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Detection of Hexavalent Chromium Ion in Water by Optode Membrane

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***Abstract*—**Chromium is a heavy metal that is often found as a water pollutant. High concentrations of hexavalent chromium (Cr(VI)) ion in nature are toxic and carcinogenic, so their presence in water needs to be monitored. Detection of heavy metals in water was carried out using an optical sensor membrane (optode). The optode was fabricated from cellulose triacetate polymer with plasticizers (oleic acid and acetophenone), aliquot 336, and the chromoionophore 1.5-diphenylcarbazide (DPC). The success synthesis of optode was evidenced by FTIR and SEM characterization. The optode performance produces a linear response in detecting Cr(VI) ion in the concentration range of 0.02-0.40 mg/L with an R^2 of 0.9930, as well as the best conditioning at pH 3. The detection and quantitation limits are 0.0055 mg/L and 0.0165 mg/L. The sensitivity of the chromium optode was excellence, with a molar absorptivity value of 8.8303×10^6 $M^{-1}cm^{-1}$. The performance test results of the chromium optode were acceptable because they meet the specified requirements for minimum detection concentration value.

Keywords*—Cellulose triacetate; Hexavalent chromium; Membrane; Optode; Pollutants*

1. INTRODUCTION

The color change between metal and ligand interactions allows for quantitative and noninstrumental analysis, namely direct eye detection of the analyte. However, most currently available chromogenic ligands bind ions efficiently in organic solvents and are poorly soluble in aqueous solutions. A more straightforward approach is the incorporation of ligands into a polymeric sensing phase known as an "optode" [1,2]. The reagent is immobilized in a solid matrix, such as a transparent membrane, for the analyte to be extracted into the probe to generate a preoperational optical signal to the change in analyte concentration. The optode utilizes the reaction of the ligand with the analyte to produce a specific color in detecting the analyte [3,4,5].

Chromium is an abundant element that ranks 21st in the earth's crust with a concentration range in soil between 1–3000 mg/kg, in drinking water worth 0–117 µg/L, and in rivers and lakes 26 µg/L to 5.2 mg/L. Chromium in nature is divided into two species, namely trivalent chromium (Cr(III)) and hexavalent chromium (Cr(VI)) [6,7]. Chromium ion contamination in the environment can originate from the activities of the leather tanning, textile manufacturing, metal plating, and dye industries. Environmental pH and temperature affect the form and toxicity of chromium ions [8].

Cr(III) has benefits as a micronutrient for humans for sugar and lipid metabolism. However, if Cr(III) is oxidized Cr(VI), it will negatively impact humans and the environment. Cr(III) can be oxidized to Cr(VI) with high manganese (Mn) oxygen concentrations [9]. Cr(VI) has high toxicity and is a carcinogen that can cause gastrointestinal, kidney, lung, and liver cancer, making it dangerous for the body [9,10]. Therefore, the Cr(VI) threshold permitted in drinking water, drinking water raw materials, and water for fisheries and livestock is a maximum of 0.05 mg/L as regulated in Government Regulation No.20 of 1990 [11].

The specific objectives of this research were to obtain the best formulation of membrane composition that will be used as an optode for the detection of the heavy metal Cr(VI) ion, to obtain the best staining test parameters, and to obtain performance test parameters for an optode membrane. The result was given a chromo ionophore to be able to detect pollution and as an indicator of water quality. The urgency of determining optodes for heavy metals is that metals are pollutants commonly found in waters due to their

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reasonably massive use. So, it can be used to indicate pollution and water quality.

2. EXPERIMENTAL SECTION

2.1. Materials

The materials used were cellulose triacetate (CTA) (CAS 9012-09-3), 1,5-diphenylcarbazide (DPC) (CAS 140-22-7), trioctylmethylammonium chloride (aliquot 336) (CAS 63393-96-4), oleic acid (CAS 112-80-1), $K_2Cr_2O_7$ (CAS 7778-50-9), H_2SO_4 (CAS 7664-93-9), acetophenone (CAS 98-86-2), methanol (CAS 67-56-1), chloroform (CAS 67-66-3), and acetone (CAS 67-64-1). All chemicals were pro analyst produced by Merck, Darmstad, Germany.

