

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

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

by

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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,