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## Determination of $Hg^{2+}$ by diphenylcarbazone compound in polymer film

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### ABSTRACT

A sensitive optical sensor for determining  $Hg^{2+}$  concentration has been prepared by incorporating the indicator dye, diphenylcarbazone compound, into cellulose acetate polymer film. To prepare the sensor, a cellulose acetate film was hydrolyzed with base and then the diphenylcarbazone compound bonded to the film. This method is easy to perform and uses acetyl cellulose as a carrier. According to the results, the prepared sensor was able to determine the  $Hg^{2+}$  concentration with a  $\pm 6\%$  error. Also, the adsorption capacity was  $3.41 \times 10^{-3}$  mmol/g.

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## 1. Introduction

One of the most popular poisonous elements in aquatic ecosystems is mercury ( $Hg^{2+}$ ) in a way that even a low amount of this element can significantly affect human health [1-8]. This is due to the  $Hg^{2+}$  accumulation in the human body from the food chain which causes serious damages to the brain, lungs, central nervous system, kidney, and the development of the fetus [9-14]. Unfortunately, the emission of mercury by humans is increasing [15, 16]. This increasing trend in environmental pollution is considered a global concern. For addressing this issue, a reliable and rapid method is needed to determine the mercury trace [17].

In this respect, a variety of sensitive analytical methods can be used to determine  $Hg^{2+}$  selectively such as inductively coupled plasma-atomic emission spectrometry (ICP-AES), inductively coupled plasma mass spectrometry (ICP-MS) [18, 19], cold-vapor atomic fluorescence spectroscopy (CVAFS) [20], and cold-vapor atomic absorption spectroscopy (CVAAS) [21-23]. Although these traditional techniques are sensitive with high accuracy, the measurement instruments are sophisticated, expensive, with high costs of operation, and the sample preparation process is complicated. These factors make these methods time-consuming for a large number of samples and are not suitable for routine monitoring in the field. Besides, during the collection, samples may be altered. Consequently, the design of an inexpensive, fast technique for the detection of  $Hg^{2+}$  is desired. Currently, some techniques are employed for field application and miniaturization including fluorimetry and colorimetry [24-31]. However, their application is still limited due to the interference of other metal ions and sophisticated synthesis of probe materials

[32, 33]. Voltammetric methods which are electrochemical techniques have a high potential for the determination of  $Hg^{2+}$  in the field compared to other methods [34, 35]. This is because of possessing some inherent characteristics, including selectivity and sensitivity, miniaturization, cost-effectiveness, and rapid analysis time [36].

So far, in spite of the increasing interest in the development of a time-saving, easy-to-operate, low-cost, and reliable technique for the determination of  $Hg^{2+}$  in the field, only a few numbers of studies have addressed the optical sensors (fluorescent and colorimetric) [25, 37, 38]. Some studies have been worked on the determination of  $Hg^{2+}$  through voltammetric methods, but they are fragmentary and incompletely [39-41]. To the best knowledge of the authors, none of the previous studies have focused particularly on the determination of  $Hg^{2+}$  through voltammetric techniques. Moreover, the application of nanomaterials in these methods has been recently gained increasing attention. This research focuses on the preparation of a highly sensitive sensor for determining  $Hg^{2+}$  concentration by incorporating the indicator dye, diphenylcarbazone compound, into a polymer film.

## 2. Experiment Procedure

### 2.1. Materials

To prepare a standard solution of mercury chloride ( $HgCl_2$ , 0.1 M), 2.715 g of  $HgCl_2$  dissolved in 100 ml distilled water in a standard flask. Diphenylcarbazone compound 0.02% solution was prepared by dissolv-

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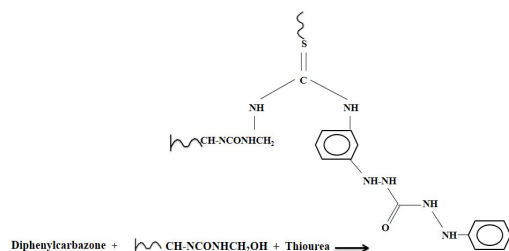


Fig. 1. The possible reaction between the activated membrane and diphenylcarbazone compound.

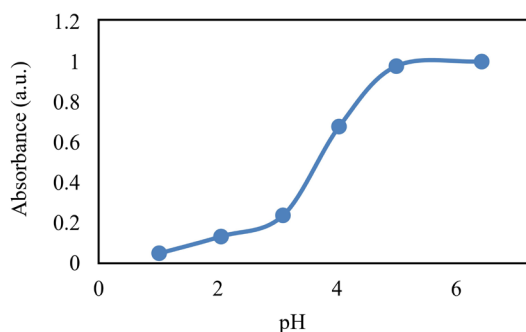


Fig. 3. Adsorption of  $\text{Hg}^{2+}$  in different pH values.

ing the  $\text{C}_2\text{H}_5\text{OH}$  dye solution with a 2.00% concentration in a 100 ml volumetric flask. 2.264 g  $\text{NH}_4\text{Cl}$  was dissolved in 100 ml distilled water to prepare  $\text{NH}_4\text{Cl}$  solution with 0.4 M concentration and 2.14 g  $\text{NaBrO}_3$  was dissolved in distilled water in a volumetric flask (250 ml) to obtain  $\text{NaBrO}_3$  solution with 0.06 M concentration. For the preparation of polyvinyl alcohol and Thiourea solutions, 0.7 g and 1g of the reagents were dissolved in 100 ml of distilled water, respectively.

## 2.2. Methods

### 2.2.1. Sensor Preparation

For de-esterification of the acetyl group and the increase in the membrane porosity, the hydrolysis of acetyl cellulose was carried out. The transparent films were immersed in  $\text{KOH}$  ( $0.1 \text{ mol.l}^{-1}$ ) for 24 hours. Subsequently, the specimens were washed with distilled water followed by the treatment with a mixture of polyvinyl alcohol (0.70 % (w/v)) and thiourea (1.00 % (w/v)) solution for 48 hours at room temperature. Then, the polymer membrane was treated with a solution of diphenylcarbazone compound (0.020 % (w/v)) at room temperature and stirred for about 20 hours. At the next step, the film was washed by rinsing with distilled water to the extent that no absorbance was observed at the dye wavelength. The drying process of the film was carried out at  $45^\circ\text{C}$  for 15 minutes.

### 2.2.2. Spectrophotometric Measurements

Shimadzu 2100 ultraviolet-visible (UV-Vis) spectrophotometer and a thermostated cell were used to measure the UV-Vis spectra at the con-

Table 1.

Determination of  $\text{Hg}^{2+}$  concentration

The standard amount of $\text{Hg}^{2+}$ (ng)	The measured amount of $\text{Hg}^{2+}$ by the proposed method (ng)				Mean $\pm$ SD
10	9	12	11		$10.6 \pm 0.1$
20	22	18	23		$21 \pm 0.1$
25	23	26	27		$25.3 \pm 0.1$

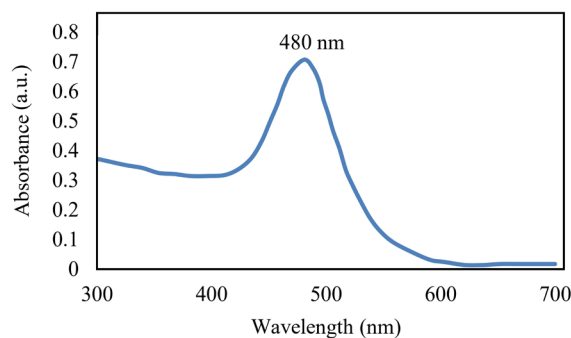


Fig. 2. UV-Vis spectrum of the polymer film functionalized with diphenylcarbazone compound.

trolled temperature of  $25^\circ\text{C} \pm 0.1$ .

## 3. Results and Discussion

The reaction between the activated cellulose film and the diphenylcarbazone compound is illustrated in Fig. 1. There is an amino group in the structure of the diphenylcarbazone compound, therefore, by special treatments, the molecules of the dye can be linked to cellulose acetate. According to Kostov et al. [42], just the dyes that have amino groups in their structure are able to be linked to cellulose acetate. With the help of thiourea, it is possible to link dyes with or without amino groups in their structure to cellulose acetate polymer.

As a result of the high activity of the carrier, the interaction of the carrier compounds having the low molecular weight and a free para-position in their structure is possible.

Therefore, indicators with a free para-position or hydroxyl group in their molecule can be employed. In addition, to link the molecules of dye to the cellulose acetate membrane, thiourea acts as a bridge. This results in the covalent bonding between the indicator and the polymer film [43].  $\text{BrO}_3^-$  can oxidize diphenylcarbazone compound in the presence of  $\text{Hg}^{2+}$  in an acidic environment ( $\text{pH} \sim 4.5$ ) [44].

### 3.1. UV-Vis Spectrum of Functionalized Cellulose Acetate

The UV-Vis spectrum of the treated cellulose acetate was obtained by measuring the intensity at a different wavelength and plotted against wavelength. The UV-Vis spectrum of the diphenylcarbazone-functionalized film obtained is shown in Fig. 2. As illustrated, the maximum absorption appeared at 480 nm. Thus, the spectrophotometric measurements were carried out at 480 nm.

### 3.2. The Effect of pH on the Adsorption of $\text{Hg}^{2+}$

The acidity of the solution affects the  $\text{Hg}^{2+}$  determination sensitivity of the diphenylcarbazone compound. The adsorption plot versus pH for the functionalized polymer film is shown in Fig. 3. The pH value was adjusted with sodium hydroxide or hydrochloric acid at an  $\text{Hg}^{2+}$  concentration of  $1.0 \times 10^{-5} \text{ mol/mL}$  and the amount of adsorbed Hg was measured by spectroscopy. The adsorption of  $\text{Hg}^{2+}$  decreases for a pH value of lower than 5. Decreasing the pH of the solution reduces the adsorption of the diphenylcarbazone compound. However, in neutral solutions, the interfering of other heavy ions increases and they produce colored compositions with diphenylcarbazone compound. When acidity increases, the diphenylcarbazone-mercury complex formed on the polymer film gradually decomposes and decolorizes [45, 46]. Therefore the determination measurement was carried out at  $\text{pH} = 5$ .

### 3.3. Determination of Micro-amounts of $\text{Hg}^{2+}$ by UV-Vis Spectroscopy

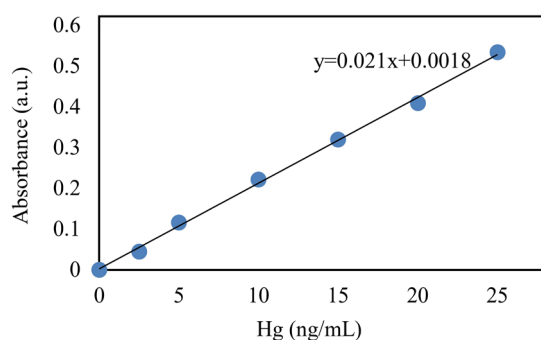


Fig. 4. Calibration curve for Hg at the wavelength of 480 nm.

The signal intensity of UV-Vis spectroscopy of the specimen was investigated at 480 nm for different  $\text{Hg}^{2+}$  concentrations in the range of 0 to 25 ng/mL to obtain the calibration curve. The calibration curve obtained is linear from 0 to 25 ng as shown in Fig. 4. Three measurements for each absorption value for each solution were carried out and the mean value was reported. By employing the plotted calibration curve, the determination of unknown concentrations of mercury was performed. The results of measurements with the prepared sample are summarized in Table 1. The error of the measurements was within  $\pm 6\%$  for samples 10 to 25 ng.

#### 3.4. Adsorption Isotherm of $\text{Hg}^{2+}$ on the Functionalized Cellulose Acetate Film

Fig. 5 illustrates the optical characteristics of the immobilized diphenylcarbazone compound on the cellulose acetate film for different concentrations of  $\text{Hg}^{2+}$ . To evaluate the binding capacity of the functionalized polymer film, a rebinding experiment was carried out by using 0.2 g of the polymer film in 25 mL phosphate buffer solution of  $\text{HgCl}_2$  (pH  $\sim 4$ ). The suspension was stirred at 25 °C for 30 minutes and the absorption amount in the range of 0 to 200  $\mu\text{g}/25\text{mL}$  was measured. After the exposure to the solution, the polymer film was removed from the solution and the concentration of remaining  $\text{Hg}^{2+}$  was analyzed. The mercury amount adsorbed on the surface of the functionalized polymer was calculated by Eq. (1):

$$Q = C_i - C_e \quad (1)$$

where  $C_e$  and  $C_i$  denote the equilibrium and initial concentrations of  $\text{Hg}^{2+}$  (25  $\mu\text{g}/\text{mL}$ ), respectively [47]. Fig. 4 shows the obtained results of the adsorbed  $\text{Hg}^{2+}$ . It is evident that with increasing the concentration of  $\text{Hg}^{2+}$  in solutions from 0 to 150  $\mu\text{g}/25\text{mL}$ , the amount of  $\text{Hg}^{2+}$  adsorbed by the functionalized cellulose acetate increased linearly. According to the adsorption curve, the functionalized cellulose acetate film has the maximum adsorption capacity of  $\text{Hg}^{2+}$  equal to  $3.41 \times 10^{-3}$  mmol/g.

## 4. Conclusions

One of the most popular poisonous elements in aquatic ecosystems is mercury and the design of a reliable and rapid method for determination of mercury is needed. In this research, an optical sensor was prepared by the functionalization of hydrolyzed cellulose acetate by diphenylcarbazone.

The UV-Vis spectra of the polymer film showed a peak at 480 nm. The maximum adsorption was achieved at pH = 5 and by the decrease in pH, the adsorption decreased. Using the calibration curve, the error in determining the concentration of  $\text{Hg}^{2+}$  was around 6 %. The film exhibited the capability of the adsorption capacity in a wide range of  $\text{Hg}^{2+}$  concentration.

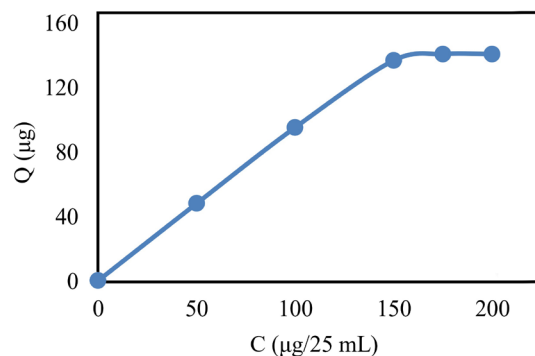


Fig. 5. Hg adsorption of the functionalized cellulose acetate film.

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## Conflict of Interest

All authors declare no conflicts of interest in this paper.

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