2.2. Instrumentations

The tools used were a screw micrometer (0.001 mm, Fowler 52-224), analytical balance (0.0001 mg, OHAUS AX224/E), magnetic stirrer (MG-78-1), sonicator (AS ONE), pH meter (Hanna HI 2211), and oven (Memmert UM 400). For characterization, the solid-state UV-Vis spectrophotometer (400-1000 nm, Ocean Optics Vis-NIR USB4000), FTIR spectroscopy (400-4000 cm^{-1}, ABR), UV-Vis spectrophotometer (200-1000 nm, Thermo Scientific), and SEM instrument (1000-30000× magnification, Hitachi S-4800 SEM) were performed.

2.3. Preparation of CTA Optode Membrane for Cr(VI) Detection

The CTA optode membrane was made using the following procedure. A cellulose triacetate (CTA) solution was made by mixing 0.1350 g of CTA into 10 mL of chloroform. The DPC solution was prepared by mixing 5 mg DPC into 5 mL methanol. The homogeneous CTA solution was added with a 0.30 mL plasticizer made from 0.03 mL of oleic acid and 0.27 mL of acetophenone. A 0.07 mL aliquot of 336 was added to the CTA solution and stirred with a magnetic stirrer for 15 min. The DPC solution that has been made was poured into the CTA solution mixture and then stirred again for 15 min. The solution mixture was homogenized with a sonicator for 15 min. The homogenized mixture was poured into a petri dish and left at air temperature for 48 h. The optode membrane that has been fabricated was then cut to a size of 3×1 cm.

2.4. Characterization and Performance Test of The CTA Optode Membrane

Membrane characterization was carried out by taking a portion of the membrane and using it for FTIR and SEM measurements. The membrane performance testing carried out included determining the optimum pH for color formation, determining the optimum contact time, determining the performance of the optode membrane (linearity test, LOD, LOQ, precision, accuracy, selectivity, and sensitivity), and then continued with Cr(VI) ions detection in water samples. Performance test measurements were carried out using UV-Vis spectroscopy of solid materials previously carried out at the maximum wavelength range.

3. RESULT AND DISCUSSION

3.1. CTA Optode Membrane Fabrication

Optical sensors (optodes) are chemical techniques that analyze analyte chemical reactions connected with spectroscopic measurements (reflectance, absorbance, fluorescence, and luminescence). The optode has a primary structure, namely a membrane, as the main sensor in detecting analytes in the sample. In a chemical sense, the principle of an optode membrane is an interface matrix for analytes and reagents to react chemically so that colored complexes can be formed. Cellulose triacetate (CTA) fabricates optode membranes as a carrier matrix for active substances in optodes. Aliquot 336 acts as an extractor or carrier of Fe(III) and Cr(VI) ions into the CTA membrane so that they can react with the active components [12]. The reaction of aliquot 336 with Cr(VI) is shown in Equation (1).

$$R_3(CH_3)N^+Cl^-_{(aq)} + HCrO_4^-{}_{(aq)} \rightarrow (R_3(CH_3)N^+)HCrO_4^-{}_{(aq)} + Cl^-_{(aq)} \quad (1)$$

Chromophore is one of the structures that make up the CTA membrane, which is used to recognize Cr(VI) analytes based on complex reactions. 1,5-diphenylcarbazide (DPC) reacts specifically with Cr(VI). The DPC complex and Cr(VI) reaction involve a two-step reaction. DPC was used because it has good ligand properties and quickly forms complexes with transition metals [13]. The complex formation reaction $[Cr(DPCO)]^+$ consists of several reactions; the first step is the oxidation of DPC with Cr(VI) to become diphenylcarbazone (DPCO), where Cr(VI) is reduced to Cr(III). The second step is the formation of a complex between Cr(III) and DPCO to form a purplish $[Cr(DPCO)]^+$ complex (**Fig. 1**) as the final reaction product [14,15].

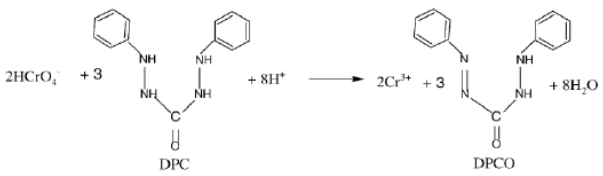

Fig. 1 Reaction for the formation of the $[Cr(DPCO)]^+$ complex [4,15]

On the other hand, the addition of oleic acid plasticizer plays a role in weakening the stiffness of the fabricated polymer membrane, increasing the flexibility

of the CTA polymer chains in the membrane, and promoting the transfer of Cr(VI) to the membrane [16,17].

