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Design and Evaluation of a Mercury (II) Optode Based on Immobilization of 5, 6 Di methyl -1- (4 methyl benzyl) -2- para tolyl-1H-benzimidazole (DMBPTBI) on a Triacetylcellulose Membrane and Determination in Various Samples

A. Mosadeghei Fard[1] and G. H. Vatankhah[1*]

[1] Department of Chemical Engineering, Islamic Azad University, Bushehr Branch, Bushehr, Iran

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ABSTRACT

The characterization of an optical sensor membrane is described for the determination of Hg^{2+} ions based on the immobilization of 5, 6 Di methyl -1- (4 methyl benzyl) -2- para tolyl-1H-benzimidazole (DMBPTBI) on a triacetylcellulose membrane. The membrane responds to mercury ions by changing color reversibly from orange to red in universal buffer solution at pH 2. Under optimum conditions, the proposed membrane displayed a linear range of 0.1-12 μg mL^{-1} with a limit of detection of, 0.02 μg mL^{-1} at a wavelength of 558 nm. The response time of the optode was about 8 -10 min, depending on the concentration of mercury (II) ions. The coefficients of variation (CV) of the sensor response for, 1.0 μg mL^{-1} of Hg(II) was, 1.8% and the CV between seven membranes was 2.3%. The sensor can readily be regenerated with the ethylene diamine solution. The optode is fully reversible and the selectivity of optode to Hg^{2+} ions in universal buffer is relatively good as interferences. The proposed optode was applied successfully for the determination of mercury (II) in various samples.

Keywords: Optode; Hg^{2+}ions; 55, 6 Di methyl -1- (4 methyl benzyl) -2- para tolyl-1H-benzimidazole (DMBPTBI); Ethylene diamine; Triacetylcellulose

1. INTRODUCTION

Mercury is one of the most abundant heavy metals in the environment, and its toxic effects have been recognized for a long time. The mercury content of air, soil and water has been increasing in the past decades, because of the greater utilization of fossil fuels and for the expanded use in industry and agriculture [1]. Due to its dangerous and harmful properties for the health of human being, the determination of mercury is very important for environmental protection [2]. A wide range of analytical methods have been used for the determination of mercury in real samples. These includes spectrophotometry [3], Hg(II) is water-soluble in water and can be converted to methylmercury in the presence of micro-organisms, which is a highly toxic form [4]. Mercury metal can be transported over long distance and may be bio-accumulated in the food chain like fish and interfere with ozone depletion in the arctic. Increased applications of Hg(II) have led to increase in possible risks to the environment, so the removal of Hg(II) becomes crucial. The treatment of waste waters from Hg(II) is one of the growing

[*]Corresponding author: gh.vatankhah@gmail.com

needs in environmental applications. However, several processes are useful to remove these heavy metals from water and wastewater including chemical precipitations, ion exchange, membrane filtration, adsorption flotation, and coagulation flocculation [5,6]. Among them, the wide application of adsorption is emerged from advantages including simplicity, low cost, high efficiency, wide adaptability and availability of different adsorbents [7]. Concern over the distinct toxicity of mercury has stimulated explorations aimed at developing price-favorable, fast, and facile methods to monitor mercury in biological, industrial and food samples [8-10]. These includes spectrophotometry[11], electrochemical techniques: atomic absorption/ emission spectroscopy[12], inductively coupled plasma mass spectrometry (ICP-MS)[13], selective cold vapor atomic fluorescence spectrometry[14], X-ray microanalysis and a variety of potentiometric ion-selective electrodes[15], chemical sensors based on measurements of optical signals are considered as advanced techniques due to their simplicity[16], reasonable selectivity[17], improved sensitivity[18], low detection limit and fieldwork applicability[19]. However these methods have good sensitivity, but they require expensive instruments, well-controlled experimental conditions, and profound sample – making. Optical sensors have drown much attention in analytical chemistry because of their possible application in biology, biotechnology and ecology[20] and because of their advantages such as small size, feasibility of miniaturization, freedom from electrical interference, low cost, good sensitivity and selectivity[21]. Development of optochemical sensors (so called optodes) [22] has been mostly based on the immobilization of the reagent by either physical (adsorption, encapsulation, sol-gel, etc) or chemical (covalent bond) methods and incorporate this in the sensor design. The immobilization can be performed directly on the surface of optical fibers (intrinsic sensors), or on a suitable material which can then act as an interface between the sample and the fibre optic system (extrinsic sensors)[23]. The sensing phase consists of reagent dyes immobilized in organic or inorganic matrices. Reaction with the analyte changes the absorbance or fluorescence behavior of the sensitive layer. Organic dyes and metalochromic indicators, which are used in the spectrophotometric determination of various metals, play a main role in the design of optodes [24].

