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Synthesis Dithizone-Immobilized in Polyvinyl Chloride Membranes for Copper Detection in Water

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Abstract

A simple, cost-effective, and environmentally friendly analytical method is needed to determine Cu (II) levels in water. Many methods have been developed by immobilizing dithizone in a polyvinyl chloride (PVC) matrix with dioctyl phthalate (DOP) as a plasticizer in a tetrahydrofuran (THF) solvent. However, the optimal composition of PVC, DOP, and THF has not been determined. The purposes of this study were to determine the optimal composition of dithizone, PVC, and DOP for the sensor membranes, evaluate the performance of the chemical sensors in detecting Cu (II) ions, and measure the copper content in conventional drinking water. The research began with the fabrication of sensor membranes, followed by absorbance testing, and concluded with method validation through characterization. Adsorption of Cu (II) caused the membrane colour to change from yellow to reddish orange, with maximum absorbance observed at 427 nm. The sensor membrane exhibited the best response to Cu (II) ions at pH 2.8. A linear calibration curve for Cu (II) was obtained in the concentration range of 0-0.6 ppm, with an R^2 value of 0.9924. The limit of detection was 1.9881 x 10^{-3} mg L^{-1}, and the limit of quantification was 6.0245 x 10^{-3} mg L^{-1}. The molar absorptivity was 9.4831 x 10^4 L mol^{-1} cm^{-1}. The proposed sensor membrane was used to measure Cu (II) in drinking water employing the internal standard addition method, with observed recoveries ranging from 98.63% to 100.29%. The copper levels in the drinking water samples tested in this study did not exceed the drinking water quality standards set by PERMENKES RI number 492/PER/IV/2010.

Keywords: sensor membrane, dithizone, validation method, polyvinyl chloride.

1. Introduction

Water is a crucial component for human life, as it takes two liters of water daily to sustain human health. It contains chemicals that are beneficial for the human body. The composition and levels of these chemical substances can vary depending on the environmental conditions of the water source [1]. Hence, there is a growing demand for clean water to meet these needs. In Jakarta, finding clean water is challenging, prompting people to rely on refill or bottled drinking water. The criteria for good quality drinking water include being odorless, colourless, tasteless, free from heavy metals, and free from microorganisms [2]. Water sources for clean water are increasingly scarce, leading people to rely more on refill or using bottled drinking water. Consequently, ensuring the quality of water consumed becomes paramount, with particular attention needed for heavy metal content. Contamination during the drinking water treatment process can elevate levels of heavy metals.

The content of heavy metals is a critical variable that requires attention. While heavy metals are essential for body metabolism at low concentrations, they can become toxic at higher levels. Thus, monitoring the composition of heavy metals in drinking water is crucial. Copper (Cu) is one of the heavy metals found in drinking water, Cu is necessary for human metabolism and various biological processes. However, excessive absorption of copper can lead to poisoning, causing damage to the kidneys and liver. According to the World Health Organization (WHO), the permissible limit for copper content in drinking water is 2 mg/L [3]. Therefore, it is imperative to develop detection methods capable of identifying the presence of copper in drinking water.

Atomic Absorption Spectrophotometry (AAS), Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES), and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) are the methods that commonly used for metal determination. These techniques require expensive instrumentation and an expert for sample analysis. Alternatively, voltametric methods and potentiometry offer more cost-effective alternatives. While these methods are suitable for metal detection and quantification, they can be time-consuming when analysing numerous samples. Therefore, there is a need for simpler semiquantitative or qualitative identification methods, such as sensor-based identification, which are more efficient [4].

In recent years, optical chemical sensor-based methods have emerged as promising alternatives to traditional sensors. Optical chemical sensors, or optodes, have shown significant advancements in ion-sensitive optical devices and their application in trace heavy metal ion analysis. These sensors utilize indicator dyes that undergo changes in optical properties upon interaction with specific ions. While methods like atomic absorption spectroscopy, plasma absorption, and mass spectrometry are effective for metal ion determination, they often require costly instrumentation and complex preparation. In contrast, optodes offer a more economical approach, requiring only a spectrophotometer or spectrofluorometer for operation. These sensors function through ligand-ion interactions that alter their optical properties.

