4 Square wave voltammetry (SWV)

Cyclic voltammetry used as insight into the electrode mechanism and impedance techniques is used to know the kinetic information of very fast electrode processes. Amongst these techniques, advanced voltammetric techniques unified the advantages of pulse techniques that probably can enhance sensitivity. Pulse technique originate from Kalousek commutator (Kalousek, 1946; Radej, Ruzic, Konrad & Branica, 1973) and Barker (Barker, Gardner, 1973; Barker & Jenkins, 1952) was reported as long ago in 1957, however back then the utility of the technique limited by the electronic technology. After that, recent advances in both analog and digital electronic have made it possible to incorporate SWV by using advances potentiostat type analyzer (Princeton, 1957; Mirceski et al., 2013).

Pulse techniques are the most technique applied for analytical applications. There are several pulse techniques that have to be some of the most useful in electroanalytical methods encompassed of the differential voltammetry (DPV), normal pulse voltammetry (NPV) and square wave voltammetry (SWV). In many cases, SWV is the most popular pulse technique and widely considered for mechanistic and kinetic studies as complementary to cyclic voltammetry and can be available alternative to more frequently used spectrometric or separation methods in multianalytes. Plus, up until now SWV technique has been used for routine quantitative analyses (Chen & Shah, 2013; Laborda, González, & Molina, 2014; Dogan Topal, Ozkan, & Uslu, 2010).





The advantages of SWV can be found at response of high scan rate, thus reducing scan time. SWV can be used to perform an experiment much faster than NPV and DPV, which typically run at scan rate of 1 to 10 millivolt per second (mV/s). Typical SWV only take 1 to 5 second for a complete cycle and can reach 1 volt per second (V/s). Furthermore, the currents different is larger than either forward or reverse currents, so the height of the peak is usually quite easy to read, thus increasing the accuracy. Additionally, the sensitivity increases from the fact that the net current is larger than either the forward or reverse components. Therefore, simplex optimization to maximize peak current by varying the waveform parameters has been examined thoroughly (Dogan-Topal et al., 2010).

In this context, the number of waveforms employed is considering by three basic groups to describe the simple SWV technique introduced by Kalousek, Barker and Osteryoung formats. Kalousek format had a lower frequency method, which measures the current only on the reverse half cycle of the square wave (SW). Barker format is the simplest to visualize where the waveform is a direct analog to sinusoidal ac voltammetry with a symmetric SW of frequency and amplitude riding on either a ramp or slow staircase waveform.

Amongst three formats, Osteryoung format is the most commonly used as the waveform differs from other SW response that the base potential increases by amplitude for each full cycle. The response also consists of discrete current-potential separated by the potential increment noted as  $\Delta E_p$  or known as peak-to-peak potential separation.  $\Delta E_p$  could be used to determine the apparent rate, which is a number of current-potential points within a certain potential range. The currents increase





proportionally to the scan rate. The response frequently is distorted by electronic noise and a smoothing procedure is necessary for its correct interpretation (Dogan-Topal et al., 2010; O'Dea, Osteryoung, & Osteryoung, 1981; Osteryoung, & Osteryoung, 1985).



😭 pustaka.upsi.edi



Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBa

) ptbups







05-4508



#### **1.3** Carbon Paste Electrode (CPE)

Great electrode is the electrode that has been widely applicable in the electrochemical studies and electroanalysis because of their advantages such as simple preparation method, inexpensive, chemical inertness, easy to handle, and biocompatibility. The electrode can be easily prepared at the laboratory. The most popular electrode materials are the mixture of carbon powder and a liquid nano-electroactive binder that is simply called carbon paste. The carbon paste electrode was invented by Ralph Norman Adams from the University of Kansas at the end of the 1950s. It has been long time since Ralph Norman Adams published a short one-page report in 1958. The idea of carbon paste built is closely connected by dropping mercury electrode (DME) technique introduce by Jaroslav Heyrovsky in 1922 (Adams, 1958; Heyrovský, 1924; Švancara, Vytřas, Kalcher, Walcarius, & Wang, 2009; Ghoreishi, Behpour, Ghoreishi, & Mousavi, 2017).