In this paper the fabrication of an optode for determination of low levels of mercury is described in which the sensing reagent is (DMBPTBI) [25] immobilized on triacetylcellulose membrane. The reaction takes place within few minutes and a color change occurs from orange to red, which is spectroscopically detected in the absorbance mode. The sensor layer can be regenerated instantly and completely with the same carrier solution and the optode is fully reversible. Experimental results showed that, this optode could be used as an effective tool in analyzing the mercury content of various samples such as alloy for dental prosthesis, omega3 tablet, soil, water, fish and vegetables. In table 1 we compare the present optode with other reported optodes for determination of mercury.

2. EXPERIMENTAL

2.1. Reagents

All the reagents such as DMBPTBI and ethylene diamine were supplied from Merck Company. The ligand DMBPTBI solution (1.0×10^{-4} M) was prepared by dissolving 0.0025 g of DMBPTBI in ethanol and diluting to 100 mL. A stock solution of 1000 μg mL^{-1} Hg^{2+} ion was

Table1. Comparison of the proposed optode with other reported optodes for determination of mercury

Reagent mmobilized on membrane	Response Time, min	Linear Renge mol.L^{-1}	Detection limit mol.L^{-1}	RSD %	References
Ditizone on Triacetylcellulose (TAC) membrane	8 - 12	7.5×10^{-4} -3.8×10^{-3}	0.02	3.2	[26]
Sulfanyl phenyl imino on Sol - Gel membrane	3	1.5×10^{-5} -2.0×10^{-2}	1.0×10^{-6}	2.7	[27]
Indigo carmine on Triacetylcellulose (TAC) membrane	8 – 10	2.4×10^{-2} -4.7×10^{-5}	7.2×10^{-6}	3.6	[28]
triazene ((E)-1-(2- ethoxyphenyl)-3-(4-nitrophenyl) triaze-1-ene) on Triacetylcellulose (TAC) membrane	15	7.0×10^{-4} -9.0×10^{-3}	6.4×10^{-7}	1.3	[29]
Rhodamine 6G – P on Triacetylcellulose (TAC) membrane	20	4.9×10^{-6} -2.5×10^{-5}	3.1×10^{-9}	2.2	[30]
Di methyl -1- (4 methyl benzyl) -2- para tolyl-1H-benzimidazole on Triacetylcellulose (TAC) membrane	8 - 10	1.0×10^{-6} -1.2×10^{-5}	0.2×10^{-9}	2.3	New weak

prepared by dissolving 0.0680 gr of $HgCl_2$ (Merck) in distilled water and diluted to the mark in a 50 mL volumetric flask. Universal buffer solutions were prepared from boric acid / acetic acid / phosphoric acid (0.04 M each). The final pH was adjusted by the addition of 0.2M sodium hydroxide. Stock solutions of 6000 μg mL^{-1} of interfering ions were prepared by dissolving appropriate amounts of suitable salts in double distilled water.

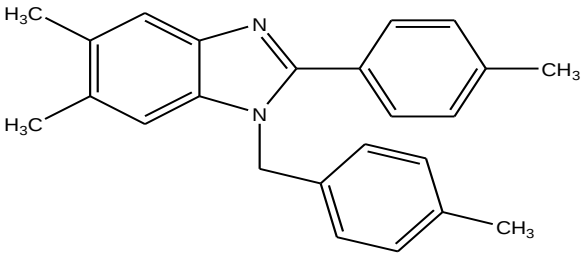
2.2. Apparatuses

A Shimadzu 1601 PC UV-Vis spectrophotometer with a 1cm cell was used for recording all spectra and absorbance measurements. A Jenway 3510 pH-meter which calibrated against two standard buffer solutions at pH 4.0 and 10.0 was used to measure the pH of the solutions.

