Optical membrane for visual screening of mercury determination in drinking water based on polyvinyl chloride and dioctyl sebacate

Choirul Amri, Sri Puji Ganefati, Sardjito Eko Windarso, Adib Suyanto

Department of Environmental Health, Ministry of Health Health Polytechnic Yogyakarta, Yogyakarta, Indonesia

Abstract

This study developed an optical membrane for detecting Hg pollution in water, using polyvinyl chloride and dioctyl sebacate (PVC-DOS). The primary aim was to assess the suitability of PVC-DOS optical membranes as a screening tool for Hg in drinking water. Specific objectives included determining optimal conditions (wavelength, reaction pH, response time) for Hg determination with PVC-DOS-based optical membranes and evaluating the visual performance (absolute and difference thresholds) for detecting Hg in drinking water. Laboratory experiments involved preparing PVC-DOS-based optical membranes composed of 1,5-diphenylcarbazone, PVC, and DOS mounted on mica paper holes. Optimisation of wavelength, response time, and reaction pH was performed (each five times). Absolute and difference thresholds were established. Optimal conditions were found to be a reaction pH of 6-9, a membrane response time of 45 minutes, and a purple Hg-positive membrane (wavelength 575-580 nm). The visual optical membrane method demonstrated an absolute threshold of 0.4 µg/L and a difference threshold of 0.5 µg/L. PVC-DOS-based optical membranes can effectively screen for Hg in water. This method involves dipping an optical membrane stick and comparing the result with a color standard.

Correspondence: Choirul Amri, Department of Environmental Health, Politeknik Kesehatan Kemenkes Yogyakarta, Jl. Tatabumi no. 3 Banyuraden Gamping Sleman Yogyakarta 55293 Indonesia.
E-mail: choirul.amri@poltekkesjogja.ac.id

Key word: analysis; membrane; mercury; water

Contributions: CA Conceptualization, Data Analysis, Methodology, Validation, Visualization, Writing – Original Draft, Review & Editing; SPG Methodology, Validation, and Writing – Original Draft, Review & Editing; SEW Methodology, Analysis, Validation, and Writing – Original Draft, Review & Editing; AS Methodology, Visualisation, Writing – Review & Editing.

Conflict of interest: the authors declare no conflict of interest.

Ethics approval and consent to participate: none.

Funding: this research did not receive external funding.

Availability of data and materials: all data generated or analysed during this study are included in this published article.

Received: 12 September 2023.
Accepted: 14 November 2023.
Early access: 24 November 2023.

Healthcare in Low-resource Settings 2023; 11:11781
doi:10.4081/hls.2023.11781

Introduction

The spectrophotometric and atomic absorption spectrophotometric methods are commonly employed to analyse mercury (Hg) in water.[1–6] However, the high cost associated with this analysis[7] limits its accessibility, and it is considered impractical by many environmental practitioners. Therefore, there is a need, especially among environmental practitioners, for an affordable and practical method to assess Hg pollution in drinking water.[5,8–12]

Numerous studies have explored the use of a specialised material known as an "Optical Membrane," constructed from Polyvinyl Chloride and Dioctyl Sebacate (PVC-DOS), to detect excessive mercury (Hg) levels in drinking water. This innovative approach has the advantage of being user-friendly and cost-effective, making it accessible to environmental experts and the general public.[13] These membranes act as miniature sensors. Some studies have developed highly sensitive sensors capable of detecting even trace amounts of mercury and lead without the need for collecting large water samples initially.[14] Other research endeavors have produced similar sensors using different materials, demonstrating their effectiveness in mercury testing for drinking water.[15] Additionally, another study devised a sensor that can distinguish mercury even in the presence of other metals.[16] These studies collectively highlight the effectiveness of these specialised sensors in accurately and easily detecting mercury in water, especially in a drinking water context. This relatively new method, with minimal prior development, offers low costs and simplicity, making it an accessible solution. Importantly, this method does not require specialised knowledge, rendering it suitable for use by environmental practitioners and the general population. Furthermore, this method allows for visual readings in the field, and it represents a novel area of research.

In order to optimise the use of the optical membrane for determining mercury (Hg) in water, it is essential to establish the ideal testing conditions.[17] The research has identified the optimal conditions, including the reaction pH and membrane response time.[18,19] To comprehensively assess the method's performance as a tool for mercury (Hg) testing in water, various performance metrics, such as the absolute threshold and difference threshold, must be determined. Therefore, this study aimed to identify the optimal conditions for PVC-DOS-based optical membranes, encompassing factors like wavelength, reaction pH, and response time. Additionally, it evaluates the method's performance visually, considering parameters like absolute threshold and difference threshold.