3.2. Characterization of the CTA Optode Membrane

Optode membrane characteristics need to be analyzed because they can affect the performance of the resulting optode membrane. The physical characteristics of the resulting optode membrane were analyzed from the uniformity of size, thickness, and pores. The size of the optode membrane is made uniform at 3×1 cm. The thickness of the optode membrane was measured using a screw micrometer and is expected to be constant. The measurement results from three different cups show the average thickness of the optode membrane.

Meanwhile, the thickness of the Cr(VI) detection membrane is 0.0421 mm with a %RSD of 3.37%. The resulting values show excellent accuracy in membrane manufacturing. Lambert-Beer's law explains the relationship between absorbance, concentration, and thickness. A homogeneous membrane thickness is expected to provide the best results in an even distribution of DPC or thiocyanate for detecting analytes because a flat membrane surface produces a homogeneous wavelength. Absorbance measurements depend only on the concentration of the analyte to be measured.

The characteristics of the functional groups contained in the optode membrane were analyzed using FTIR. The IR spectrum was recorded at wavenumbers between 4000–400 cm^{-1}. The measured absorption spectrum will produce good absorption at a value of 80-20%T. Characteristic peaks in the Cr(VI)-detecting CTA-based membrane (**Fig. 2**) were observed at wave numbers 2928, 1738, and 1235 cm^{-1}, which were associated with the C–H, C=O, and C–O stretching vibrations, respectively. In addition, the optode membrane spectrum appears to have a weak peak at 3487 cm^{-1} of O–H stretching vibration. The results show that there is no significant difference in wave numbers. The IR spectrum decreases in absorbance after C-H sp^3 stretching in **Fig. 2c**, which is generally caused by the formation of complex compounds [16]. Immersing the optode membrane into a standard solution, Cr(VI), does not cause chemical changes to the optode membrane or a shift in the resulting IR spectrum. The wave numbers of the fabricated optode membrane read in the IR spectrum all meet the range by the literature, as shown in **Table 1** [14,18,19].

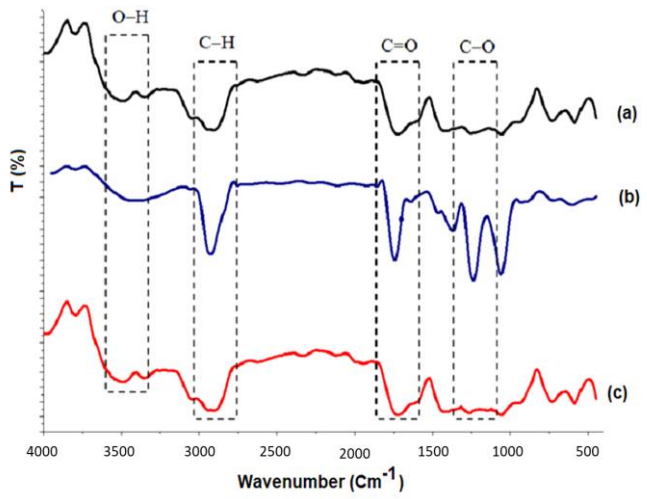

Fig. 2 IR spectrum of the Cr(VI) detection optode membrane CTA+DPC (a), CTA+DPC+Cr(VI) (b), and CTA [18] (c)

Table 1. Comparison of Cr(VI) detection membrane with the literature

This research (cm^{-1})	Li et al. [19] (cm^{-1})	Groups	Type of vibration
3383	3430	O–H	Stretching
2926	2939	C–H sp^3	Stretching
1747	1720	C=O	Stretching
1231	1221	C–O	Stretching

Optode membrane pores were analyzed using SEM to determine the surface morphology of the resulting membrane. The CTA optode membrane was characterized using SEM with different magnifications, and the results are presented in **Fig. 3**. The surface morphology of the CTA optode membrane was observed to have a homogeneous surface. The cavities visible at 30,000× magnification on the membrane surface are due to the interaction between the CTA polymer and thiocyanate. The thiocyanate is well distributed throughout the membrane cross-section [20].