A Hamilton syringe (10 μl) was used to deliver small volumes of reagent into the cell. The reference cell was contained a membrane without any indicator. All measurements were made in the absorbance mode.

2.3. Synthesis of Ligand DMBPTBI.

A mixture of 4 methyl benzaldehyd (2mmol), 4,5 di methyl 1,2 orto phenylene diamine (1mmol) and was added silica-bonded N-propylsulfamic acid (0.1 g) in solvent free condition at 80^{0C} for the appropriate time. and heated at 80^{0C} in an oil bath. After completion of the reaction, as indicated by Thin Layer Chromatography (TLC), the reaction mixture was filtered and remaining washed with warm ethanol (2-5mL). After cooling, the corresponding products were obtained which purified by recrystallization from hot ethanol. The recovered catalyst was dried and reused for subsequent runs. The product was purified by column chromatography on silica gel [eluent: EtOAc/n-hexane (3:7)] to give pure 5, 6 Di methyl -1- (4 methyl benzyl) -2- para tolyl-1H-benzimidazole (DMBPTBI) in 90% yield. (Scheme 1) was synthesized according to literature [25].



Schem 1. Mp(°C)= 177
IR(KBr): 3020, 2900, 1610, 1507, 1436, 1381 (Cm^{-1}).
^{1}H NMR:(400MHz , $CDCl_3$): δ 1.95 (s, 6H), 2.50 (s, 6H), 5.39 (s, 2H) , 7.13 (d,2 H, J=8.34 Hz), 7.29 (d, 2H, J=8.34 Hz), 7.34-7.41 (m,2H,), 7.49 (d, 2H, J=8.34 Hz).
^{13}C NMR(125MHz , $CDCl_3$): δ 20.35, 20.62, 21.12, 21.45, 48.11, 110.62, 119.64, 125.37, 125.78, 126.90, 129.10, 129.32, 129.44, 129.73, 132.27, 134.50, 137.37, 139.98,153.26.

2.4. Preparation of the sensor membrane

The immobilized indicator on triacetylcellulose was prepared according to the following procedure. The transparent triacetylcellulose membranes were produced from waste photographic film tapes that were previously treated with commercial sodium hypochlorite for several seconds to remove colored gelatinous layers. The films were treated with a clear solution of (DMBPTBI) (20 mg) in 20 mL ethylene diamine for 5-7 min at ambient temperature. Then they were washed with water for removing ethylene diamine and loosely trapped indicator. The membranes were finally washed with detergent solutions and water. Prepared membranes were kept under water when not in use [26].

2.5. Samples preparation

2.5.1. Water samples

River water, natural mineral and spring water samples were collected in acid-leached polyethylene bottles. Hg water samples was collected from (Bushehr, Iran). Filtered through 0.45 μm Millipore cellulose acetate membrane filters to remove particles and diluted with distilled water to the ratio of 1:1. The samples were then adjusted to pH3.5 and immediately analyzed [31].

2.5.2. Soil samples

Accurately weighed 1.0 g of soil samples from near Bushehr petrochemical center (less than 200 meshes), dried at 110 °C were poured into a 250 mL beaker and 10 ml concentrated nitric acid was added to it. The mixture was gently heated under a hood until drying. After complete dry and the mixture was cooled to room temperature, A second 10-mLportion of concentrated nitric acid was added and the procedure. Then 10 mL concentrated hydrochloric acid was added to the beaker and the mixture was gently heated until complete drying. After cooling, the residue was dissolved in 10 mL of 1 M HCl and the solution was then filtered into a 100 mL calibrated flask, using a syringe filter (0.45 μ m pore sized). The sample was neutralized by proper amounts of a 1 M NaOH solution and finally diluted to the mark with water [32].

2.6. Absorbance measurements

The prepared membranes were put in a buffer solution of pH 2 for 30 min to reach equilibrium. Then membrane was placed vertically inside in sample cuvette containing 3 mL buffer solution of pH 2, and a blank membrane (without indicator) was put in the reference cuvette containing the buffer solution. The sample cell was finally titrated with mercury (II) ions solution and the absorbance value of system was measured over the wavelength range of 400- 800 nm after 10 min (equilibrium time). Absorbance of

membrane before and after the sample solution was added, at 558 nm and 473 nm was measured.