Materials and Methods

In alignment with the research objectives, this study aims to determine the optimal conditions for PVC-DOS-based optical membranes and assess their performance in determining mercury (Hg) in water. Each optimisation was conducted five times.

Preparation of an optical membrane based on PVC-DOS

The membrane solution comprised the following components: 5% 1,5-diphenylcarbazone (DPC), 30% PVC, and 65% DOS. In 2 mL of tetrahydrofuran (THF), 100 mg of this membrane composition were dissolved14,20. Mica sheets with a thickness of 0.4 mm were cut into 0.7 x 5.0 cm squares. A hole punch with a diameter of 0.5 cm was used to create a hole 0.9 cm from the end of each sheet. The membrane solution was dripped into the holes on the mica sheet, and after drying, the mica sheet was removed, leaving behind a transparent membrane.

Optimisation of wavelength

The optical membrane was immersed in 5 mL of Hg solution (1.0 μg/L) in a test tube for a few minutes until it turned red-purple. A spectrophotometer with a wavelength range of 400–700 nm was utilised to measure the absorbance of the optical membrane, with measurements taken at 5 nm intervals.

Optimisation of response time

The optical membrane was immersed in a 1.0 μg/L Hg solution for various durations (5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, and 60 minutes). A spectrophotometer, set at the maximum wavelength determined during wavelength optimisation, was used to measure the absorbance of each optical membrane.

Optimisation of pH

The optical membrane was immersed in 12 test tubes, each containing 5 mL of Hg solution (1.0 μg/L), for varying durations (5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, and 60 minutes). The absorbance of each optical membrane was read using a spectrophotometer at the wavelength optimised earlier during wavelength determination.

Results

Optimisation of wavelength

The results of wavelength optimisation for measuring the absorbance of the 1.0 μg/L Hg solution are listed in Table 1. The optimal absorbance is achieved at a wavelength of 575-580 nm.

Optimisation of response time

Optimisation results for response time are presented in Table 2. The response time for the optical membrane to detect Hg is 45 minutes.

Table 1. Results of wavelength (λ) optimisation.

λ (nm)	Abs	λ (nm)	Abs	λ (nm)	Abs	λ (nm)	Abs
400	0.000	550	0.442	585	0.492	640	0.135
430	0.022	560	0.480	590	0.485	655	0.081
460	0.055	565	0.490	595	0.470	670	0.058
490	0.116	570	0.497	600	0.454	685	0.042
520	0.250	575	0.501	610	0.409	700	0.032
535	0.346	580	0.501	625	0.256		

Table 2. Results of response time optical membrane.

Time (minute)	Abs-1	Abs-2	Abs-3	Abs-4	Abs-5	Abs average
5	0.094	0.124	0.099	0.102	0.108	0.103
10	0.253	0.222	0.214	0.238	0.246	0.235
15	0.318	0.312	0.320	0.336	0.339	0.325
20	0.388	0.390	0.406	0.410	0.417	0.402
25	0.540	0.528	0.514	0.519	0.520	0.524
30	0.597	0.605	0.628	0.622	0.613	0.613
35	0.690	0.659	0.668	0.679	0.672	0.674
40	0.757	0.749	0.743	0.735	0.729	0.743
45	0.782	0.754	0.774	0.762	0.768	0.768
50	0.749	0.762	0.756	0.781	0.769	0.763
55	0.769	0.783	0.754	0.763	0.796	0.768
60	0.784	0.762	0.759	0.776	0.769	0.770

Optimisation of pH

Optimisation results for the pH of the optical membrane reaction are presented in Table 3. The optical membrane reaction for detecting Hg occurs at an optimum pH of 6-9.

Discussion

For varying durations, the optical membrane was immersed in a 1.0 µg/L Hg solution (5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, and 60 minutes). A spectrophotometer, set at the maximum wavelength determined during the optimisation process, was used to measure the absorbance of each optical membrane.