Optical chemical sensors offer more advantages over conventional electrical-based sensors, including selectivity, immunity to electromagnetic interference, and more safety when handling flammable and explosive compounds. They are also noted for being sensitive, cost-effective, non-destructive, and versatile. Unlike potentiometry, optodes do not necessitate a reference cell. However, alongside these advantages, optical sensors also present certain drawbacks. They can be susceptible to ambient light interference, have a limited dynamic range, require mass transfer of analytes from the sample to the indicator phase to generate an analytical signal, and may exhibit lower selectivity in some cases.

Several studies have explored the use of optical chemical sensors by immobilizing-coloured complexing reagents on polymer membranes. For example, cellulose acetate membranes immobilized with compounds like 1-(2-pyridylazo)-2-naphthol (PAN), 2-amino-cyclopenten-1-dithiocarboxylic acid (ACDA), and dithizone (DTZ) have been employed for detecting Cd (II), Ni (II), Zn (II), Pb (II), and Co (II) [6, 7]. These sensors offer robustness and specificity in heavy metal ion detection.

From previous studies, this research aims to analyse Cu (II) ions at various concentrations using cellulose acetate membranes immobilized with DTZ. The method will undergo validation and characterization through Scanning Electron Microscopy (SEM) and Fourier-Transform Infrared Spectroscopy (FTIR). Subsequently, the membrane will be used for detecting Cu (II) in drinking water.

2. Materials and Method

Polyvinyl chloride (PVC), dithizone, tetrahydrofuran (THF), dioctyl phthalate, hydrochloric acid 37% p.a, nitric acid 65% p.a, aquadest, mineral water, $Cu(NO_3)_2.3H_2O$ p.a, sodium acetate trihydrate p.a, buffer solution pH 4.

2.1 Preparation of sensor membrane

Polymer membrane was made by mixing polymer PVC, ligand (complexing agent), plasticizer (DOP) and THF with various amounts. In this study, PVC polymer was used with a polymer weight variation of 0.45-0.50 grams. Weight of dithizone ligand was 3-6 mg, volume of DOP was 130-170 µL and THF was 10 mL. All mixtures were stirred for 5 hours until homogeneous. Next, the solution was poured into a glass mold measuring (5×12) cm^2 and left for several hours (until dry). The finished membrane was cut into pieces with a size of 2.0×0.8 cm^2. The optimum membrane was used for the next work step.

2.2 Time and pH optimization

Time optimization was started by soaking the membrane with 0.5 ppm Cu (II) solution as much as 2 mL. Then, the absorbance was measured every 30 minutes, until the optimum time was obtained. For pH optimization, the membrane was soaked with 0.5 ppm Cu (II) solution as much as 2 mL for 150 minutes with varying pH.

2.3 Determination of maximum wavelength

Calculating the maximum wavelength of DTZ-PVC membrane using UV-Vis Spectrophotometry in the range of 400-800 nm. The membrane used in this step has been soaked with 0.5 ppm Cu (II) solution.

2.3 UV-Vis spectrophotometer and AAS calibration curve preparation

The formed sensor membrane was immersed into each Cu (II) solution with a concentration variation of 0-0.6 ppm. Then the absorbance was determined using UV-Vis spectrophotometry. Make a calibration curve and calculate the regression equation. For the AAS calibration curve, the formed sensor membrane was immersed into each Cu (II) solution with a concentration variation of 0-0.6 ppm. Then the absorbance was determined using AAS. Make a calibration curve and calculate the regression equation.