3. RESULTS AND DISCUSSION

3.1. Properties of DMBPTBI as a chromoionophore

The complexation reactions of DMBPTBI as a chromoionophore with metal ions are well known to be strongly dependent on the pH [33]. The extraction of Hg (II) from the aqueous sample solution into the membrane phase and its complexation by the indicator (DMBPTBI) involved the loss of one proton from the hydroxyl group of one DMBPTBI molecule. This ion-exchange process depends on the electroneutrality conditions in the organic membrane phase. The overall equilibrium between the aqueous sample solution (aq) and the organic membrane phase (org) is:

$$HL\ (org) + Hg^{2+}(aq) + 2X\ (aq) \leftrightarrow HgLX\ (org) + X\ (aq) + H^{+}(aq)$$

where HL is DMBPTBI. It may be assumed that a 1:1 Hg (II) - DMBPTBI complex is formed in the optode membrane since this was the stoichiometry found in aqueous solution for DMBPTBI [34].

3.2. Spectral characteristics

Figure 1 shows the absorption spectra of free and immobilized DMBPTBI, which were obtained after being equilibrated in buffer solution (pH 2) containing different concentrations of mercury. The spectral change (increase in absorption band at 558 nm and decrease in absorption band at 473 nm) is result of increase of mercury ions concentration in the membrane, which is due to the extraction of mercury ion into the membrane and complex formation. The absorbance maxima of the immobilized DMBPTBI are located at 558 nm and those of free dye at 550 nm. It is important to note that the absorption spectra of immobilized dye is red shift in comparison to those of their soluble form (558 instead 550 nm). This suggests that the structural conformation of the immobilized dye is more planar than that of its solution analogue [35]. The wavelength of 558 nm was selected for future studies because of higher selectivity and sensitivity at this wavelength.

3.3. Effect of pH on response of the optode

Figure 2 shows the effect of pH values on the response of the optode membrane. The absorbance measurements were made for 1.5 μg mL-1 mercury ion in the pH range of 1 – 5 at 558 nm. The absorbance measurements were expressed as absorbance difference, which was defined as the difference between the absorbance of the immobilized DMBPTBI alone and the absorbance of the Hg - DMBPTBI complex at 558 nm. As can be seen in Fig.2, the pH increases from 1 to 5.0 as the value of the difference in absorbance increases. At pH values more than 2, the response decreases. This phenomenon might be due to the fact that at lower pH values (pH<2), complexation is weak. At pH values higher than 2, Hg^{2+} forms different hydroxide species which make it unable to form complex with DMBPTBI [36]. Thus, pH=2 was selected for furthure studies.

3.4. Response time

The response time of the optode is controlled by the time required for the analyte to diffuse from the bulk of the solution to the membrane interface and to associate with the indicator [37]. The response time of the present optode was tested by recording the absorbance change at 558 nm from a pure buffer (pH 2) to a buffered mercury solution of 12 μg mL^{-1}. The membrane was found to reach 95% of

the final signal at 8-10 min depending on the concentration of the Hg^{2+} (Fig. 3). In general, the response time is lower in concentrated solutions than dilute solutions.