Lindquist (1973) reported that carbon paste electrodes have low background currents compared to other electrodes such as solid graphite or noble metal electrodes while Olson and Adams (1960) stated that most carbon paste electrode can achieve background currents of about 200 nano-ampere or else lower than that depend on the adsorbed electroactive species or analytes. Apart of that, carbon paste electrode also be recommended and become considerable attention because of it can exhibit wide electrochemical potential window. Apparently, typical potential range of common carbon paste electrode depends naturally on the type of medium or supporting electrolyte used. The potential range can be at both positive and negative potentials which the measurements can be performed in the acidic electrolyte range varies -1.0





V to +1.5 V vs Ag/AgCl, neutral electrolyte between -1.3 V and +1.4 V and alkaline electrolyte between -1.2 V and +1.2 V (Olson, C., Adams, 1963).

The binder or pasting liquid played as the second main important role of carbon paste which influences the properties of the carbon paste electrode. The commonly use binding agents for preparation of carbon pastes are paraffin oil, silicon oil, mineral oil such as nujol or uvasol, ceresin wax, bromoform or bromonapthalene. The practical use of the binder is due to its insolubility in the aqueous solution under measurement, chemical inertness, mechanically stable, electro-inactivity and long lifetime. Generally, the presence of binder at the surface will decrease the transfer rates, at the same time can lower the kinetics and causing a higher over-potential compared to homogenous electrodes. Even so, the binder showing as successful class that has attractive properties of high ion-pairing ability and suffer from atypical signal-to-noise characteristics (Kalcher, 1990; Kalcher et al., 1995; Vytras, Švancara, & Metelka, 2009).

There are several types of carbon material that have been widely used for the preparation of solid electrode include glassy carbon, carbon black, carbon fiber, several form of graphite powder to the highly oriented pyrolytic graphite and carbon nanotube. Amongst of them, carbon paste electrode is the most frequent types of working electrode due to the ease of their construction. Carbon nanotube pastes are soft and non-compact, and need to be kept in a holder. Common types of the holders are short Teflon tube, glass tube, and polyethylene syringe which then must electrically contacted via a conducting wire. The refilling the carbon paste into the holder must be with or without reservoir (Vytras et al., 2009).





Carbon paste electrode can be classified into two forms; unmodified carbon paste electrode which is simply called bare electrode and modified carbon paste electrode. The intention of modification carbon paste electrode is to counter the problems of poor sensitivity and selectivity faced at bare electrode. In some case, analysis is not possible with unmodified electrode. Since the unmodified electrode often suffers from the fouling effect and signal-to-noise sometimes insufficient to determine the trace level of analyte. The comparison between modified and unmodified carbon paste electrode can be differentiate based on it fabrication. Typically unmodified carbon paste electrode is a combination of carbon powder and a binder; meanwhile modified carbon paste electrode is fabricated by adding one or more electroactive material know as modifier into the bare electrode (Sajid et al., 2016; Mobin, Sanghavi, Srivastava, Mathur, & Lahiri, 2010).

The effects incorporation of modifier into bare electrode can lowering redox potential required for the electrochemical, provided ability to promote electrontransfer process, thus the modified carbon paste electrode can be used to lower of magnitude of detection limit as compared to the bare carbon paste electrode. Besides, modified electrode can enhance the sensitivity and selectivity of the detection method so that it can exhibit electrocatalytic toward analyte (Jing et al., 2015; Beitollahi, Karimi Maleh, & Khabazzadeh, 2008).



### 1.4 Multi-walled Carbon Nanotubes

Iijima group from Japan who was the first discover carbon nanotube in late 1991 and the discovery of carbon nanotube (CNT) have been the target to numerous investigations due to its unique properties (Iijima, 1991). CNT can be defined as cylinders composed of rolled-up graphite planes with diameters in nanometer scale. CNTs are highly isotropic, and it is this topology that figure out nanotubes from other carbon structures and gives them their unique properties. CNT become ideal candidate of nanofiller in preparation of various electrochemical sensors. CNT attract particular interest due to its unique morphology, nano-sized scale, novel physico-chemical properties, high surface-to-volume ratio, enhanced magnetic and electrical properties and flexible applications (Ribeiro, Botelho, Costa, & Bandeira, 2017; Yunqiao Gao,

Wang, Yang, Sun, & Zhao, 2014). Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah

Generally, there are three categories of CNT have been reported in the literature which are single-walled carbon nanotube (SWCNT), double-walled carbon nanotube (DWCNT), and multi-walled carbon nanotube (MWCNT). SWCNT is made of single graphite tubules rolled up into seamless cylinder with diameter of 1 to 2 nm diameters and several micrometers in length. DWCNT consist of only two tubes having similar sizes to SWCNT. Meanwhile, MWCNT consist of several coaxial cylinders, each are concentric and closed graphite tubules with multiple layers. The hole typically from 2 to 25 nm separated between tubes to the interlayer spacing in graphite approximately 0.34 nm. The outer diameter of MWCNTs ranges from 2 to 100 nm and inner diameter is in the range of 1 to 3 nm. The length is one of several micrometers. Figure 1.6 showed the visualized of SWCNT, DWCNT and MWCNT

05-45068





(Rivas et al., 2007; Qureshi, Kang, Davidson, & Gurbuz, 2009, Pandey & Dahiya, 2016).



*Figure 1. 6.* Example of carbon nanotube shape of single-walled carbon nanotube (SWCNT), double-walled carbon nanotube (DWCNT) and multi-walled carbon nanotube (MWCNT) (adapted from Nakashima & Shiraki, 2016)

Amongst of three categories of CNTs, multiwalled carbon nanotubes (MWCNTs) have captivating much attention due to extraordinary mechanical, electrical, chemical, thermal and structural properties. To date, their unique properties on having large surface area and provide high electrical conductivity are considered promising materials in the fabrication electrode since their application as conducting beneficial in field electron emitting devices would improves performance of sensors. Additionally, the wider surface of MWCNT also provide a more efficient internal encapsulation and external functionalization with active molecules since the decoration of MWCNT suitable for depositing nanoparticles on the MWCNT's walls or ends, bonded by physical interaction which then provide wide potential







applications in catalysis, biosensors, biomedical, magnetic data storage and electronic devices (Tsierkezos et al., 2016; Pandey & Dahiya, 2016).

MWCNT are considered promising material for future nano-electronics and field-emission displays since their application as conducting or electron emitting devices improves their performances and simultaneously reduces significant their size. In addition, the electronic properties of MWCNTs are strongly connected to their delocalized electron system, and thus, the chemical modification of MWCNT influences their electronic properties. Consequently, with the proper choice of type of modification, the electronic properties of MWCNTs can be purposely adjusted. There are numerous attempts have been made for the modification via MWCNT with other modifiers, thus the various modifications will be explained thoroughly in the next for protected under the modification.





05-4506

ptbup 27

#### 1.5 Layered double hydroxide

Layered double hydroxides (LDHs) are family member of anionic clays consisting of positively charged brucite-like layers separated by charge balancing anions between the layers among which are located anions and water molecules. One of the most important properties of LDH is LDH provide anionic exchange capacity where the anion and water molecules intercalated into LDH interlayers can be replaced with other organic anions and polar molecules. LDHs is also known as ionic clays possess general formula that represents this class of material are  $[M^{2+}_{1-x}M^{3+} x(OH)_2]^{x+} A^{m-}_{x/m}.nH_2O$ , where  $M^{2+}$  is a divalent cation (Ca<sup>2+,</sup> Mg<sup>2+,</sup> Zn<sup>2+</sup>, Co<sup>2+,</sup> Ni<sup>2+</sup>, Cu<sup>2+,</sup> Mn<sup>2+</sup>),  $M^{3+}$  is a trivalent cation (Al<sup>3+</sup>, Cr<sup>3+</sup>, Fe<sup>3+</sup>, Co<sup>3+</sup>, Ni<sup>3+</sup>, Mn<sup>3+</sup>), A<sup>m-</sup> is an interlayer anion (Cl<sup>-</sup>, NO<sup>3-</sup>, ClO<sup>4-</sup>, CO<sup>3-</sup>, SO4<sup>-2-</sup> and many other inorganic anions).The x value is equivalent to the charge density is equal to the molar ratio,  $M^{3+}/(M^{2+}+M^{3+})$ . Figure 1.7 showed the schematic structure of layered double hydroxide (Hussein, Hashim, Yahaya, & Zainal, 2010; Huanshun Yin et al., 2011).