2.4 Determination of sensitivity, LOD and LOQ, and accuracy

Through the previous linearity test, the sensitivity can be determined to determine the sensitivity of a method can be known through the slope value obtained on the linearity curve obtained on the linearity curve. Limit of Detection (LOD) is the smallest test parameter owned by an instrument to measure certain analytes owned by an instrument to measure certain analytes. The lowest concentration or amount of analyte that still shows an absorbance value on the instrument is the definition of the limit of detection, while Limit of Quantification (LOQ) is the limit of quantification of an analyte that can be calculated accurately and thoroughly. In addition, LOQ also shows the sensitivity of the analytical method used. To obtain the LOD and LOQ values, the absorbance of the Cu (II) analysis blank solution was determined for 7 repetitions. Finally, accuracy is carried out by the standard addition method or standard addition, namely by adding several samples to be analysed with an analyte solution that has a known concentration. Accuracy was determined by comparing the Ca, Cs, and Cb values obtained by the standard addition method.

2.5 Sensor membrane characterization

The dithizone-immobilized membrane was characterized using FTIR spectrophotometry and SEM. Testing the chemical properties of the membrane after dithizone immobilization was characterized using an IR spectrophotometer to determine whether dithizone immobilization went well which can be seen from the functional groups that appear in the spectrum, SEM to determine the surface morphology and cross-sectional area of the membrane.

2.6 Concentration testing of Cu (II) ions in the sample solution

In this study, as much as 2 mL of drinking water sample was added a few drops of acetate buffer until the pH of the sample became 2.8. Then the membrane was dipped into the sample solution, then the absorbance was measured using UV-Vis spectrophotometry at the maximum wavelength. Measurements were repeated 3 times to improve the accuracy of the results and reduce errors in the study.

2.7 Sample testing with AAS using standard addition

In this study, AAS was used to validate the UV-Vis Spectrophotometric Method. Into a 10 mL volumetric flask, 0.3 mL of 10 ppm Cu (II) solution and 0.3 mL of sample were added, then 0.1 M HNO_3 was added until the limit mark. Then the membrane was dipped into the sample solution, then measured the absorbance using AAS at the maximum wavelength.

3. Results and Discussion

The flexibility of the membrane in this study is influenced by DOP, which acts as a plasticizer. Stirring the solution for 5 hours aims to achieve homogeneity. As shown in Table 1, using 150 µL of DOP resulted in the best membrane texture: clear, dry, smooth, and easily released from the mold. Thus, the amount of plasticizer significantly affects membrane characteristics; higher DOP concentrations yield more flexible membranes with plastic-like properties. However, excessive DOP can cause the membrane to clump like glue. DOP interacts coordinatively with PVC, maintaining a dispersed phase within the predominantly PVC continuous matrix. This interaction influences the mechanical properties of the dithizone complex. The mechanical properties are dependent on the degree of dipolar interaction. Additionally, the presence of PVC disrupts interchain attractions, acting as a barrier between PVC chains. This disruption further impacts the mechanical properties of the complex compound. Conversely, excessive PVC addition can diminish these properties.

Table 1. Optimization of DOP.

No	DOP (µL)	Characteristics
1	130	Clear, dry, attached to the mold
2	140	Clear, dry, attached to the mold
3	150	Clear, stiff, easy to move frim the mold
4	160	Clear, smooth, slightly wrinkled
5	170	Clear, smooth, slightly wrinkled

3.1 Optimization of dithizone composition

The membrane was prepared by mixing 0.5 g of PVC, 10 mL of THF, 150 µL of DOP, and the amount of dithizone was varied from 3.0; 3.8; 4.6; 5.4 and 6.0 mg. The texture of the resulting membrane is shown in Table 2.

Table 2. Optimization of dithizone.