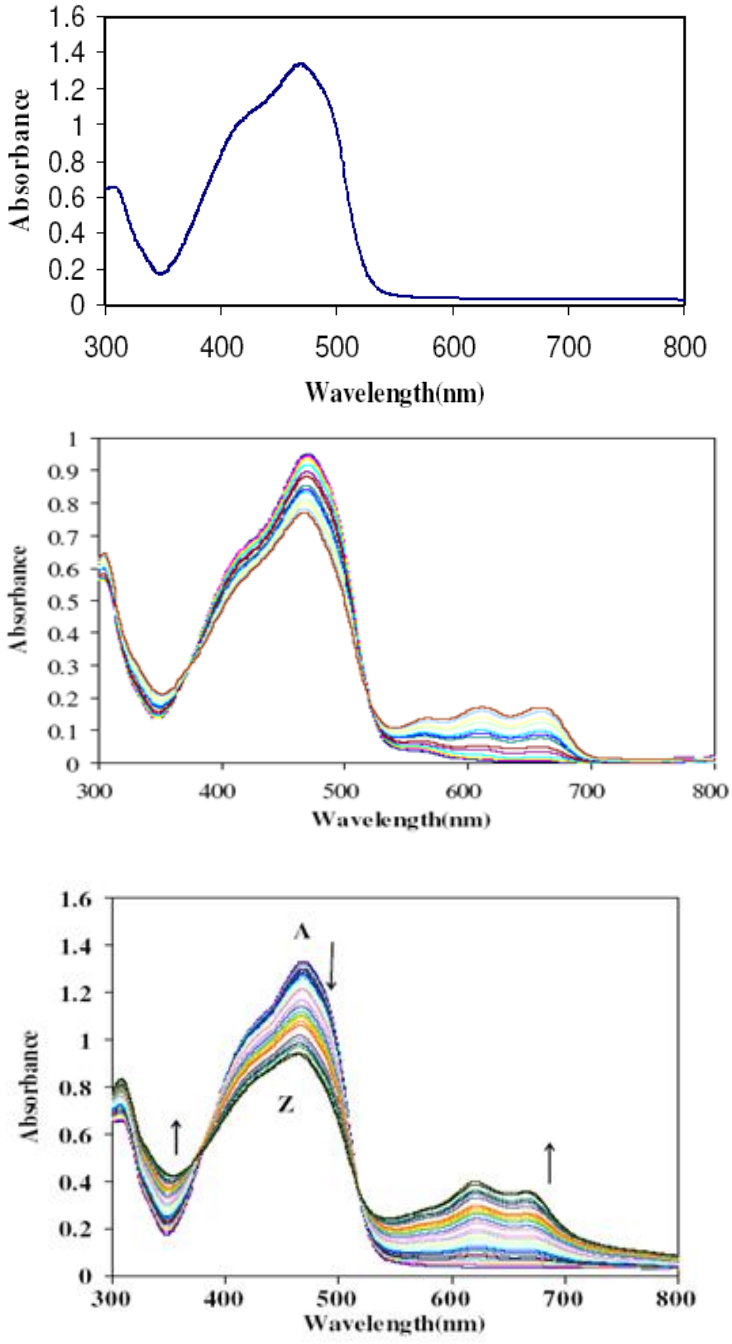


Fig.1. **(a)** Absorption spectra for a 1.0×10^{-4} M DMBPTBI solution in the presence of (0 - 28 μg mL^{-1}) Hg^{2+} at pH 2 (A-Z show increase in concentration of Hg^{2+} by addition of 1.7 ng ml^{-1} Hg^{2+} in each interval) **(b)** Absorption spectra of optode film in the presence of (0-28 μg mL-1) Hg^{2+} at pH 2. (A-Z show increase in concentration of Hg^{2+} by addition of 2.3 ng ml^{-1} Hg^{2+} in each.

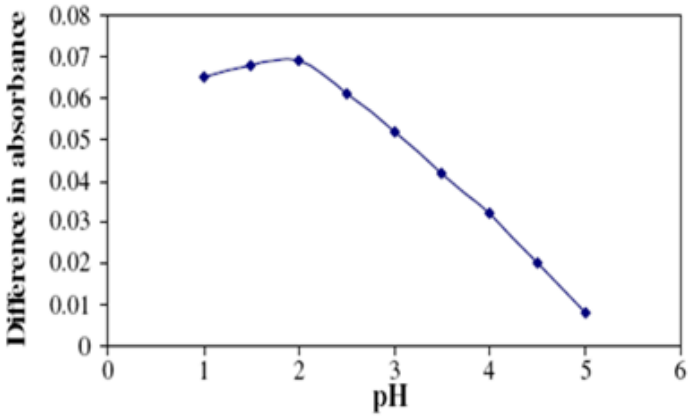


Fig.2. Effect of pH on the response of membrane in the presence of 1.5 μg ml^{-1} mercury at 558 nm.

