

**DEVELOPMENT OF A PORTABLE
MEMBRANE-COLOR-SENSOR FOR
DETECTION OF HEAVY METAL**

NUR ATIAH BINTI AZMI

UNIVERSITI SAINS MALAYSIA

2019

**DEVELOPMENT OF A PORTABLE
MEMBRANE-COLOR-SENSOR FOR
DETECTION OF HEAVY METAL**

by

NUR ATIAH BINTI AZMI

**Thesis submitted in fulfilment of the
requirements for the degree of
Doctor of Philosophy**

July 2019

ACKNOWLEDGEMENT

In the Name of Allah, the Most Gracious, the Most Merciful. All praise is to Allah, the Lord of all the worlds; and peace and blessings are upon our Prophet and Messenger Muhammad and His family and all His companions.

My greatest appreciation goes to my supportive parent Hj. Azmi bin Mat and Hjh. Siti Khairiah binti Hamdzan. Both of you are the pillar of strength and encouragement of my life. You've been an awesome parent and always ready to support me in every situation. Life has been hard, and at times, I've wanted to give up, but you have always been there to remind me of my worth and encourage me to reach for the stars. Thank you for believing in your daughter. I will always love you. May Allah bless both of you till 'Jannah'.

I would like to express the deepest appreciation to my main supervisor Assoc. Prof. Dr. Low Siew Chun for her time and effort despite her busy schedule to offer feedback, advice and discussion throughout the research. I am really thankful for her invaluable guidance, support and inspiration during the most critical period of my PhD journey. Without her persistent help, this thesis would not have been possible. My sincere thanks for my co-supervisor Dr. Zeinab Abbas Jawad for the moral support, advice and assistance in finishing this research within time.

I would like to extend my sincerest thanks and appreciation to my beloved brothers and sisters; Azilawaty, Awatif, Alif and Akmal for their endless support and prayers along this journey. Saving the most important for last, I wish to give my heartfelt thanks to my husband, Mior Muhammad Saifuddin, who unconditionally

love, patience, and support of my academic endeavors over the past several years enabled me to complete this thesis.

I also would like to take this opportunity to say warm thanks to all my beloved friends, who have been so supportive along the way of doing my thesis. A special thank also goes to my lab partner; Roswani who was generous enough to share her knowledge and information with me. My appreciation also extends to those who helped up in collecting data. Not forgetting, thanks to all technical and administrative staff from the School of Chemical Engineering their cooperation during this research.

Finally, I would like to acknowledge the financial support by the Ministry of Higher Education Malaysia (MOHE) for MyPhD (MyBrain15) scholarship and Research University Grant USM (RUI)1001/PJKIMIA/814230.

Nur Atiah Azmi

July 2019

TABLE OF CONTENTS

	Page
ACKNOWLEDGEMENT	ii
TABLE OF CONTENTS	iv
LIST OF TABLES	vii
LIST OF FIGURES	ix
LIST OF ABBREVIATIONS	xiv
LIST OF SYMBOLS	xvi
ABSTRAK	xvii
ABSTRACT	xix
CHAPTER ONE INTRODUCTION	1
1.1 Heavy metals	1
1.2 Optical chemosensor	3
1.3 Chromophore	4
1.4 Membrane as the sensing platform for a colorimetric sensor	5
1.5 Problem statements	7
1.6 Research objectives	11
1.7 Scope of study	11
1.8 Organization of thesis	13
CHAPTER TWO LITERATURE REVIEW	15
2.1 Contamination of heavy metals	15
2.2 Conventional techniques of heavy metals sensing	23