No	**Dithizone (mg)**	**Characteristics**	
		Membrane colour	Solution Colour
1	3.0	Not changing	Not changing
2	3.8	Changing	Not changing
3	4.6	Not changing	Changing
4	5.4	Not changing	Changing
5	6.0	Not changing	Changing

The amount of dithizone on the membrane significantly influences its sensitivity to measured ions. Using 3.0 and

3.8 mg of dithizone resulted in membranes with clear textures that were easily removed from the mold. Increasing the dithizone to 4.6 and 5.4 mg produced membranes with a cloudy texture, still easily removable from the mold but with a darker colour. Using 6.0 mg of dithizone resulted in a cloudy texture, again easily removed from the mold but with an even darker colour. The cloudier texture observed with higher dithizone amounts indicates that the membrane's capacity for immobilizing dithizone may have been exceeded.

From the data, it was observed that using 3.0 and 3.8 mg of dithizone yielded the best membranes: clear texture and easy mold release. Subsequently, these membranes were tested by soaking them in a 0.5 ppm Cu (II) solution. With 3.0 mg of dithizone, there was no change in the membrane or solution color. With 3.8 mg, the membrane changed color while the solution did not, aligning with literature expectations.

Using 4.6, 5.4, and 6.0 mg of dithizone, the membrane colour did not change, but the solution turned orange. This colour change indicates leaching, where ions previously complexed with dithizone on the membrane dissolve back into the solution. This leaching process, also known as diffusion, involves solute exiting inert solid pores and mixing with the surrounding solvent [9].

3.2 Optimization of the PVC composition

In PVC optimization, 150 µL DOP, 3.80 mg dithizone, and 10 mL THF were used with stirring for 5 hours. The PVC used varies from 0.45; 0.48; and 0.50 g. The resulting membrane texture is shown in Table 3.

Table 3. Optimization of PVC composition.

No	PVC (gr)	Characteristics
1	0.45	Clear, thin, rather easy to remove from the mold
2	0.48	Clear, thin, easy to remove from the mold
3	0.50	Clear, thicker, stiff

Furthermore, 0.48 g of PVC was utilized to produce a thin membrane that meets the criteria for a sensor membrane. The thickness of the membrane is a crucial factor to consider as it directly influences the rate of interaction between the ligand and Cu (II). Thin membranes facilitate quicker changes because Cu (II) can interact more rapidly with immobilized ligands. This increased interaction is facilitated by the ease with which Cu (II) can penetrate thinner membranes.

3.3 Optimization Soaking Time

Soaking time optimization aims to determine the optimum time for the membrane to react with Cu (II) solution. For that, the membrane was cut into small pieces with a size of about 0.8 x 2.0 cm, soaked with 0.5 ppm Cu (II) solution as much as 2 mL. Then, the absorbance was measured every 30 minutes, the relationship between the immersion time and absorbance value is shown in Figure 1. The highest absorbance is obtained when the membrane is soaked for 150 minutes where the membrane has finished binding to the Dithizone ligand so that the absorbance produced is stable.

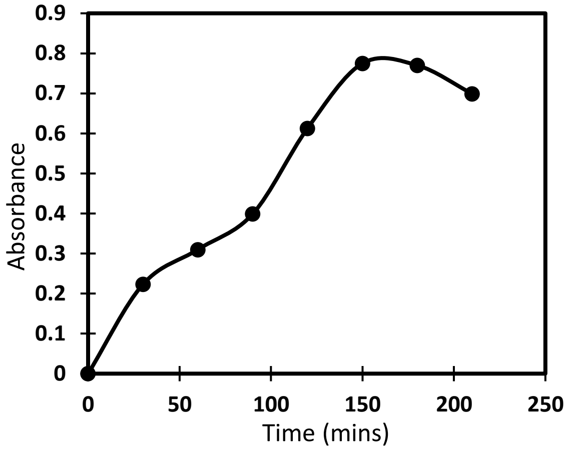

Figure 1. Soaking time optimization.