Fig. 3 shows the morphology of the Cr(VI) detection membrane, which displays a dense and compact structure. The membrane pores appear to be filled with chromophore molecules (carriers). The pore distribution is almost homogeneous and asymmetric. However, no pores could be observed on the top surface of the CTA membrane by SEM under 30,000× magnification. The membrane, at 30,000× magnification,

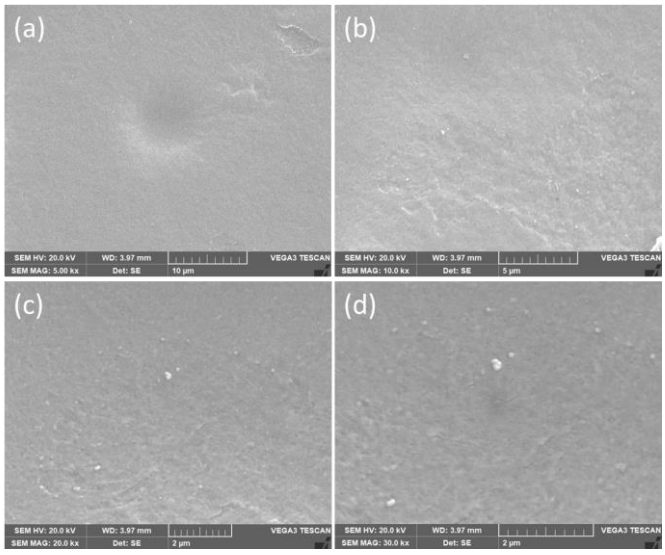

Fig. 3 Surface morphology of the Cr(VI) detection optode membrane at magnifications of 5,000× (a), 10,000× (b), 20,000× (c), and 30,000× magnification (d)

cannot display the pore size in the structure, so the pore size distribution (PSD) cannot be calculated. These pores are filled with plasticizer and carrier. Membrane porosity can be determined using the gravimetric method, which is defined as the pore volume fraction divided by the total membrane volume [20-22]. The morphology of the CTA membrane (top surface) shows that this membrane is formed by cellulose triacetate polymer presenting a porous structure. The distribution of pores is homogeneous, with a porosity value of 43.72 ± 1.64%. The greater the porosity, the higher the flux value produced so that the porous membrane allows water to penetrate it easily. It maximizes the diffusion rate of Cr(VI) into the CTA membrane (matrix).

3.3. Optimization of pH and Contact Time

Analyte concentration measurement with a CTA-based membrane optode that combines chemical reactions with spectroscopic measurements. The optode membrane changes color when interacting with the analyte. The resulting color can be measured using visible wavelengths. The signal response in the form of absorbance produced by this measurement provides maximum conditions at the maximum wavelength (λ_{max}). This condition provides good sensitivity values and low detection limits and can reduce measurement errors.

λ_{max} on the Cr(VI) detection membrane was obtained by measuring the absorbance in the 400–700 nm wavelength range. Measurements were carried out in two conditions: pH 1.5 and pH 3. The measurement results showed that the membrane tested in a standard Cr(VI) solution gave a maximum absorption peak at a wavelength of 621 nm at pH 1.5 and 585 nm at pH 3 (**Fig. 4**).

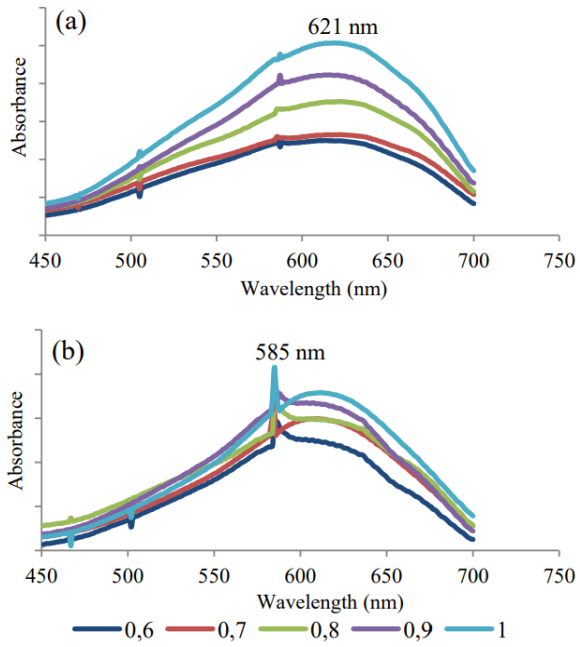

Fig. 4 Maximum absorbance results of the optode membrane at pH 1.5 (a) and pH 3 (b) with various Cr(VI) concentrations

The intensity of the color formed with maximum absorbance is shown at pH 3. Measurements at pH 1.5 show that the intensity of the color formed is fainter than measured at pH 3, so the measured absorbance is lower than at pH 3 (**Fig. 4**). This is because the color change occurs during the formation of the DPC and Cr(VI) chromophore complex on the membrane, changing the standard solution to a purplish color. Conditioning at pH 3 is ideal and is used to determine subsequent analytical performance. Measurements at pH >3 are slow and time-consuming. This behaviour, that pH influenced color and ion formations, also occured on several heavy metals [23,24].