2.3	Chemical Sensor	24
2.3.1	Electrochemical sensor	28
2.3.2	Optical chemosensor	30
2.4	Design of an optical chemosensor for heavy metal	36
2.4.1	Interaction of chromophore with metals solution	37
2.4.2	Selection of chromophore	39
2.5	Development of optical colorimetric membrane-based sensor	43
2.6	Research gaps	56
CHAPTER THREE MATERIALS AND METHODOLOGY		58
3.1	Research flowchart	58
3.2	Raw material and chemicals	60
3.3	Membrane synthesis as a sensing platform	61
3.3.1	Synthesis of porous CA/CS membrane	61
3.3.2	Glutaraldehyde coating as crosslinking agent on the membrane surface	62
3.3.3	Improvements of membrane porousness	64
3.3.4	Membrane characterizations	65
3.3.5	Immobilization of chromophore onto CA/CS membrane platform	66
3.3.6	Performance of membrane-based sensor to detect heavy metals	67
3.3.7	Color assessment of a membrane sensor	68
3.4	Selection of chromophores	69
3.4.1	Responses of chromophores at different pH	69
3.4.2	Effects of DTz concentrations towards immobilization on the membrane surface	70
3.5	Influences of heavy metals testing conditions on the sensor's performance	71
3.5.1	Effect of heavy metal pH	71
3.5.2	Effect of different type of heavy metal prepared at different concentrations	72
3.5.3	Determining the sensor's sensitivity: membrane sensor's response time	72
3.5.4	Effect of mixed heavy metals solution	72

3.6	Sensor's performance on real sample applications	73
3.6.1	Environment sample (river water)	73
3.6.2	Cosmetic samples	75
CHAPTER FOUR RESULTS AND DISCUSSION		79
4.1	Membrane synthesis as sensing platform	79
4.1.1	Synthesis of porous CA/CS membrane	81
4.1.2	Improvement of membrane porousness	98
4.2	Selective of chromophores	111
4.2.1	Response of colorimetric indicator at different pH on heavy metals	111
4.2.2	DTz immobilization conditions	124
4.3	Influences of heavy metals testing conditions on sensor's performance	132
4.3.1	Effect of heavy metal pH	132
4.3.2	Membrane sensor responses toward different type of heavy metal	133
4.3.3	Determining the sensor's sensitivity: membrane sensor's response time	137
4.3.4	Effect of mixed heavy metals solution	140
4.4	Sensor's performance on real sample applications	146
4.4.1	Environmental sample (river water)	146
4.4.2	Cosmetic samples	152
4.4.2(a)	Sample preparation	153
4.4.2(b)	Performance test in lipsticks samples	155
CHAPTER FIVE CONCLUSIONS AND RECOMMENDATIONS		159
5.1	Conclusions	159
5.2	Recommendations	161
REFERENCES		163
APPENDICES		
LIST OF PUBLICATIONS		

LIST OF TABLES

		Page
Table 2.1	Acceptable conditions for discharge of industrial effluent for mixed effluent of standards A and B	21
Table 2.2	Malaysian National Pharmaceutical Regulatory Agency (NPRRA) cosmetic guidelines for heavy metals	22
Table 2.3	Chemosensor classification	26
Table 2.4	Color of visible light spectrum at specific wavelength	34
Table 2.5	Optical chemosensor	45
Table 3.1	List of materials and chemicals used	60
Table 3.2	Preparation of CA/CS-membranes to use as the sensor's platform at different polymer dope composition in the formic acid solvent. Total polymer dope weight is 40g	62
Table 3.3	Membrane-based sensor (Mem-6: 17% CA + 1wt% CS) polymer dope preparation in 0 wt.%, 20 wt.%, 30 wt.% and 40 wt.% of non-solvent additive (deionized water)	65
Table 3.4	DTz chromophore classification for low, medium and high concentration at unadjusted pH solution	71
Table 4.1	Effects of polymers composition to affect GA binding capacity onto CA/CS membranes	82
Table 4.2	Pore diameter distribution for CA/CS membranes prepared using DI non-solvent with a) 0 wt.%, b) 20 wt.%, c) 30 wt.% and d) 40 wt.% DI water	105
Table 4.3	Color changing performances of colorimetric membrane sensors prepared using different chromophores for the detection of 3 ppm and 10 ppm Pb(NO ₃) ₂	123
Table 4.4	The color changes of DTz-CA/CS membranes (4.0cm x 0.5cm) for detection of a) Pb ²⁺ ions in 3 ppm Pb(NO ₃) ₂ , b) Hg ²⁺ ions in 3 ppm Hg(NO ₃) ₂ .H ₂ O, c) Cu ²⁺ ions in 3 ppm	139