3.4 Optimization pH and determination of maximum Wavelength

pH optimization was carried out by immersing the membrane in 2 mL of 0.5 ppm Cu (II) solution with various pH for 2.5 hours. Then, the absorbance was measured using a UV Vis spectrophotometer. The pH relationship of the solution Cu (II) 0.5 ppm solution with its absorbance value is shown in Figure 2. The relation between the pH and its absorbance value is shown in Figure 3. The highest absorbance was obtained in Cu (II) solution with a pH of 2.8.

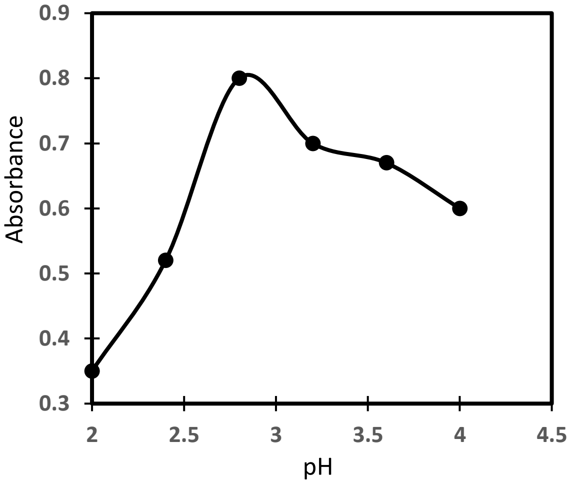

Figure 2. Optimization of pH.

Measurement of the maximum wavelength of the membrane that has been made is done by measuring the absorbance of the wavelength of 400 - 700 nm. This treatment was carried out on the membrane before and after being degassed by Cu (II) solution. From the graph that illustrates the relationship between absorbance and wavelength the wavelength, obtained data that the maximum absorbance was obtained at wavelength. For the membrane before soaking with Cu (II) solution is 616 nm and after soaking with Cu (II) solution 427 nm, as shown in Figure 3.

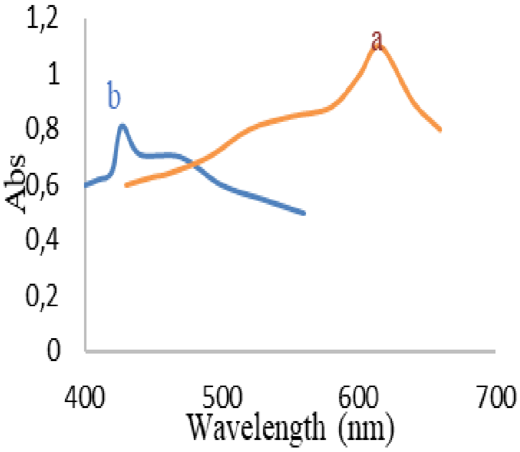

Figure 3. Maximum wavelength of (a) membrane and (b) membrane soaked with Cu (II) solution

The change in maximum wavelength is due to the formation of colour change on the membrane. Where the membrane before soaking is light green, and after soaking it is orange. Membrane hypochromic shift, meaning that the wavelength of the membrane becomes smaller after the membrane is soaked with Cu (II) solution. This can be effect by the reaction coordination complex with Cu (II) solution, so the membrane will be leaching to the bulky compound and make the size become larger, so that the wavelength of the complex compound become decreases and make the wavelength come to the bathochromic effect. The pH effect of the membrane will affect because of immobilized ligand leaching from the membrane sensor.

3.5 Characterization

3.5.1 SEM

From Figure 4, it is evident that there is a difference in pore size between the membrane before and after immersion in a Cu (II) solution, magnified 3,000 times. Initially, the membrane exhibited pores ranging from 0.5 to 1 µm. However, after immersion, the pores appear to have shrunk. This phenomenon is attributed to the penetration of Cu (II) ions into the membrane pores, resulting in their reduction in size. The coordination covalent reaction between Cu (II) ions and the membrane's components causes the formation of complex compounds, which are larger in size. This interaction leads to a reduction in pore size, as the complex compounds occupy space within the pores.