Figure 1. 7. Schematic structure of layered double hydroxide

05-450



28

Unique layered structure, intercalation, catalyst and anion-exchange capability of LDH is worthy of great intention and showed promising fabricating organicinorganic nanocomposite materials for intercalation processes. The stability of LDH structure comes from electrostatic interaction and hydrogen bonding between the layer and interlayer contents. Thus, several of anions have been used for the intercalation process to enhance the performance of LDH in the various fields of applications. Amongst beneficial organic anions such as drugs, pesticides, plant growth regulators and fertilizers (Mamat, Kusrini, Yahaya, Hussein, & Zainal, 2013). LDH have been applied in diverse applications such as pesticides (Bruna et al., 2009), drug release and delivery system (Kong et al., 2010; Bi, Zhang, & Dou, 2014), controlled released formulation (Silion, Hritcu, Lisa, & Popa, 2012), and sensors (Illyas M. Isa et al., 2013).

Large number of studies has shown that LDHs are attractive materials for fabrication of sensors. The requirements of LDH as a modifier in the electrodes are required for monitoring process in various analytes. LDHs can improve sensitivity and selectivity of detection as they allow immobilizing electrocatalytic reagents toward the detection of certain target analytes. Therefore, numerous organic-inorganic hybrid and bio-hybrid LDH materials have also raised the attention of the community of electrochemical sensors for the development of new applications of LDH-based modified electrodes. Next sections will reviewed the articles from previous applications of LDH-modified electrochemical sensor for various analytes monitoring (Mousty & Prévot, 2013; Baig & Sajid, 2017). 05-4506

### 1.6 Introduction to Bisphenol A and Uric Acid

Bisphenol A (BPA) with chemical name 2, 2-(4, 4-dihydroxydiphenyl) propane is an organic compound consisting of two phenolic rings connected by a single carbon carrying two methyl groups as shown in Figure 1.8. BPA is not found naturally in the environment, therefore it is man-made molecule. The first invertor of BPA is by the Russian chemist Alexander Dianin in 1981. BPA was created by the reaction of phenol with acetone following a 2 to 1 ratio in the presence of an acid catalyst leaving water as the sole by-product. The usefulness of BPA is use in high production volume chemical in the production of polycarbonate and epoxy resins and as an additive in polyvinyl chloride became evident by the middle of the 20<sup>th</sup> century. However, late 1938, chemists from London led by Dodds and Lawson, who detected an estrogenic activity from BPA when they were tested on rats at a dose of 100 mg. Therefore, there is first report of accidental free BPA came in 1993 about BPA leaching from polycarbonate plastics and arise a major concern in BPA exposure and safety (Dodds & Lawson, 1938; Krishnan, Permuth, Stathis, Feldman, and Tokes, 1993; Allard, 2014).



Figure 1. 8. The structure of bisphenol A



BPA is used primarily in an industrial chemical reagent, the plastic monomer and plasticizer is one of the highest yield chemical produced worldwide. BPA mainly used in the production of polycarbonate plastics, polyester resins, epoxy resins, thermo plastics and other special plastics. BPA-based products include home appliances, water bottles, infant bottles, food storage containers, beverage cans, sport equipment, kitchen utensils, electronic devices and dentistry appliances such as dental fillings and sealant. Exposure to BPA can occur from many different sources, but most common way is through packaged foods, beverages or feeding bottles. Owing to the generous use of BPA-based products in daily living, BPA leaching is promoted by acidity from the food stored, elevated temperature, vigorous mechanical cleaning and use of detergents for the cleaning packaging (Ragavan, Rastogi, & Thakur, 2013; Poorahong et al., 2012; Johnson, Saxena, & Sahu, 2015).

In the body, hormones act by an endocrine mechanism so that they are secreted by cells of an endocrine gland and carried by the blood to the target cells in the distant organ. At the target sites, the bioavailable hormones binds to cellular receptors, then relay the signal to the cell to enable the response. Unfortunately, endocrine disruptors can disturb any of these processes. Therefore, BPA is considered to be a typical endocrine disrupter that capable interfering with the human endocrine system. Over exposure to BPA had led to the closely related with various adverse health effects include of lowering the immune function, altering the development of the male and female reproductive tract, increasing the incidence of various cancers for instance testicular, prostate and breast cancer even at very low concentration and causing birth defects, infertility (Salian, Doshi, & Vanage, 2011; Zhan, Song, Tan, & Hou, 2017; Darbre, 2015; Huang, Liu, Li, Zhang, & Yao, 2015).