Cu(NO₃)₂·3H₂O and d) Zn²⁺ ions in 3 ppm ZnCl₂ solution at pH7. Metals volume: 4mL; shaking speed: 100 rpm; immobilized DTz concentration on the membrane surface: 100ppm

Table 4.5	Performances of DTz-CA/CS membrane sensors tested with common constituents in river water. Samples were prepared according to maximum permissible constituents concentration allowed by Malaysian Department of Environment standard and regulation. All solutions were adjusted to pH7 for a fair comparison with earlier studies	147
Table 4.6	Responses of DTz-CA/CS membrane sensors by adding coexistence heavy metals ions into the samples of Kerian River water. The added metal concentration was based on the maximum permissible contents from the standard guideline by Department of Environment, Malaysia. All samples were adjusted to pH 7	152
Table 4.7	Detection of Pb ²⁺ ions in different aqueous lipstick samples using DTz-membrane sensor	156
Table 4.8	Detection of Pb ²⁺ ions content in aqueous lipstick samples using ICP-OES analysis	158

LIST OF FIGURES

		Page
Figure 1.1	Colorimetric membrane-based sensor color changes performance after reaction with the target analyte	6
Figure 2.1	Online newspaper alerts on the banned cosmetic product that contain toxic content	17
Figure 2.2	Framework for lead exposure	18
Figure 2.3	Schematic of typical chemosensor principal	24
Figure 2.4	Experimental set-up for potentiometry system using ion-selective electrodes with solid membranes	29
Figure 2.5	The electronic controlling circuit of a potentiostatic set-up to imposing a predetermined voltage between terminals of working and reference electrodes. The function generator provides the reference voltage as a function of time	30
Figure 2.6	Schematic diagram represent the signal emitted by the signalling subunit of optical chemosensor binding with target analyte (cation)	31
Figure 2.7	Electromagnetic spectrum	32
Figure 2.8	General arrangement of spectroscopic principles: a) reflection, b) refraction, c) absorption and d) fluorescence emission	33
Figure 2.9	Scheme of nanofibers modified by distinct nanomaterials for applications for heavy-metal detection in optical sensors. The lower part of the figure provides a schematic showing the principles of optical detection by the fluorescence quenching (left) or by the color change (right) the presence of the heavy metal ion	35
Figure 2.10	Organic chromophores used in optical chemosensor	39
Figure 2.11	Chemical structure of 8-(4-n-dodecyl-phenylazo) 2,4-quinolinediol chromophore	40

Figure 2.12	Chemical structure of diphenylthiocarbazone chromophore	41
Figure 2.13	Chemical structure of 4-(2-pyridylazo) resorcinol (PAR) chromophore	42
Figure 2.14	Chemical structure of 1-(2-pyridylazo)-2-naphthol (PAN) chromophore	43
Figure 3.1	Flowchart of overall experimental works	59
Figure 3.2	Experimental set-ups for membrane sensor's color assessment	69
Figure 3.3	Map showing the location for natural Kerian River water sampling	74
Figure 3.4	The sampling technique used for natural Kerian River water collection	75
Figure 3.5	Preparation protocols for Method 1 by: 1) adding ethanol into solid lipstick samples and 2) solid-liquid phase direct heating with continuously stirred on the magnetic hot plate at 50°C	76
Figure 3.6	Lipstick preparation protocol for Method 2 using 1) a bain-marie technique to melt solid lipstick, 2) addition of ethanol solvent to form aqueous lipstick sample and 3) direct heating until dryness before dilution using distilled water	77
Figure 4.1	Schematic diagram based on the hypothesis of developed optical membrane-based sensor mechanism when using a) CA and b) CA/CS as the membrane platform.	80
Figure 4.2	SEM images and pores distribution of a) CA Mem-1 as the control membrane, b) CA/CS Mem-6 as the optimum membrane for GA coating	85
Figure 4.3	Analysis of the membrane surface pores distribution using image-J software (a) high contrast image to differentiate membrane pores (dark spot area) and polymer matrix (white and grey spot area) (b) drew boxes were used to indicate the gap area in between the membrane pores	87
Figure 4.4	ATR-FTIR spectra of CA/CS membrane a) with and b) without GA coating	88