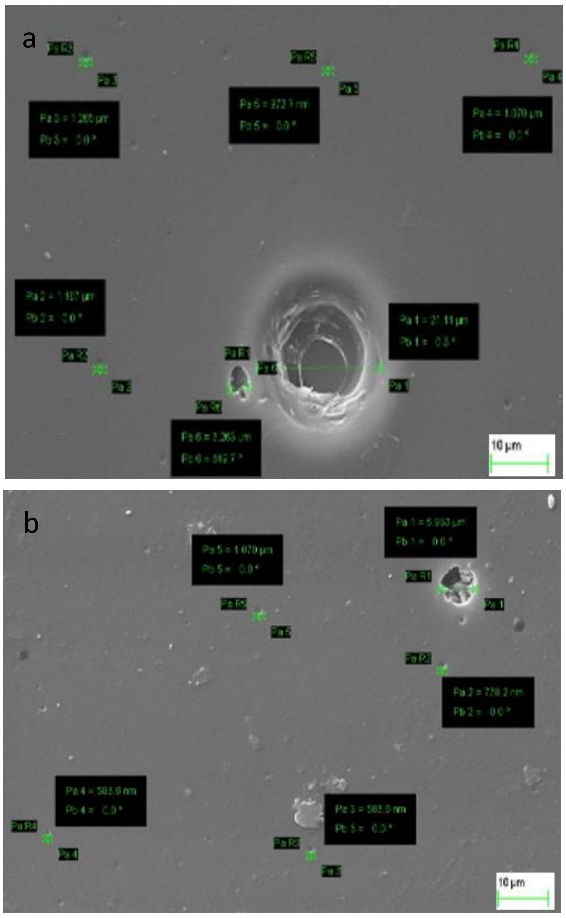

Figure 2. SEM characterization of the membrane (a) before immersed in Cu (II) solution and (b) characterization of the membrane after Cu (II) immersion.

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3.5.2 FTIR

Based on Figure 5, the spectra of FTIR obtained exhibit consistent patterns indicating the presence of PVC compounds, as compared with reference spectra [10]. Specifically, peaks were observed at 634.5 cm^{-1} and 605.5 cm^{-1}, indicating the presence of a C-Cl group. Additionally, a peak at 1425.13 cm^{-1} suggests the presence of a C-H group, which further supports the identification of PVC compounds in the membrane. Moreover, the presence of dithizone in the membrane is indicated by peaks at 1255.4 cm^{-1}, 1511.9 cm^{-1}, and 1641 cm^{-1}, corresponding to C-N and N-H groups. Notably, the peak at 1722.1 cm^{-1} signifies the presence of the C=O aldehyde group, characteristic of DOP as a plasticizer in the membrane.

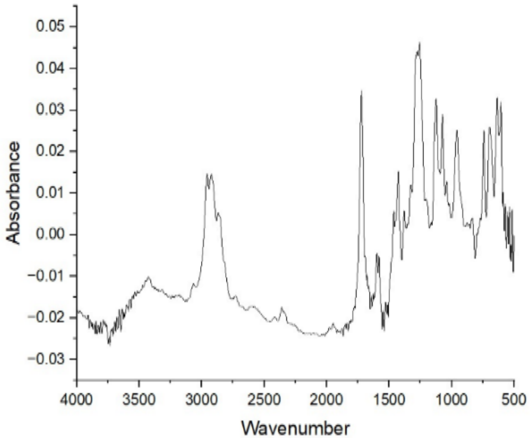

Figure 3. FTIR spectra of PVC-DTZ membrane.