Consequently, the BPA have been banned in several industrialized countries like France, Canada, Belgium, Denmark, Sweden and others countries including Malaysia. In 2008, Canada was the first country that banned the import, sale and advertising of plastic feeding bottle containing BPA and officially classifies BPA as toxic substance. In Malaysia on 15 March 2011, Minister of Health had announced a ban on polycarbonate bottles containing BPA due to BPA's risk to infant hormone systems. In order to avoid the potential toxic effects of BPA, United States Environmental Protection Agency (EPA) has set maximum allowable level of BPA as 0.05 mg kg<sup>-1</sup> body weight per day, while European Union (EU) regulations allow lower limit of BPA residues to be positive at 3 mg kg<sup>-1</sup>. The dissolved BPA from food contact materials in EU should follow Regulation 10/2011/EU (Shi, Liang, Zhao, Liu, & Tian, 2017a; Johnson et al., 2015; Cao, Corriveau, & Popovic, 2009; Bernama, 2012; Jiang, Ding, Luan, Ma, & Guo, 2013).

Uric acid (UA) or also called (2,6,8-trihydroxypurine) is the organic heterocyclic compound represented by the formula  $C_5H_4N_4O_3$  as shown in Figure 1.9 with molecular weight of 168 Dalton. The occurrence of UA in human urine is somewhat of an abnormality. UA first discovered by the Swedish chemist Carl Wilhelm in 1742 to 1786. The first method developed for uric acid analysis was introduced by Offer in 1894. This method is based on the chemical oxidation of uric acid ( $C_5H_4N_4O_3$ ) to allantoin ( $C_4H_6N_4O_3$ ), which reduces phosphotungstic acid to a tungsten blue chromophoric compound. However, this method suffers from several problems especially the problem of interferences due to other species capable of producing the same reaction (Galbán, Andreu, Almenara, De Marcos, & Castillo, 2001). In 1941, Bulger and Johns introduced a method for the determination of uric







acid based on the use of uricase enzyme. This method is the determination of the reduction, by protein-free filtrates of an alkaline ferricyanide solution, before and after the destruction of uric acid by uricase. The process of spontaneous precipitation of UA in normal urine will be explained in the next paragraph (Bulger & Johns, 1941; Ghoreishi, Behpour, Ghoreishi, & Mousavi, 2017; Erden & Kiliç, 2013; Maiuolo, Oppedisano, Gratteri, Muscoli, & Mollace, 2016).



O 05-4506832 O pustaka upstack *Figure 1. 9.* The structure of uric acid

UA is known by the primary product of purine metabolism in the human body and a major nitrogenous compound in the urine. The lack of uricase makes UA the end product of purine metabolism. The enzyme uricase or urate oxidase further oxidizes uric acid to allantoin. However, human cannot oxidize uric acid to more soluble compound allantoin due to lack of uricase enzyme. Normally, UA undergoes further metabolism in human and is secreted by kidneys and intestinal tract. UA majorly exists in urine in a state combination with bases as urates. It is transit through urinary channels and encounters a diversity of physical and chemical conditions, which are calculated to affect the stability of the urates.





ptbuj 33

UA can be seen as pale, watery and poor in salts and at other times it is concentrated, rich in salts, and high-colored. These variations may occur in quick succession as it is accumulates in the bladder with mixture of urines of all these several character. Normally, UA is dissolved in blood and passed through the kidney into urine, where it is eliminated. If there is an increase of UA or if the kidney does not eliminate enough UA from the body, levels of it build up in the blood. As urate concentration increases in blood, UA crystal formation increases. In human blood, the normal reference interval of UA is around 1.5 to 6.0 mg/dL in women and 2.5 to 7.0 mg/dL in men. In water, the solubility of UA is low, while in human, the average concentration of UA in blood is close to the solubility limit (6.8 mg/dL). As the level of UA is higher than 6.8 mg/dL, crystal of UA form as monosodium urate (MSU) (Roberts, 1890; Maiuolo et al., 2016).