Figure 4.5	Effect of volume of GA used for GA coating on CA/CS membrane. Mem-6 obtained from Table 4.1 was tested, with the sample testing size of 1cm x 1cm and constant GA concentration of 0.25 wt.% in phosphate buffer for 1 hour at a constant temperature of 37°C	89
Figure 4.6	Stability analysis of GA-coated on the CA/CS membrane (Mem-6) over long period storage	90
Figure 4.7	SEM surface images for CA/CS-GA a) before and b) after DTz-chromophore immobilization on membranes	91
Figure 4.8	Color appearance of DTz chromophore a) before and after interact with aqueous b) GA, c) GA and $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, d) GA and $\text{Pb}(\text{NO}_3)_2$, e) GA and ZnCl_2 and f) GA and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$	92
Figure 4.9	Color changes of CA/CS-GA-DTz membrane sensors when used to detect different metal ions (10 ppm)	93
Figure 4.10	Color intensity on CA/CS-GA-DTz membranes when interact with different concentration of a) $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, b) $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, c) $\text{Pb}(\text{NO}_3)_2$ and d) ZnCl_2	95
Figure 4.11	Color changes of CA/CS-DTz membrane sensors when used to detect different heavy metal ions (10 ppm)	96
Figure 4.12	Schematic representations of (a) CA/CS membrane formation, (b) DTz interaction with CA/CS membrane and (c) formation of the DTz-metal (Pb^{2+}) complex	98
Figure 4.13	SEM photograph of CA/CS membranes with a) 0 wt.%, b) 20 wt.%, c) 30 wt.% and d) 40 wt.% of non-solvent additive (deionized water) in polymer dope	102
Figure 4.14	Performances of DTz-CA/CS membrane sensors prepared at different content of DI non-solvent a) 0 wt.%, b) 20 wt.%, c) 30 wt.% and d) 40 wt%. RGB triplet values were measured after tested with 1 ppm and 3 ppm $\text{Pb}(\text{NO}_3)_2$	106
Figure 4.15	Color value at R-axis for DTz-CA/CS colorimetric sensors tested with 1 ppm and 3 ppm of $\text{Pb}(\text{NO}_3)_2$ solution. Membranes were prepared using different content of non-solvent additive (0 wt.%, 20 wt.%, 30 wt.% and 40 wt. %)	110

Figure 4.16	UV–visible absorption spectrum and color change of DTz chromophore a) before and b) after detection with Pb^{2+} ion in 1ppm $Pb(NO_3)_2$ at different pH conditions. Note: pH 4.11 was the original prepared DTz solution without pH adjustment using NaOH or HCl	112
Figure 4.17	DTz structure during acid-base reaction a) H_2DTz produced blue-greenish in color and b) conjugate base $HDTz^-$ produce orange-yellowish in color	115
Figure 4.18	UV–visible absorption spectrum and color change of PAN a) before and b) after detection with Pb^{2+} ions in 1 ppm of $Pb(NO_3)_2$ at different pH conditions. Note: pH 5.57 was the original prepared PAN solution without pH adjustment using NaOH or HCl	118
Figure 4.19	UV–visible absorption spectrum and color change of PAR a) before and b) after detection with Pb^{2+} ions in 1 ppm of $Pb(NO_3)_2$ at different pH conditions. Note: pH 5.71 was the original prepared PAR solution without pH adjustment using NaOH or HCl	121
Figure 4.20	Color of DTz solutions prepared in different concentration (1 ppm to 150 ppm)	125
Figure 4.21	Color of membrane sensors when immersed in different concentration of DTz solutions. 0 ppm was referred to the control CA/CS membrane without immersed in DTz solution and 150 ppm was referred to the CA/CS membrane immersed in 150 ppm of DTz solution	127
Figure 4.22	Mass of DTz immobilized on CA/CS membrane (4cm x 1cm) prepared using different concentrations of DTz solutions	128
Figure 4.23	Color changes of the membrane sensors after detection with Pb^{2+} in 3 ppm $Pb(NO_3)_2$. The membrane sensors were prepared using different concentrations of DTz (25 ppm to 150 pm)	129
Figure 4.24	Densitometer color density of membrane sensors prepared at different immobilization time of 1 to 20 min. Note: DTz concentration was fixed at 100ppm	131
Figure 4.25	Color changing performances of DTz-CA/CS membranes (0.5 cm x 4.0 cm) when interact with Pb^{2+} in 3ppm $Pb(NO_3)_2$	132