Determination of the contact time between optodes was carried out by observing the absorbance pattern at its maximum wavelength in the time range 0–30 min. The time is 1, 5, 10, 15, 20, 25, and 30 min. The optimum contact time for the optode was obtained at 15 min because it produced the highest absorbance value, meaning that the most stable complex was formed at that time (**Fig. 5**). The absorbance value continues to increase from the 1st min to the 15th min. After 15 min,

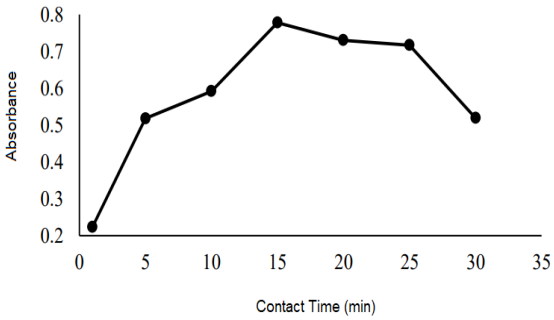

Fig. 5 Absorbance vs contact time in optode

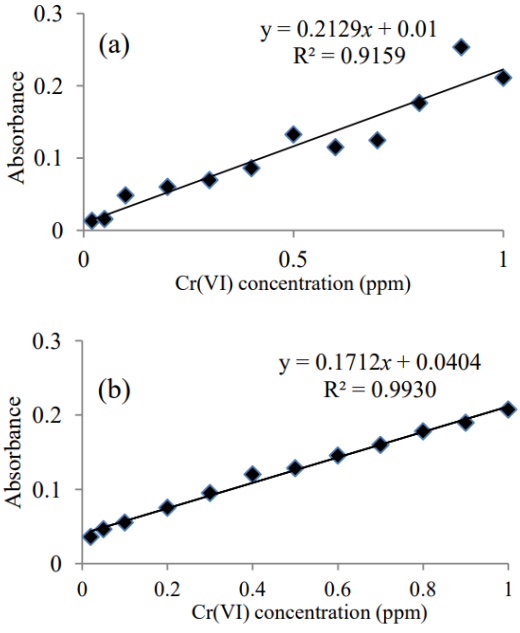

Fig. 6 Optode membrane standard curve in the range of 0.02–1.00 mg/L at pH 1.5 (a) and at pH 3 (b)

the absorbance value decreased, and the complex color formed slowly faded. Contact time that is too fast causes the formation of the complex not to be maximum, while the color of the complex fading is caused by the redissolving of the complex that has been formed into the solution [8].

The predetermined working range can be used to determine the linearity performance of the membrane (**Fig. 6**). Linearity was determined using six concentrations that provided the best correlation coefficient (R^2) of various concentrations. The highest linearity of the Cr(VI) detection optode membrane was in the range of 0.02–0.40 mg/L at pH 3, with a coefficient of determination (R^2) of 0.9968 (**Fig. 7**). According to AOAC [25], the R^2 value can have better linearity if it is close to 1.0000 or > 0.9900. The linear response results show that the optode created can produce a linear relationship between the absorbance and the concentration of the solution being measured (**Fig. 7**).

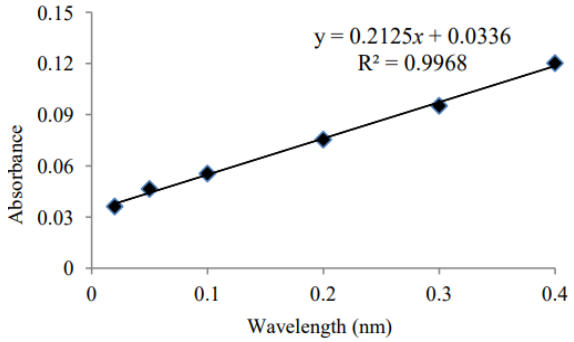

Fig. 7 Optode linearity standard curve in the working range of Cr(VI) concentration 0.02–0.40 mg/L replication 1

3.4. Detection and Quantitation Limits

The detection limit (LOD) in this study is expressed as the ability of the optode membrane to detect the analyte, namely Cr(VI), in a standard solution. The limit of quantification (LOQ) is the smallest amount of analyte concentration that can be estimated with acceptable reliability. LOD and LOQ were determined based on the standard deviation and slope of the standard curve with three repetitions. LOD is expressed as the concentration at a signal-noise ratio of 3:1. At the same time, LOQ is the lowest amount of analyte concentration that can be quantified, having a signal-noise ratio of 10:1 [26].