Extreme abnormalities of UA in biological fluids is a marker of several disorders such as gout, hyperuricemia, Lesh-Nyhan syndrome, metabolic syndrome, kidney stones, cardiovascular disease, and renal disease while lower serum value of UA have been associated with multiple sclerosis, Parkinson's disease, Alzheimer's disease, and optic neuritis. Recent studies however have provided evidence that UA may actually play a role in the development or progression of such diseases. Monitoring the concentration of UA in biological fluids can be used as an early warning sign of this disease. As a result, it is clinically important to monitor the concentration of UA in biological fluids for the early stage warning of these conditions and for the diagnosis of patients. To that end, a simple, reliable and inexpensive detecting system, especially in the form of point of care testing, is highly desirable to use for the determination concentration of UA (Compans & Cooper,







2008; Merriman, Choi, & Dalbeth, 2014; Lakshmi, Whitcombe, Davis, Sharma, & Prasad, 2011; Ghoreishi et al., 2017; Jin et al., 2012).



pustaka.upsi.ec



Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBa

ptbups







05-450



#### **1.7 Problem statement**

BPA is the most commonly used in the production of polycarbonate and epoxy resin in the chemical industrial worldwide. Exposures to BPA become adverse effect in natural environment and bring major concern as it induces negative health effects to human. Manufacturing of BPA products is one of the cause how BPA being inadvertently released into the environment and flow through effluent to contaminate the rivers and ground water. On the contrary, BPA has been found leached out into environment from bottles, packaging and plastic plants, landfill leachates when expose under certain condition like over high temperature (heating) or cleansed with rough detergent or those contain acidic. Consequently, BPA migrate into food and drinking water from a wide variety of food contact materials as when human swelled the food or drink water that containing BPA, BPA will accumulate in the human body system and thus routinely ingest trace amount of BPA (Shi, Liang, Zhao, Liu, & Tian, 2017b; Li et al., 2016).

Yet, there are large number of recent *in vitro* studies have been reported on the exposure to BPA are mediated by both genomic and non-genomic estrogen-response mechanisms. Studies have showed that exposure to high level BPA can result in harmful effects on human due to estrogen-like functionality. Even at low doses of 1 pM (0.23 ng <sup>-1</sup>) BPA may disrupt the cell functioning that linked to the sexual dysfunction, lowered sperm quality, cardiovascular diseases, endometrial hyperplasia, recurrent miscarriages, neurotoxicity problem, polycystic ovarian syndrome, abnormal development and various cancers including testicular, prostate and breast



cancer. Therefore, BPA has been declared as a toxic substance (Deng, Xu, & Feng, 2013; Saal & Hughes, 2005; Zhan, Song, Li, & Hou, 2016; Zhan et al., 2016).

Up until now BPA is banned for the use in many countries including Malaysia. Canada was the first country that declared BPA as a toxic substance and banned the use of BPA in baby bottles. Then followed by EU, China and Malaysia announced the ban on the use of chemical substances containing in baby bottles. Based on the reported on year 2009 to 2010 from National Health and Nutrition Examination Survey (NHANES), United State found that almost 90% of the individuals aged 6 years and older had detectable higher BPA in their urine compared to adolescents or adults. Specific migration limit (SMT) has been set by EC Directive in food or food stimulant at 3 mg kg<sup>-1</sup> and 0.6 mg kg<sup>-1</sup>. Even U.S EPA and the European Food Safety Authority have set the daily limit intake of BPA. The tolerable daily intake (TDI) for BPA was set at 50  $\mu$ g kg<sup>-1</sup> of body weight per day while Health Canada set the provisional tolerable daily intake (pTDI) for BPA at 25  $\mu$ g kg<sup>-1</sup> of body weight per day (Soto & Sonnenschein, 2010; Cao et al., 2008; Jing et al., 2015; CDC, 2014).