Optimum wavelength

The optimum wavelength is the one at which electronic excitation occurs while absorbing the most energy. It is determined by the energy required to excite an electron from the ground level to an excited level.[20,21] Identifying the correct wavelength is crucial to prevent measurement errors. If the wavelength used is too short, it will generate excessive energy, which can break molecular bonds. On the other hand, if the wavelength is too long, the energy produced is insufficient to excite electrons from lower to higher energy levels. Selecting the appropriate wavelength enhances sensitivity, as small changes in absorbance at these wavelengths increase sensitivity.[22,23]

A purple complex is formed when a PVC-DOS-based optical membrane reacts with Hg. DOS, in addition to serving as a plasticiser, also acts as an organic solvent in the membrane.[7,24] To determine the precise wavelength of the complex in the solvent on the optical membrane, wavelength optimisation was conducted within the 400–700 nm range. Figure 1 illustrates the wavelength spectra of the reaction product complex, with the maximum wavelength occurring at 575–580 nm.

The pH of the complex formation reaction

The pH of the reaction determines whether or not a complex compound is formed between 1,5-diphenylcarbazone and Hg.[25,26] Therefore, the pH of the reaction must be optimised to determine the pH at which complex compound formation can occur. Figure 2 illustrates the results of optimising the pH of the reaction.

The optimal pH range for the reaction between Hg and a PVC-DOS-based optical membrane is displayed in Figure 2. Given that most water falls within the normal pH range of 6-9, detecting Hg in water is highly advantageous when the pH conditions are within the optimum range of 6–9. However, it is advisable to check the pH of the sample water before conducting the determination. If the pH is not within the range of 6–9, it should be adjusted to ensure that the water's pH falls within that range.

Table 3. Results of pH optimisation

pH average	Abs-1	Abs-2	Abs-3	Abs-4	Abs-5	Abs
1	0.099	0.108	0.112	0.103	0.106	0.106
2	0.312	0.299	0.304	0.307	0.316	0.308
3	0.397	0.402	0.408	0.412	0.405	0.405
4	0.587	0.572	0.581	0.578	0.593	0.582
5	0.732	0.729	0.698	0.725	0.710	0.719
6	0.765	0.773	0.758	0.770	0.778	0.769
7	0.772	0.764	0.768	0.782	0.785	0.774
8	0.771	0.759	0.770	0.782	0.769	0.770
9	0.762	0.784	0.774	0.760	0.759	0.768
10	0.725	0.712	0.709	0.716	0.712	0.715
11	0.528	0.508	0.517	0.509	0.532	0.519
12	0.286	0.292	0.306	0.302	0.291	0.295
13	0.135	0.122	0.132	0.118	0.138	0.129

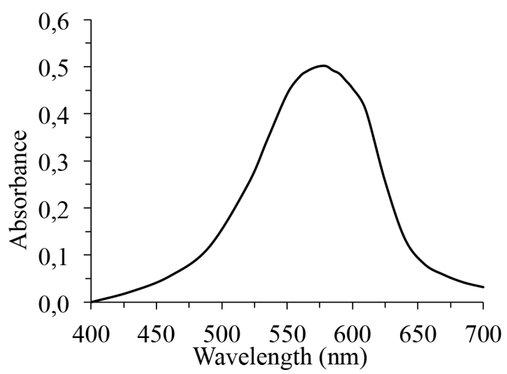

Figure 1. Wavelength spectra of reaction product complexes in PVC-DOS-based optical membranes.

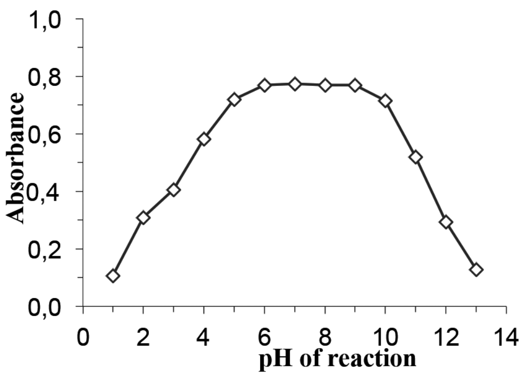

Figure 2. The complex absorbance at various reaction pH at a Hg concentration of 1.0 µg/L in water.

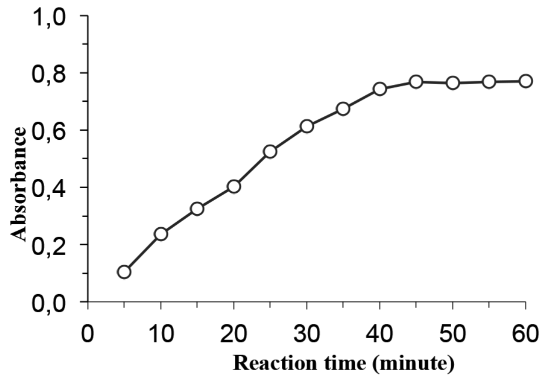

Figure 3. At a Hg concentration of 1.0 μg/L, membrane response time and absorbance were measured.