The calculated LOD for the CTA-based optode membrane as a Cr(VI) detector is 0.0055 mg/L with a LOQ of 0.0165 mg/L. This means that the CTA-based membrane optode can detect Cr(VI) below the maximum threshold set by the Indonesian National Standard (SNI) 01-3553-2006 concerning consumed drinking water, drinking water raw materials, water for fisheries and livestock, Cr(VI) concentration the maximum allowable is 0.05 mg/L. However, if the sample's Cr(VI) concentration is below the LOD value, the sample signal response cannot be distinguished from a blank signal or noise. Error problems with analyte detection and quantification can result from matrix effects, sample concentration, or other conditions, such as instrument sensitivity and reagent purity.

3.5. Precision and Accuracy

Precision is the closeness between individual test results in a series of measurements and a homogeneous sample. Precision can be expressed as repeatability or reproducibility. Repeatability is the accuracy of a method if it is carried out repeatedly by the same analyst under the same conditions and within a short time interval. The precision in this study is in the repeatability category with six repetitions with the new CTA optode membrane. This parameter helps evaluate an optode's ability to prove accurate and consistent results even when drawn from different optode sets. Precision is generally expressed as relative standard deviation (%RSD) [22,27,28]. The research results on the Cr(VI) detection membrane show that the %RSD precision value of the optode in standard solutions is 1.88%. Based on AOAC (2013), a %RSD value ≤ 8% indicates the best precision, RSD shows that the ability of the optode membrane to detect Cr(VI) in standard solutions is entirely consistent [25].

Accuracy measures how close the analysis results are to actual or acceptable values. This analysis can be an individual score, the average of a series of values, or the average of many series of values [29]. Accuracy is expressed as the recovery rate of the added analyte (%recovery). Accuracy can be expressed in terms of the standard addition method or the general standard addition method. The standard addition method adds a large amount of standard analyte corresponding to a specific concentration to analyze the sample [29]. Accuracy tests help check the accuracy of the results of the analysis carried out. The recovery rate requirement for AOAC [25] is 80–120%. The average % recovery value obtained on the Cr(VI) detection membrane with three different concentrations was 102.21% (**Table 2**). Recovery indicates that the optode accurately detects Cr(VI) in standard solutions. These

Table 2 Determination of the accuracy of CTA optode membranes in Cr(VI) standard solutions

$[Cr(VI)]_{standard}$ (mg/L)	Repe-tition	$[Cr(VI)]_{exp}$ (mg/L)	% Recovery	Average % Recovery
0.05	1	0.0598	119.53	97.57±19.23
	2	0.0447	89.41	
	3	0.0419	83.76	
0.20	1	0.1986	99.29	99.76±4.25
	2	0.1915	95.76	
	3	0.2085	104.24	
0.40	1	0.4174	104.35	109.29±7.47
	2	0.4715	117.88	
	3	0.4226	105.65	

results indicate that the optode membrane detects Cr(VI) as an analyte in the actual sample, and the analysis results are close to acceptable actual values.

3.6. Sensitivity Testing

Sensitivity is the ability of a sensor to differentiate the amount of analyte between two different samples [30]. The sensitivity of the optode can be determined by the specific absorptivity value calculated from the Lambert-Beer equation. The average specific absorptivity obtained was 16.9827 $(mg/L)^{-1} mm^{-1}$, and the molar absorptivity was 8.8303×10^6 M^{-1} cm^{-1}. The absorbance values obtained were more significant than the values reported by Lace et al. [23], which value 2.0210×10^4 $M^{-1} cm^{-1}$.

CONCLUSION

The CTA optical sensor (optode) for detecting Cr(VI) with the DPC chromophore was successfully fabricated. The thickness, pores, and functional groups resulting from the characterization were specific characteristics of the CTA optode membrane. The optimum time was 15 min, and the pH of the CTA optode membrane for detecting Cr(VI) ions was 3. Evaluation of the optode membrane's performance produces detection and quantitation limits with linear results to detect concentrations below the predetermined iron and chromium threshold values. The selectivity, precision, and accuracy obtained were also evidenced excellence value. The excellent performance results show that the optode membrane has the highly potential to detect Cr(VI) in environmental water samples.