solution at different pH conditions

- Figure 4.26 Color appearance of membrane sensors after interact with metal cations at different concentration of $\text{Pb}(\text{NO}_3)_2$, $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and ZnCl_2 solution at pH7. Metal concentration: 1ppm – 10ppm; Membrane dimension: 0.5 cm x 4.0 cm; DTz concentration: 100 ppm; DTz immobilization time: 10min 134
- Figure 4.27 RGB triplet values of DTz-CA/CS membrane sensors tested using different metals ions of $\text{Pb}(\text{NO}_3)_2$, $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and ZnCl_2 solution at concentration 3 ppm to 10 ppm buffered to pH 7 136
- Figure 4.28 Membrane color changes tested with mixed a) 75 % v/v Hg^{2+} , b) 50% v/v Hg^{2+} and c) 25% v/v Hg^{2+} in 3 ppm $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ over Pb^{2+} ions in 3 ppm $\text{Pb}(\text{NO}_3)_2$ solutions. Note: 100% v/v is equal to 4 mL the amount of 3ppm single metals solution at pH 7 141
- Figure 4.29 Membrane color changes tested with mixed a) 75% v/v Cu^{2+} , b) 50% v/v Cu^{2+} and c) 25% v/v Cu^{2+} in 3 ppm $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ over Pb^{2+} ions in 3 ppm $\text{Pb}(\text{NO}_3)_2$ solutions. Note: 100% v/v is equal to 4 mL the amount of 3 ppm single metals solution at pH 7 143
- Figure 4.30 Membrane color changes tested with mixed a) 75% v/v Zn^{2+} , b) 50% v/v Zn^{2+} and c) 25% v/v Zn^{2+} in 3 ppm ZnCl_2 over Pb^{2+} ions in 3 ppm $\text{Pb}(\text{NO}_3)_2$ solutions. Note: 100% v/v is equal to 4 mL the amount of 3 ppm single metal solution prepared at pH 7 145
- Figure 4.31 Membrane sensor's color changes when used to analyse water quality of Kerian River (adjusted to pH 7) and its accordance water analysis by AAS 151
- Figure 4.32 Concentrations of Pb^{2+} ions in lipstick samples that extract by different sample preparation protocols. Results display was based on the color changes from membrane sensors and AAS analysis. Lipstick sample Brand A was used in this experiment 153

LIST OF ABBREVIATIONS

AAS	Atomic absorption spectroscopy
BCA	Bicinchoninic acid assay
BSA	Bovine serum albumin
CA	Cellulose acetate polymer
Ca	calcium
Cd	Cadmium
CS	Chitosan polymer
Cu	Copper
DALYs	Disability-adjusted life years
DI	Deionized water
DOE	Department of Environment
DW	Distilled water
DTz	Dithizone chromophore
FA	Formic acid
FDA	Food and Drug Administration
FTIR	Fourier transform infrared spectroscopy
GA	Glutaraldehyde
Hg	Mercury
ICP-OES	Inductively coupled plasma optical emission
LOD	Limit of detection
Mg	magnesium
N ₂	Nitrogen
NaOH	Sodium Hydroxide
Ni	Nickel
PAR	4-(2-pyridylazo)-resorcinol
PAN	1-(2-pyridylazo)-2-naphthol
PVA	Poly (vinyl alcohol)
PVC	Polyvinylchloride
PVDF	Polyvinylidene difluoride

