



# Investigating film structure of membrane-based colorimetric sensor for heavy metal detection



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## ABSTRACT

A stable and relatively long lifetime optical membrane sensor for determination of heavy metal ions was prepared by covalent immobilization of dithizone (DTZ) on cellulose acetate membrane. Present work was aimed at gaining a quantitative understanding of the influence of membrane morphologies towards the immobilization of DTZ on the membrane surface. Experimental results indicated that the developed membrane by using 1 wt.% chitosan and 17 wt.% cellulose acetate showed to have the highest binding capacity and high binding stability up to 90 days of measurement. The prepared DTZ-membrane sensor exhibited quick (within 1 min) color change and was found to be capable of displaying distinctive color changes responses to the presence of mercury, copper, and zinc in aqueous solutions. The color intensity increases with increasing metal ions concentration, showed the potential practical applications for on-site quick detection of metal ions.

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## 1. Introduction

Metal ions are biological toxicity to living organisms and can bioaccumulate in the food chain, which causes several health problems such as kidney deficiency, lung problems, hypertension and nervous system failure [1,2]. Environmental measurements of heavy metals in waters are common practice using the spectroscopic analytical techniques such as Atomic Absorption Spectrophotometry (AAS) [3], Inductive Couple Plasma (ICP) [4], and High-Performance Liquid Chromatograph (HPLC) [5]. These methods are effective in detecting heavy metals ions, however, they are time and cost consuming, besides specific skills with specific methods are required [6,7].

Hence, the possibility for quick and in situ detection of heavy metal ions in water or wastewater has attracted considerable research interest. Among the effects, optical sensors appear to be especially attractive due to their simple, naked-eye recognition nature and requires less sophisticated equipment [8]. The basic strategy of an optical sensor is to use an optical indicator that can induce the visual changes in the presence of metal ions species. The detection of heavy metal ions through visual determination of the optical sensor can classify into three criteria: color phase, bright-

ness, and color saturation. Of these criteria, change in color phase is the most distinguish by human sight [9].

The optical indicator or sensing phase consists of reagent dyes that can be immobilized or entrapped within the organic and inorganic matrices. Diphenylthiocarbazone, also known as dithizone (DTZ) is an organic colorimetric reagent that could react as the optical indicator in an optical sensor. It is used to monitor ultrafast colorful photochromic reaction in metal ions solution [10]. Dithizone contains many N-donor atoms,  $-NH$  as well as  $-SH$  group that forms stable water-insoluble complexes with metal ions such as  $Pb(II)$ ,  $Cu(II)$ ,  $Cd(II)$  and  $Hg(II)$  under proper condition [11,12]. Zargosh and Babadi [13] have developed an optical membrane sensor by covalent immobilization of dithizone as the sensing phase on the agarose membrane. The prepared optical membrane was applied to detect  $Hg(II)$  and  $Pb(II)$  in industrial wastes, spiked tap water, and natural waters without any pre-concentration step.

One of the important elements in the production of a rapid optical sensor is the membrane utilized as the sensing platform. In the detection of metal ions, microporous membranes are used as scaffolds to immobilize the optically active probe molecules that provide recognition and signal transduction [14]. Without the membrane, the optical sensor is literally not functioning. The membrane specific surfaces are used as the binding sites for the adsorption of optical ligand and to maintain their stability and activity over the shelf-life of the sensor.

Chitosan (CS) is a well-known adsorbent in various applications since it has a strong chelation potential for heavy metals

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**Table 1**  
Preparation of membrane-based sensor at different polymer dope composition.

Membrane id	Casting dope composition (wt.%)		
	CA	CS	FA
Pure CA	15.0	0.0	85.0
Blend I	15.0	1.0	84.0
Blend II	15.0	1.5	83.5
Blend III	15.0	2.0	83.0
Blend IV	14.0	1.0	85.0
Blend V	17.0	1.0	82.0

due to the presence of amine and hydroxyl groups in the polymer [15–17]. However, pure chitosan membrane is poor in mechanical strength and has low chemical stability. To improve the mechanical strength of chitosan, blending of chitosan with another polymer such as cellulose acetate (CA) has been found to be an effective way. Throughout the blending process, CA acts as the mechanical support while CS contributes amino group to the membrane matrix. Indeed, CA and CS consists of the similar chemical structure which providing the possibility of producing homogeneous blends that combined the unique properties of both polymers [18]. For the instant, Takahashi and co-workers [19] have prepared a DTZ-loaded membrane by dispersing the DTZ nanofibers on the surface of the cellulose ester membrane through filtration. The DTZ sensing phase was able to selectively captured Hg(II) ions and showed different color intensities at different Hg(II) concentration. Unfortunately, the detailed conformational integrity of DTZ on the membrane surface was not discussed.

The most practical scheme to realize the effectiveness of an optical sensor is to study the conformational integrity of the optical indicator (DTZ in present work) that immobilized on the membrane surface. In this work, the conformational integrity of DTZ-membrane and its effect on adsorption of heavy metal ions (induce color changes as optical signals in response to the presence of certain metal species) were discussed. The study was focused on the membranes structural that affects the immobilization of DTZ as well as its immobilization stability over the shelf-life of the sensor. The assessments on color changes of the membrane samples with adsorbed metal ions were analyzed using the photography images and reflectance spectra with a densitometer.

## 2. Experimental

### 2.1. Materials

Chitosan, cellulose acetate polymer (with an acetyl content of 40%) and albumin bovine serum fraction V were supplied by Sigma-Aldrich (St. Louis, MO). Formic acid (98–100%) and 25% glutaraldehyde (GA), purchased from Merck (Darmstadt, Germany) were used as the solvent for membrane preparation and cross-linker for sensor development, respectively. Ethanol, diphenylthiocarbazon (dithizone, DTZ), mercury (II) nitrate monohydrate, copper (II) nitrate trihydrate and sodium hydroxide (NaOH) were supplied by Merck (Darmstadt, Germany). All chemicals used were analytical grade standards and used without further purification.

### 2.2. Membrane preparation

The different microstructure of the membrane sensing platforms were prepared by dissolving specific concentration of CA and CS polymer in formic acid (FA) solution, as the membrane casting formulations were tabulated in Table 1. The polymer dopes were stirred at 200 rpm for 4 h and then degassed to remove air bubbles. Subsequently, the casting dope was cast onto a glass plate

with a 500  $\mu\text{m}$  clearance gap of casting blade. The cast-film was then immersed into the distilled water coagulation bath containing 2 wt.% NaOH overnight. The prepared membrane was air-dried and stored in a sealed plastic bag prior to further use for characterizations, functionalization and performance tests.

### 2.3. Immobilization of dithizone (DTZ) on the membrane surface

Prior immobilize DTZ optical indicator on the membrane surface, glutaraldehyde (GA) was first coated to the membrane matrix to increase the binding capacity of DTZ for heavy metal detection. The samples were first  $\text{N}_2$ -dried and treated using 0.25 wt.% GA prepared in 0.05 M phosphate buffer solution, under a shaking condition (100 rpm) for 1 h. Subsequently, the GA-activated membranes were rinsed using phosphate buffer solution and ready for DTZ immobilization. The coated GA on the membrane surface was confirmed through Thermo Scientific FTIR spectroscopy system (NICOLET iS10, USA).

For membrane immobilization ability tests, the GA-activated membrane was immersed in 1 mg/mL BSA solution (pH 7, prepared in 0.5 M phosphate buffer) for 1 h at 27 °C. The effectiveness of GA coating is proven if the BSA binding is found relatively higher for the GA-activated membrane than the non-GA activated membrane. Total protein content was measured using the micro-BCA protein assay kit (Merck, Darmstadt, Germany), in compliance with an ultraviolet–visible spectrophotometer (Pharo 300 Spectroquant®, Darmstadt, Germany) at a wavelength of 562 nm. The amount of the protein binds onto GA-activated membranes were calculated using the following equation:

$$\text{Protein Binding } (\mu\text{g}/\text{cm}^3) = \frac{W_g}{A \times h}$$

$W_g$  is the weight of the protein grafted onto the membrane ( $\mu\text{g}$ ),  $A$  is the surface area of the membrane ( $\text{cm}^2$ ) and  $h$  is the membrane thickness (cm).

DTZ immobilization was done by immersing the GA-activated membrane in a freshly prepared 1000 ppm DTZ solution in ethanol for 20 min. The success DTZ-immobilized membrane appeared in orange color and ready to be used for trace analysis of metal ions. Membrane surface morphologies before and after DTZ immobilizations were observed using scanning electron microscope (Hitachi TM3000, Tokyo, Japan). All samples were first platinum-coated to prevent the accumulation of static charges at the specimen.

### 2.4. Trace analysis of heavy metal ions using DTZ-membrane optical sensor

The DTZ-membrane optical sensor was first immersed in the heavy metal solutions (ranged from 1 mg/mL to 100 mg/mL) for 10 min to ensure the complete color changes in response to the presence of certain metal species. The assessments on color changes of the membrane samples by naked-eye recognition were made by taking photos using a digital camera. For quantification, color intensities of the stained heavy metal ions on the membrane surfaces were scanned using the Heiland Electronics GmbH densitometer (TRD 4, Germany) at a wavelength of 560 nm in reflectance mode. Each value represents an average value of six measurements and the standard error was reported.

## 3. Results and discussion

The optical sensor makes use of the polymer membrane containing the optical indicator that reacts with the analyte to produce a distinctive color change. The main factor that determines the efficacy of such a membrane-based sensor is the binding mechanism between the optical indicator (DTZ in present work) and

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