SUPPORTING INFORMATION

There is no supporting information of this paper. The data that support the findings of this research are available on request from the corresponding author (ZA).

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CONFLICT OF INTEREST

The authors have no conflict of interest in this publication.

AUTHOR CONTRIBUTIONS

RM conducted the experiment. ZA conducted the experiment and data calculation. ZA, ER, and MR wrote and revised the manuscript. All authors agreed to the final version of this manuscript.

REFERENCES

[1] Łukasik, N., Wagner-Wysiecka, E., & Małachowska, A. 2019. Iron(iii)-selective materials based on a catechol-bearing amide for optical sensing. *The Analyst*. 144(9), 3119–3127. doi: 10.1039/C9AN00188C.

[2] Ghaedi, M., Shahamiri, A., Hajati, S., & Mirtamizdoust, B. 2014. A novel PVC-membrane optical sensor for high sensitive and selective determination of Cu^{2+} ion based on synthesized (E)-N'-(pyridin-2-ylmethylene)isonicotin-ohydrazide. *J. Mol. Liquids*. 199, 483–488. doi: 10.1016/j.molliq.2014.07.013.

[3] Isha, A., Yusof, N.A., Ahmad, M., Suhendra, D., Yunus, W.M.Z.W., & Zainal, Z. 2007. Optical fibre chemical sensor for trace vanadium (V) determination based on newly synthesized palm based fatty hydroxamic acid immobilized in polyvinyl chloride membrane. *Spectro. Acta - Part A: Mol. and Biomol. Spectro.* 67(5), 1398–1402. doi: 10.1016/j.saa.2006.10.031.

[4] Scindia, Y.M., Pandey, A.K., Reddy, A.V.R., & Manohar, S.B. 2004. Chemically selective membrane optode for Cr(VI) determination in aqueous samples. *J . Anal. Chem. Acta*. 515(2), 311–321. doi: 10.1016/j.aca.2004.03.074.

[5] Łukasik, N., & Wagner-Wysiecka, E. 2017. Salicylaldimine-based receptor as a material for iron(III) selective optical sensing. *J. of Photochem. and Photobio. A: Chem.* 346, 318–326. doi: 10.1016/j.jphotochem.2017.06.011.

[6] Urek, S.K., Francic, N., Turel, M., & Lobnik, A. 2013. Sensing heavy metals using mesoporous-based optical chemical sensors. *J. Nanomater*. 2013, 1–13. doi: 10.1155/2013/501320.

[7] El-Feky, H.H., El-Bahy, S.M., Hassan, A.M.E., & Amin, A.S. 2021. Utility of a novel optical sensor design for ultra-trace detection of chromium colorimetrically in real environmental samples. *Int. J. Environ. Anal. Chem.* 16, 4031-4048. doi: 10.1080/03067319.2021.1921759 .

[8] Kong, F. & Ni, Y. 2009. Determination of Cr(VI) concentration in diluted samples based on the paper test strip method. *Water Scie. and Technol*. 60(12), 1088-1097. doi: 10.2166/wst.2009.741.

[9] Oliveira, H. 2012. Chromium as an environmental pollutant: insights on induced plant toxicity. *J. Botany*. 375843, 1-8. doi: 10.1155/2012/375843.

[10] Wiryawan, A., Suntari, R., Kusuma, Z., Retnowati, R., Burhan, R.Y.P., & Syekhfani. 2018. Method of analysis for determination of the chromium (Cr) species in water samples by spectrophotometry with diphenylcarbazide. *J. Environ. Engin. Sustain. Technol.* 5(1), 37-46. doi: 10.21776/ub.jeest.2018.005.01.6.

[11] Government Regulation No. 22. 2001. *Penyelenggaraan Perlindungan dan Pengelolaan Lingkungan Hidup*. Jakarta: Ministry of State Secretariat

[12] Suah, F.B.M., Ahmad, M., & Heng, L.Y. 2015. A novel polymer inclusion membranes based optode for sensitive determination of Al^{3+} ions. *Spectro. Acta Part A: Mol. and Biomol. Spectro.* 144, 81–87. doi: 10.1016/j.saa.2015.02.068

[13] Douglas-Gould, W., King, M., Mohapatra, B.R., Cameron, R.A., Kapoor, A., & Koren, D.W. 2012. A critical review on destruction of thiocyanate in mining effluents. *Minerals Eng.* 34, 38–47. doi: 10.1016/j.mineng.2012.04.009

[14] Verma C, Tapadia K, & Soni AB. 2017. Determination of iron (III) in food, biological and environmental samples. *Food Chem*. 221, 1415–1420. doi: 10.1016/j.foodchem.2016.11.011

[15] Duffy G, Maguire I, Heery B, Gers P, Ducree J, & Regan F. 2018. ChromiSense: A colourimetric lab-on-a-disc sensor for chromium speciation in water. *Talanta*. 178, 392-399. doi: 10.1016/j.talanta.2017.09.066.