3.6 Linearity

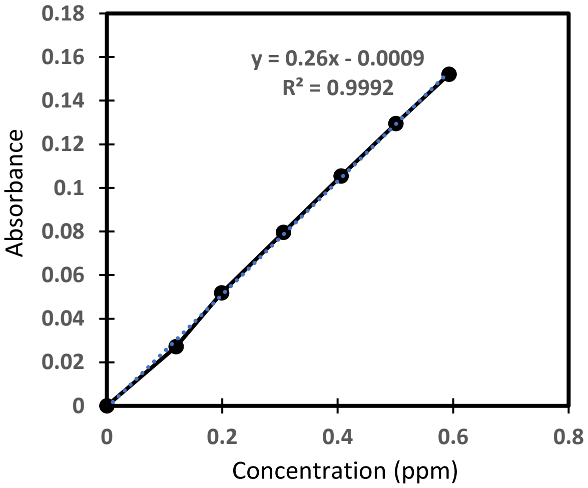

Figure 4. Calibration curve of Cu (II) sensor membrane at 427 nm of wavelength by UV-Vis spectrophotometry.

The calibration curve was constructed by immersing the PVC-DTZ membrane in Cu (II) solutions with concentrations ranging from 0 to 0.6 ppm. As depicted in Figure 7, there is a direct proportional relationship between concentration and absorbance. The absorbance increases with higher Cu (II) concentrations, as shown in Figure 6, where the regression equation is 1.5457x + 0.016 and the R^2 value is 0.9952. This indicates a high degree of linearity in the relationship between absorbance and concentration, with a sensitivity value of 9.4831 x 10^4 mol^{-1} cm^{-1}. According to the previous study, the regression linearity was at 0.96 with the equation y = 0.7249x + 0.0781, and the molar absorptivity was 4.42 x 10^5. Comparatively, the calibration curve in this study shows higher sensitivity likely due to the strong complex formation between the precursor and ligand, which enhances method validation, particularly in terms of regression curve accuracy and sensitivity.

The colour change of the membrane is also noticeable; as shown in Figure 7, the intensity of the membrane colour increases with higher concentration. The membrane immersed at 0.6 ppm specifically exhibits the greatest colour change intensity.

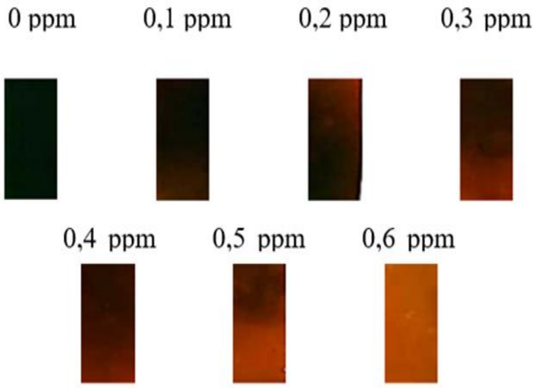

Figure 5. Progress of sensor membrane colour change along with increase in Cd (II) concentration.

In Figure 8, the results of the calibration curve generated using AAS can be observed. The equation of the line derived from the Cu (II) solution calibration curve is 0.26x + 0.0009, with an R^2 value of 0.9992. This high R^2 value indicates a highly linear relationship between Cu (II) concentration and the resulting absorbance.

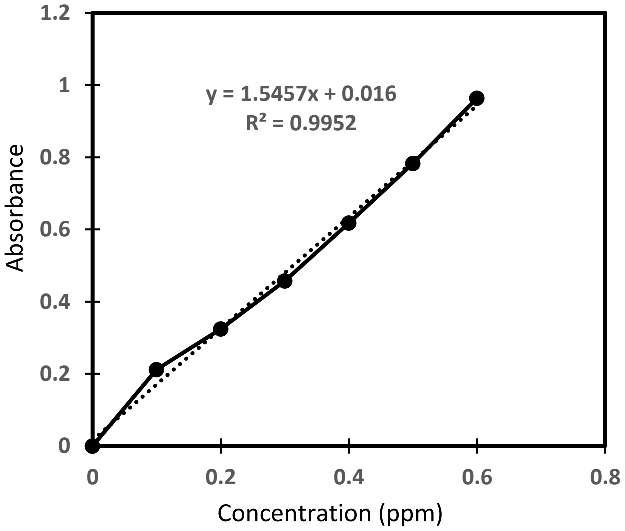

Figure 6. Calibration curve of Cu (II) solution measured using atomic absorption spectrometry.