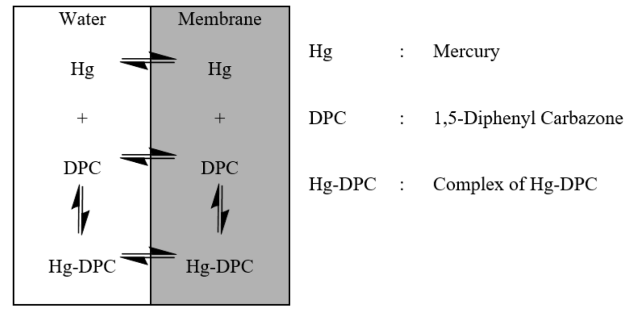

Figure 4. At a Hg concentration of 1.0 μg/L, membrane response time and absorbance were measured.

Response time of the membrane

When a chemical compound reacts with another, one of three outcomes can occur: i) no reaction, ii) an immediate reaction, or iii) a delayed reaction. To determine the time required for the reaction between the optical membrane and Hg to form a complete complex, it is necessary to optimise the reaction time or membrane response time. In this study, the response refers to the action of the membrane in the presence of Hg in water, resulting in the formation of a colored complex. The response time is the duration from the moment the membrane is immersed in an Hg-containing solution until a specific time is reached, at which point a relatively constant absorbance and color are produced. Figure 3 illustrates the membrane response time and absorbance at a concentration of 1.0 μg/L Hg. The response time in this membrane application is relatively long, approximately 45 minutes. This extended duration is attributed to the fact that the complex formation reaction occurs primarily on the membrane's surface in distinct phases, namely the aqueous phase and the organic phase. Figure 4 provides a model that can elucidate the potential of a complex formation reaction on the membrane's surface, including: i) it is improbable that Hg will penetrate the membrane and react within it; and ii) a reaction takes place on the membrane surface, and the resulting complex enters the membrane, which is the more plausible scenario.

Performance and standards for visual optical membranes

The determination of Hg using this method is essentially the same as the optical membrane method using spectrophotometry, except that the observation is done visually, i.e., directly using the sense of sight. Because of the absorption of certain wavelengths of light by a substance, the sense of sight can distinguish colors and color intensities. The color produced by the eye's impression is not the color absorbed by the substance, but rather the color that is reflected. The complex formed on the PVC-DOS membrane absorbs light at a wavelength of 575–580 nm, which corresponds to the visible spectrum's green color. As a result, the complex absorbs green light while reflecting light of other wavelengths. The color evoked by the eye's impression is violet, the complementary color of green.

This study's analysis by visual observation of color is intended to make it easier for ordinary people to perform Hg analysis with optical membranes.[27] Observation with a spectrophotometer is possible for those who have the necessary equipment and special expertise in its use and maintenance; however, it is also costly. The optical membrane method, which is observed visually, has many advantages for ordinary people because it does not require equipment or special skills, is simple to perform, and can eliminate measurement errors caused by the use of equipment. As a comparison, this method necessitates a set of color standards. It is hoped that the row of color standards will be able to distinguish between concentrations from one another. A different threshold test is required for this purpose. According to this test, the smallest difference in Hg levels that can still be clearly distinguished is 0.5 μg/L, while the lowest Hg concentration that can still be visually detected with the optical membrane (absolute threshold) is 0.4 μg/L. Based on the data obtained in this research, when using optical membranes for measuring Hg in water, it is necessary to ensure that the water is at a pH of 6-9 and that the optical membrane immersion time is at least 45 minutes.

Conclusions

The optimal conditions for determining Hg in water using PVC-DOS-based optical membranes were as follows: wavelengths of 575–580 nm, a reaction pH of 6–9, and a membrane response time of 45 minutes. The optical membrane method for determining Hg in water has a visual performance with an absolute threshold of 0.4 μg/L and a difference threshold of 0.5 μg/L. Optical membranes based on PVC-DOS can be used as a screening test tool for determining Hg in water. To utilise this method effectively, it is necessary to ensure that the water is within the pH range of 6-9 and that the optical membrane immersion time is at least 45 minutes. Subsequently, the color should be compared with the standard visually.

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