[16] Vieira, M.G.A., Silva, M.A., Santos, L.O., & Beppu, M.M. 2011. Natural-based plasticizers and biopolymer films: a review. *Euro. Polym. J.* 47(3), 254–263. doi:10.1016/j.eurpolymj.2010.12.011

[17] Alfanaar, R., & Notario, D. 2019. Sintesis senyawa koordinasi astaxanthin dengan bantuan gelombang ultrasonik. *J. Kimia dan Kemasan*. 41(2), 88–94. doi: 10.24817/jkk.v41i2.3366.

[18] Pavia, D.L., Lampman, G.M., Kriz, G.S., & Vyvyan, J.A. 2009. *Introduction to Spectroscopy 4th Edition*. Washington: Brooks/Cole Cengange.

[19] Li, F., Sun, M., Cheng, Q., & Yang, B. 2016. Preparation and characterization of graphene oxide/cellulose triacetate forward osmosis membranes. *MATEC Web. Conf.* 67, 1–6. doi: 10.1051/matecconf/20166701015.

[20] Ingole, P.G., Kim, K.H., Park, C.H., & Choi, W.K., 2014. Preparation, modification and characterization of polymeric hollow fiber membranes for pressure retarded osmosis. *RSC Adv.* 4(93). 1-5. doi: 10.1039/C4RA07619B.

[21] Xing, X.Y., Gu, L., Jin, Y., Sun, R., Xie, M., & Wu, Q. 2019. Fabrication and characterization of cellulose triacetate porous membranes by combined nonsolvent-thermally induced phase separation. *Cellulose*. 26(1002), 1-16. doi: 10.1007/s10570-019-02347-7

[22] Rastegarzadeh, S., Nahid, P., & Zahra, J. 2013. Design of a sensitive membrane optode for iron determination. *Inst. Sci. and Tech.* 41(3), 290–300. doi: 10.1080/10739149.2012.729242

[23] Lace, A., Ryan, D., Bowkett, M., & Cleary, J. 2019. Chromium monitoring in water by colorimetry using optimised 1,5-diphenylcarbazide method. *Int. J. Environ. Res. Public Health*. 16(10), 1803-18017. doi: 10.3390/ijerph16101803.

[24] Chong, K.W. & Cho, K.H. 2023. Chemical Regeneration of Activated Carbon After Adsorption of Ni(II) Ions. *Indones. J. Chem. Stud.* 2(1), 1–8. doi: 10.55749/ijcs.v2i1.20.

[25] Association of Official Analytical Chemist. 2013. *Official Method of Analysis of AOAC International 20th Ed.* Washington: AOAC Pr.

[26] Chikanbanjar, N., Semwal, N., & Jyakhwa, U. 2020. A review article on analytical method validation, *J. Pharma. Innov.* 1(1), 48-58.

[27] Regulation of the Minister of Health of the Republic of Indonesia Number 32. 2017. *Standar Baku Mutu Kesehatan Lingkungan dan Persyaratan Kesehatan Air untuk Keperluan Higiene Sanitasi, Kolam renang, Solus Per Aqua, dan Pemandian Umum*. Jakarta: Ministry of Health.

[28] Firooz, A.R., Movahedi, M., & Sabzyan, H. 2019. A new selective optode for the determination of iron(III) based on the immobilization of morin on triacetylcellulose: A combined experimental and computational study. *J. Mat. Scie. & Eng.* 94, 410-416. doi: 10.1016/j.msec.2018.09.031.

[29] Harmita. 2004. Petunjuk pelaksanaan validasi metode dan cara perhitungannya. *Majalah Ilmu Kefarmasian*. 1(3), 117-135. doi: 10.7454/psr.v1i3.3375.

[30] Harvey, D. 2016. *Analytical Chemistry 21.* New York: McGraw-Hill Companies.