UA is an end product of purine metabolism, and considered as a species of great importance in human diagnosis. UA is important for the detection of abnormal level of UA in the human body. Extreme abnormalities of UA level may accumulate in human body, and excessive amount in body fluid may form solid state urate and lead to gout or kidney stones, hyperuricemia as an independent risk factor for the development of cardiovascular and renal disease and Lesh-Nyhan syndrome. Meanwhile, lower UA concentration had been linked to multiple sclerosis, Parkinson's disease, Alzheimer's disease and optic neuritis. Gout occurs when sodium







urate crystals are deposited in the joints, soft tissue, bursae and tendons (Lakshmi et al., 2011; Erden & Kiliç, 2013; damanisha & Guo, 2008; Alderman & Aiyer, 2004; Nyhan, 1997).

UA exists majorly as urate, the salt of UA. As the urate concentration increase in blood, UA crystal formation increases. The normal reference interval of UA in human blood is 1.5 mg/ dL to 6.0 mg/dL in women and 2.5 to 7.0 mg/dL in men. The solubility of UA in water is low, and in humans, the average concentrations of UA in blood close to the solubility limit of 6.8 mg/dL. In case, the level of UA is higher than 6.8 mg/dL, crystals of UA form as monosodium urate (MSU). Main product of the electrochemical oxidation is 4, 5-dihydroxyluric acid, which is unstable and mostly decomposes into allantoin (Chao, Ma, & Li, 2012). However, human cannot oxidize UA to the more soluble compound allantoin due to the lack of uricase enzyme. Most daily UA disposal occurs via kidney. Therefore, it is important monitoring the concentration of UA in biological fluids so that it can be used as an early warning of the presence of the UA in urine (Jin et al., 2012; Maxwell et al., 1997; Beitollahi, Hamzavi, Torkzadeh-Mahani, Shanesaz, & Maleh, 2015).

Up to now, many analytical methods include traditional analytical method and modern analytical method for BPA and UA measurements have been built. Modern analytical methods which include high performance liquid chromatography (HPLC), liquid chromatography–tandem mass spectrometry (LC–MS), enzyme-linked immunoassay (ELISA), gas chromatography coupled with mass spectrometry (GC-MS). Meanwhile traditional analytical method is electrochemical analysis. All above analytical methods, desirable to have simple and direct method for measurement the







concentration of BPA and UA is electrochemical method. This choice is because electrochemical method known as low cost, high sensitivity and selectivity, good precision, simple apparatus use making them suitable for rapid monitoring compare to modern analytical methods (Halle, Claparols, Garrigues, Franceschi, & Perez, 2015; Cunha, Pena, & Fernandes, 2015; Maiolini et al., 2014; Manjunatha, Deraman, Basri, & Talib, 2018; Pan, Gu, Lan, Sun, & Gao, 2015).









### 1.8 Significant study

This study is in the field of electrochemical method bring special interest for *in vivo* practical application because it is simple, quick, inexpensive and require no additional apparatus and not much attention is needed in design and development of the electrode. Since the electrode can be used for universal monitoring of the various diseases, toxic substances, and environmental component in short period of time. Therefore, it is desirable to apply such advancement of electrode in solved the real problem (Jadon, Jain, & Sharma, 2016; Chitravathi & Munichandraiah, 2015).

Modification of electrode offer remarkable advantages to electrochemical sensor as it resolve slow kinetic of many plain or bare electrodes. Conscious choice of electrode modifier added advantages for routine analysis as it generate desirable performance of the electrochemical sensor in the analytes. Contribution of CNT in electrochemical sensor promotes electron-transfer reactions for the analytes, making them as perfect candidate for detection platform for electroactive species. Yet, addition of LDH show better performance in electro-catalysis and provide compact detection in analytes by overcoming the poor response in analytes. LDH obviously can be attractive material for the modified electrode in electrochemical analysis (Amiri, Raoof, & Ojani, 2016; Arvand, Ansari, & Heydari, 2011; Song et al., 2017; Zhan et al., 2016).







### **1.9** Objectives of the study

The objectives of this study are as follow:

- To determine the electrochemical characterization of the modified MWCNT paste electrode by using cyclic voltammetry and electrochemical impedance spectroscopy (EIS) techniques.
- To optimize the performances at optimize experimental variables by using SWV response of UA and BPA at the modified MWCNTs paste electrodes.
- To validate modified MWCNTs paste electrodes in the determination of UA and BPA in various real samples analysis



purtaka upai odu m

Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah