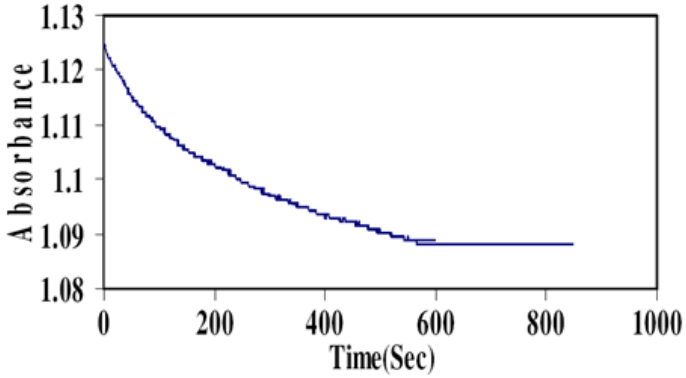


Fig.3. Typical response curve of the film optode at 558 nm as a function of time when film was exposed to 12 ng mL^{-1} Hg^{2+} ion.

3.5. Dynamic range

Fig. 4 shows the absorbance signals of the optode film to various concentrations of Hg^{2+} ions in the range of 0-14 μg mL^{-1} that exhibits a linear range from 0.1 to 12 μg mL^{-1} and 14 μg mL^{-1} was found as the concentration of Hg^{2+} ion that saturates the film.

The regression equation was: $\Delta A = 0.0068\ C + 0.0783$ with a correlation coefficient of 0.9991, where ΔA is the increase in absorbance of the film at 558 nm for a fixed time of 10 min, the C is the concentration of Hg^{2+} in μg mL^{-1}.

The detection limit which was estimated as the concentration of analyte producing an analytical signal equal to three times the standard deviation of the blank signal was found to be 0.02 ng mL^{-1}.

3.6. Regeneration of the optode membrane

Some reagent including HCl, NaOH, EDTA, H_2SO_4, HNO_3, SCN, ethylene diamine and uric acid were studied as regenerating reagents. It was found that the best result was obtained by applying ethylene diamine which gave short membrane regeneration times (10-30 S). After this regeneration and for the next mercury concentration measurement, the optode should be placed in buffer (pH 2) for 10-15 min.

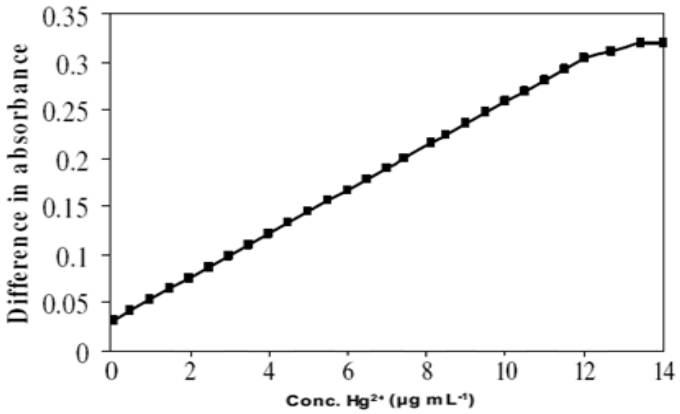


Fig.4. Calibration curve of the membrane at 558 nm in the range of 0-14 µg mL^{-1}.

3.7. Selectivity

The major property of the optode membrane, its selectivity, reflects its relative response to the analyte ion and to the other ions present in solution. Thus, the influence of a number of common metal ions on the absorbance of the proposed Hg^{2+} [38] optical sensor was carried out. To determine of selectivity of the optode membrane, the membrane was tested for the determination of 10.0 µg $mL^{-1}$of Hg^{2+} ions in the presence of some metal ions, including Cd^{2+}, Ni^{2+}, Cu^{2+}, Pb^{2+}, Co^{2+}, Sn^{2+}, Ag^{+}, Fe^{2+}, Zn^{2+} and Fe^{3+} The species were considered as interference if they caused an analytical variation of 5% or more when compared to the analytical signal obtained in the absence of the interfering species. At the applied pH value, no interference was observed from even 50-fold excess of the interfering ions.

3.8. Reproducibility and Repeatability

These parameters of the sensing phase membrane in the determination of mercury was evaluated by repeatedly exposing the sensing phase membrane to a 1.0 µg mL^{-1} mercury solution and a 1.0 × 10^{-4}M ethylene diamine solution. The repeatability was evaluated by performing seven determinations with the same standard solution of Hg^{2+}. The relative standard deviation (R.S.D) for the response of one membrane towards a 1 µg mL^{-1} of mercury solution was 1.8% (n=7).

The reproducibility of the response of different membranes was also studied. Seven different membranes were prepared from the same batch and they were evaluated by performing the determination of 1 µg mL^{-1} mercury. The relative standard deviation for the response of between membranes was 2.3%. The results show that the reproducibility is satisfactory and the membrane could be regenerated easily by using ethylene diamine solution.

3.9. Life time and stability

The lifetime of membrane was determined by adding a buffer solution (pH 2) in a cuvette including the film. The signal was recorded at wavelength of 558 nm over a period of about 10 h. No significant loss of the indicator and no drift in signal occur during this time and the sensing phase was stable over the experiment with no leaching of the indicator. It should be noted at pH 2, DMBPTBI exists its neutral form (yellow). Additionally the stability of response of the film was investigated over six weeks under water, which indicated that the film was stable over this period[39].

3.10. Accuracy and Analytical applications

The proposed optical sensor was found to work well under laboratory conditions. To test the practical application of the present sensor, The mercury content of water and soil digest were analyzed by standard addition method and then determined by the proposed optode (table 2). From the data given in Table 2 this paper is readily seen that the present optical sensor is useful for the determination of mercury in real samples.

3.11. Determination of mercury (II) in an alloy

The certified composition of the alloy was Ag 34.38%, Zn 16.05%, Cu 6.88% and Hg 42.69%. The average value of five determination by the proposed optode was 41.52% mercury (n=5, standard deviation = ± 0.83). The recovery of the experimental mean obtaind in relation to the known certified value was 97.3%.

4. CONCLUSION

The optode described in this work is easily prepared and provides a simple and inexpensive means for the determination of Hg^{2+} ions. The membrane responds to mercury ions by changing color reversibly from orange to red. The sensor can be regenerated readily with ethylene diamine solution and has a long life time. The response of the optede was reproducible and the optode presented a good selevtivity for Hg^{2+} over other metal ions. Since the sensor does not require solvent extraction, it can compete with standard optical fibers. The sensor can be applied for the analysis of various samples. Also by comparison of this method with some of the other sensors for determination of Hg^{2+} ions, has been recognized that the proposed method has more sensitive and selective. It has wide dynamic range and even more easy fabrication and low cost.

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REFERENCES

[1] A. Ensafi, M. Fouladgar, Sens. Actuators B 136 (2009) 326.
[2] R. Voegborlo, A. El-Methnani, M. Abedin, Food Chem. 67(1999) 341.
[3] H. Shafiekhani, F. Nezam, S.H. Bahar, J. Serb. Chem. Soc. 82 (2017) 317.
[4] P.A. Ariya, et al. The Arctic: A Sink for Mercury. Tellus B, 56 (2004) 403.
[5] S. Malamisa, E. Katsoua, E. Journal of Hazardous Materials, 252-253 (2013) 461.
[6] J.D. Clercq, International Journal of Industrial Chemistry 17 (2012) 3.
[7] S. Abedi, H. ZavvarMousavi, A. Asghari, Desalin. Water Treat. 31 (2015) 9.

Table2. Determination of Hg^{2+} in soil and water samples

Sample	Added ($\mu g\ mL^{-1}$)	Founded ($\mu g\ mL^{-1}$)	RSD %	Recovery %
Tap water	0	10.33	1.1	---
	20	16.19	1.8	103.1
River water	0	6.18	1.1	---
	20	16.43	1.3	95.3
Soil	0	2.21	2.1	---
	20	16.69	1.8	102.4