Pb	Lead
RGB	Red; Green; Blue
SEM	Scanning electron microscopy
UV	Ultraviolet
WHO	World Health Organization
XRF	X-ray fluorescence spectrometry
Zn	Zinc
HCl	Hydrochloric acid
ppm	Part per million
ppb	Part per billion

LIST OF SYMBOLS

λ	Wavelength
~	Approximately
ca.	Approximately
e.g.	For example
etc.	And so forth
i.e.	Which is
wt. %	Weight percentage
% v/v	Volume per volume percentage
°C	Degree Celsius
R^2	Linear regression correlation coefficients
cm	centimeter
nm	nanometer
μ	micro
g	gram

PEMBANGUNAN MEMBRAN-PENDERIA-WARNA MUDAH ALIH UNTUK PENGESANAN LOGAM BERAT

ABSTRAK

Satu keperluan asas bagi penderia permeteran warna berasaskan membran adalah untuk membenarkan sasaran analit untuk mencapai kepada kromofor sementara mengekalkan imobilisasi kromofor yang kuat pada permukaan membran. Kajian ini membuktikan persepsi asas bagi morfologi membran dan pengaruh mereka terhadap pengikatan kromofor untuk mengesan logam berat terlarut. Membran kepingan rata terdiri daripada campuran polimer selulosa asetat (CA) dan kitosan (CS) bertindak sebagai pelantar penderiaan untuk pengikatan kromofor. Membran dengan 17 wt.% CA dan 1 wt.% CS menunjukkan mempunyai kapasiti pengikatan tinggi dan kestabilan pengikatan yang tinggi sehingga 90 hari pengukuran. Penambahan air ternyahion (DI) sebagai bahan tambah bukan-pelarut juga telah menunjukkan penambahbaikan liang-liang membran, yang menambahbaikan kepekaan penderia. Perubahan warna yang boleh dilihat oleh membran pemeteran warna dari biru-kehijauan kepada merah jambu telah diperhatikan apabila permeteran warna bersentuhan dengan ion Pb^{2+} dalam 1 ppm $Pb(NO_3)_2$. Pemilihan kromofor (Dithizon, 1-(2-pyridylazo) 2-naftol and 4-(2-pyridylazo)-resorsinol) yang sensitif dan strategi imobilisasi penderia membran juga telah dijalankan. Dithizon (DTz) pada pH yang tidak diselaraskan mampu menghasilkan satu peralihan warna yang jelas yang diperhatikan melalui spektrum penyerapan UV dan pengecaman mata kasar. Untuk imobilisasi yang optimum adalah memerlukan kepekatan DTz pada 100 ppm dan masa imobilisasi selama 10 minit. Untuk menilai kepekaan dan kememilihan penderia permeteran warna di

dalam larutan ion logam berat terlarut tunggal dan campuran, keadaan penderiaan seperti pH, jenis ion logam berat (Pb^{2+} , Hg^{2+} , Zn^{2+} and Cu^{2+}), kepekatan dan masa tindak balas telah diuji. Pembangunan penderia DTz-membran dalam kerja ini telah mempamerkan perubahan warna yang cepat (dalam masa 1 minit) dan mampu memaparkan perubahan warna tersendiri dari biru-kehijauan kepada merah jambu, kuning-keorenan merah-unggu dan coklat kemerahan dalam tindak balas terhadap kehadiran Pb^{2+} , Hg^{2+} , Zn^{2+} dan Cu^{2+} dalam larutan akueus. Analisis kuantitatif menggunakan data RGB (R:Merah; G:Hijau; B:Biru) telah menunjukkan bahawa setiap ion logam yang diuji menunjukkan fasa corak pengecaman RGB mereka sendiri tanpa kesan gangguan penting diantara ion logam. Ini menunjukkan potensi untuk aplikasi yang praktikal bagi pengesanan cepat di tapak sama ada ion logam berat tunggal atau campuran. Penderia membran DTz-CA/CS ini telah menunjukkan perubahan warna yang tersendiri dalam mengesan ion logam berat sintetik di dalam air yang diperoleh daripada Sungai Kerian. Ion logam berat sintetik ini telah disediakan pada had maksimum dibenarkan (0.1 ppm Pb^{2+} , 2.0 ppm Zn^{2+} and 0.2 ppm Cu^{2+}) untuk efluen perindustrian (Piawai A) oleh Jabatan Alam Sekitar Malaysia. Penderia membran ini telah berjaya digunakan untuk penentuan ion-ion logam berat bukan sahaja kepada penilaian kualiti air sungai tetapi juga termasuk analisis produk kosmetik (sampel gincu) dengan menunjukkan perubahan warna pada jejak ion logam berat yang rendah.

DEVELOPMENT OF A PORTABLE MEMBRANE-COLOR-SENSOR FOR DETECTION OF HEAVY METAL

ABSTRACT

A basic requirement of colorimetric membrane-based sensors is to allow the target analyte to access to the chromophore while retaining a strong chromophore immobilization on the membrane surface. This study elucidates the fundamental perceptive of membrane morphologies and their influences on the binding of chromophores to detect aqueous heavy metals ions. Flat sheet membranes consist of mixed polymer cellulose acetate (CA) and chitosan (CS) was acts as the sensing platform for chromophore binding. Membrane with 17 wt.% CA and 1 wt.% CS showed to have the high binding capacity and high binding stability up to 90 days of measurement. The addition of deionized water (DI) as the non-solvent additive has also shown to improve the membrane porousness, which improved the sensor's sensitivity. Visible color changes of the colorimetric membrane from blue-greenish to peachy-pink was observed when it was in contact with the Pb^{2+} ions in 1 ppm $\text{Pb}(\text{NO}_3)_2$. Selection of sensitive chromophore (Dithizone, 1-(2-pyridylazo) 2-naphthol and 4-(2-pyridylazo)-resorcinol) and its immobilization strategy on the membrane sensor has also been carried out. Dithizone (DTz) at unadjusted pH was capable to produce an obvious color transition observed through UV-visible absorption spectrum and naked eyes recognition. The optimum immobilization of DTz required the concentration of 100 ppm and 10 minutes immobilization time. To determine the sensitivity and selectivity of the developed colorimetric sensor in the single and mixed aqueous heavy metals ions solution, the sensing conditions such as pH, type of heavy metals (Pb^{2+} , Hg^{2+} , Zn^{2+} and Cu^{2+}), concentration and response

time were evaluated. The developed DTz-membrane sensor in this work has exhibited quick (within 1 minute) color change and was able to display distinctive color changes from blue-greenish to peachy-pink, yellowish-orange, red-violet and reddish-brown in the response to the presence of Pb^{2+} , Hg^{2+} , Zn^{2+} and Cu^{2+} in aqueous solutions. The quantitative analysis using RGB (R:Red; G:Green; B:Blue) data showed that each tested metal ions have demonstrated their own RGB's recognition pattern phase without significant interfering effects among the heavy metal ions. This showed the potential for practical applications of on-site quick detection on either single or mixed heavy metal ions. The DTz-CA/CS membrane showed a distinctive color changed in the detection of synthetic heavy metals ions in the water that obtain from Kerian River. The synthetic heavy metals ions was prepared the at maximum permissible limit of 0.1 ppm Pb^{2+} , 2.0 ppm Zn^{2+} and 0.2 ppm Cu^{2+} for industrial effluent (Standard A) by Malaysian Department of Environment. This membrane sensor was successfully applied for the determination of heavy metals ions not only limited to river water quality assessment but also included the cosmetic product analysis (lipstick samples) at the low trace level of heavy metals ions.

CHAPTER 1

INTRODUCTION

1.1 Heavy metals

The rapid economic development has increased the environmental pollution occurred through the toxic substances released from agriculture, towns, mining industry, factories or human activities. Environmental pollutant such as fungicidal sprays, household bleach, and caustic chemicals have the potential to produce the toxic heavy metals (Rezaee *et al.*, 2005, Tangahu *et al.*, 2011). Heavy metals are defined as metallic elements with relatively high atomic weights and those having a specific density of more than 5 g/cm (Fergusson, 1990, Järup, 2003). Lead, arsenic, mercury, cobalt, zinc and chromium are among of the toxic metals that are highly soluble in water, contributing towards contamination of the ecosystems especially in the water pollution issue.

Heavy metals enter our bodies and causes poisoning via food, drinking water and air. For instance, by drinking the contaminated water from a lead contaminated pipe or consumption of heavy metal contaminated seafood will cause serious damage to the human central nervous system, endocrine system, kidneys, bones and livers (Bansod *et al.*, 2017). Heavy metals contamination can be cause by both natural and anthropogenic activities such as mining operations, wastewater, industries and metallurgical processes (Nobi *et al.*, 2010). The natural phenomena including weathering process and volcanic eruptions have also been reported to significantly contribute to heavy metal contamination (Michelozzi and De' Donato, 2014, Sun *et al.*, 2016).

Cosmetics have cast a spell over cultures to enhance physical beauty throughout history. Despite its effectiveness, recent news reports on the warning about the high trace of heavy metals element in cosmetic products such as lipstick which is persistent and recurring (Mansouri *et al.*, 2017, Monnot *et al.*, 2015, Zakaria and Ho, 2015). In 2012, the U.S. Food and Drug Administration (FDA) released the test results of 400 lipstick samples and found an average of 1.11 ppm of lead in the lipstick sample, with a maximum lead level of 7.19 ppm obtained (Hepp, 2012). This heavy metal might be intentionally added to cosmetics products or present as impurities in the finished products (Pinto *et al.*, 2018). However, long term usage of cosmetic can cause heavy metals bio-accumulation in the body which is dangerous for organs; disrupt the normal bodily functions and lead to a chronic disease. Besides, the cumulative effect from repeated applications of cosmetic can add up its concentration to significant heavy metals exposure.

DALYs, or disability-adjusted life years, are the standard public health metric used by the World Health Organization (WHO) to assess the sum total of morbidity and mortality in a given population as a result of a particular disease or condition (Lackner *et al.*, 2018). DALYs measures health gaps between a current situation and an ideal situation where everyone lives up to the age of the standard life expectancy in perfect health. In year 2012, WHO had reported lead exposure that is responsible for ca. 0.67 million deaths and 13.9 million DALYs of the world population, which attributed by 9.8% idiopathic intellectual disability, 4% ischaemic heart disease and 4.6% stroke cases (Havens *et al.*, 2018, WHO, 2016).

Concern over the distinct toxicity of heavy metal has stimulated the development of a cost-effective, and facile methods to control the heavy metal

exposure in different industries, including but not limited to, chemical precipitation, adsorptive membrane (Sitko *et al.*, 2016), and electrochemical treatment technologies (Fayazi *et al.*, 2016, Mahmoudian *et al.*, 2016, Osipova *et al.*, 2000, Zhang *et al.*, 2014). The heavy metals content in waters are commonly analyzed using spectroscopic analytical techniques such as Atomic Absorption Spectrophotometry (AAS) (Ghaedi *et al.*, 2007), Inductive Coupled Plasma (ICP) (Milne *et al.*, 2010), and High-Performance Liquid Chromatograph (HPLC) (Malik *et al.*, 2006). These methods are effective in detecting heavy metals ions, however, they are time and cost consuming, besides involving a complicated sample treatment and pre-concentration steps that can only be carried by professionals (Bontidean *et al.*, 2004, Sartore *et al.*, 2011). This will prohibit the screening for heavy metals trace and thus hinders the objective of preventing heavy metal contamination as early as possible in the production chain. Hence, further efforts to control and rapid monitoring the released heavy metals are required to reduce its exposures. Under such a scenario, the optical chemosensor has emerged as a potential detection system for an effective monitoring of heavy metal.

1.2 Optical chemosensor

In the recent year, sensors have gained considerable research and development by expertise as an application with the purpose to detect trace analyte based on its simple analytical procedures and short detection time (Elmizadeh *et al.*, 2019, Liu *et al.*, 2018). A chemical sensor (chemosensor) is a simpler approach to chemical analysis; which provide responding output without sample treatment and pre-concentration steps. It can be classified into optical, electrical, electrochemical,