3.7 LOD and LOQ

LOD and LOQ using a specific instrument was carried out with at least seven repetitions [11, 12]. In this study, the detection limit for Cu (II) was found to be 1.9881 x 10^{-3} mg/L. The LOQ, which represents the lowest analyte quantification limit that can be calculated accurately and thoroughly, also indicates the sensitivity of the analytical method used. The LOQ was determined to be 6.0245 x 10^{-3} mg/L. According to previous study, their study reported a smaller LOD value than this research. This indicates that although the lower quantification and minimum detection limits in this study were higher, the LOD and LOQ values are still acceptable.

3.8 Accuracy

Accuracy testing aims to determine whether the analysis method used can produce reliable and consistent results. By evaluating the percent recovery value, the closeness of the analysis results to the actual values can be assessed. In this study, the standard addition method was added, which involves adding known concentrations of an analyte solution to several samples for analysis. As shown in Table 4, the average recovery value was found to be 100.491%. This value meets the criteria of the acceptable accuracy range of 80-110%, indicating that the method meets accuracy requirements. According to previous study, the percent recovery was found to be 98.88%. This research demonstrates greater accuracy compared to previous studies, suggesting that the PVC-immobilized dithizone membrane is effective method for analysis metal detection.

Table 5. Determination of accuracy using conventional drinking water.

Concentration (ppm)	Abs	Ca	Cb	Cs	Recovery (%)
0.1	0.205	0.1262	0.00636	0.1215	98.63374
0.2	0.313	0.2012	0.00636	0.1938	100.5366
0.3	0.443	0.2902	0.00636	0.2809	101.0466
0.4	0.604	0.3980	0.00636	0.3887	100.7583
0.5	0.765	0.5086	0.00636	0.4965	101.1560
0.6	0.947	0.6297	0.00636	0.6183	100.8151
Average					100.4907

3.9 Determination Cu (II) content in the sample

To assess the effectiveness of AAS and spectrophotometry in measuring Cu (II) ion content in the sample, the content of Cu (II) ions was measured using both methods. The test results indicate that the Cu (II) ion content determined by AAS was 0.0027 ppm, while spectrophotometry measured it at 0.0021 ppm. This data demonstrates that both AAS and UV-Vis spectrophotometry yield comparable results, indicating that either instrument can be reliably used to measure Cu (II) ion content in the sample. According to the Decree of the Indonesian Minister of Health No. 492/MENKES/Per/IV/2010, which stipulates a maximum copper (Cu) level of 2 ppm for drinking water, the drinking water samples tested are well within the acceptable limit and are thus deemed suitable for consumption.

3.10 Recapture test

The recovery test aims to determine the efficiency of the PVC-DTZ membrane in measuring Cu (II) ions. The test results are shown in Table 5. From Table 5, it can be concluded that the results obtained using the sensor membrane method are almost identical to those obtained with the AAS method. This demonstrates that the sensor membrane can be effectively used to determine Cu (II) levels in water.

4. Conclusion

Immobilization of dithizone in PVC membranes was carried out under optimum conditions, using 3.8 mg of dithizone, 10 mL of THF, 0.48 g of PVC, and 150 µL of DOP. This resulted in a membrane with a clear, thin texture that was easily removed from the mold and exhibited no leaching. Membrane performance was validated with various parameters, ensuring its suitability for detecting Cu (II) content in drinking water. The level of Cu (II) in drinking water was measured at 0.0021 ppm using UV-Vis spectrophotometry. According to the Decree of the Minister of Health of the Republic of Indonesia No. 492/MENKES/Per/IV/2010, which stipulates that the acceptable Cu (II) level in drinking water is 2 ppm, this result shows that the sample is safe for consumption.

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