[8] G. K. Darbha, A. Ray, P. C. Ray, ACS Nano 1 (2007) 208.
[9] B. Tang, L. J. Cui, K. H. Xu, L. L. Tong, G. W. Yang, L. G. An, ChemBioChem 9 (2008) 1159.
[10] M. Shamsipur, M. Hosseini, K. Alizadeh, N. Alizadeh, A. Yari, C. Caltagirone, V. Lippolis, Anal. Chim. Acta 533 (2005) 17.
[11] H. Tavallali, M. Yazdandoust, Eurasian Journal of Analytical Chemistry, 3 (2008) 284.
[12] C. Y. Li, X. B. Zhang, L. Qiao, Y. Zhao, C. M. He, S. Y. Huan, L. M. Lu, L. X. Jian, G. L. Shen, R. Q. Yu, Anal. Chem. 81 (2009) 9993.
[13] J. V. Ros-Lis, M. D. Marcos, R. Mártinez-Máñez, K. Rurack, J. Soto, Angew. Chem. Int. Ed. 44 (2005) 4405.
[14] E. M. Nolan, S. J. Lippard, Chem. Rev. 108 (2008) 3443.
[15] M. H. Lee, S. W. Lee, S. H. Kim, C. Kang, J. S. Kim, Org. Lett. 11 (2009) 2101.
[16] B. Leng, L. Zou, J. Jiang, H. Tian, Sens. Actuators B 140 (2009) 162.
[17] C. Sanchez-Pedreno, J. Ortuno, M. Albero, M. Garcia, M. Valero, Anal. Chim. Acta 414 (2000) 195.
[18] B. Kuswandi, R. Narayanaswamy, J. Environ. Monit. 1 (1999) 109.
[19] W. H. Chan, R. H. Yang, K. M. Wang, Anal. Chim. Acta 444 (2001) 261.
[20] A. Clark, R. Kopelman, R. Tjalkens, M.A. Philbert. Anal. Chem. 71 (1999) 4837.
[21] A. Afkhami, N. Sarlak, Sens. Acuators B Chemical 124 (2007) 285.
[22] [22] W. Simon, Technology and application of chemical sensors and biosensors-Quo-Vadis .Chimia 44 (1990) 395.
[23] W.R. Seitz, Chemical sensors based on immobilized indicators and fiber optics, CRC Crit. Rev. Anal. Chem. 19 (1998) 135.
[24] M. Amini, B. Khezr, A. Firooz, Sens. Actuators B 131 (2008) 470.
[25] K. Niknam, D. Saberi, J. Can. J. Chem. 88 (2010) 167.
[26] A. Safavi, M. Bagheri, Sens. Actuators B 90 (2004) 143.
[27] K. Alizadeh, R. Parooi, P. Hashemi, B. Rezaei, M. R. Ganjali, J. Hazard. Mater.186 (2011) 1794.
[28] H. Tavallali, E. Shaabanpur, P. Vahdati, Spectrochim. Acta A 89 (2012) 216.
[29] H. Tavallali, H. Shafiekhani, M. K. Rofouei, M. Payehghadr, J. Braz. Chem. Soc. 25 (2014) 861.
[30] N. Thakur, S. A. Kumar, K. A. Kumar, A. K. Pandey, S. D. Kumar, A. Reddy, Sens. Actuators, 11 (2015) 346.
[31] M. R.; Froudi Jahromi, S. Zandifar, E. Pakdaman, F. TavakoliS. Bagheri. J. Phys. Theor. Chem. IAU Iran. 12 (2016) 297-306.
[32] V. Mrvic, M. Jakovljevic, D. Stevanovic, D. Cakmak, M. Zdravkovic, J. Serb. Chem. Soc. 73 (2008) 673.
[33] N. Alizadeh, A. Moemeni, M. Shamsipour, Anal. Chem. 464 (2002) 187.
[34] T.P. Jones, M.D. Porter, Anal. Chem. 60 (1988) 404.
[35] J. Lurie, Handbook of Analytical Chemistry, English translated by: N. Bobrov, Moscow (1978).
[36] A. Safavi, M. Sadeghi, Sens. Actuators 107 (2005) 53.
[37] A. Safavi, M. Sadeghi, Talanta 71 (2007) 339.
[38] C. Sanchez- Pedreno, J.A. Ortuno, M.I. Albero, M.S. Garcia, M. V. Valero, Anal. Chem. Acta 414 (2000) 195.
[39] B. Kusvandi, R. Narayanaswamy, Sens. Actuators B 74 (2001) 131.