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Simple Synthesis of Cellulose Triacetate from HVS Paper Waste and Its Application for Optode

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Abstract—The optode membrane is a membrane that can identify ions in an aqueous solution. One of the most widely used optode membranes is cellulose triacetate based. Cellulose triacetate (CTA) has the characteristics of hydrophobic, transparent, elastic, and affordable. There are sources of cellulose triacetate that can be utilized and waste paper is one of them. Waste paper is extracted to obtain the cellulose, then by acetylization reaction to produce cellulose triacetate. The resultant cellulose triacetate has a degree of substitution (DS) of 2.89 and an acetyl group percentage (% AG) of 43.64. The standard and synthesized CTA optode membrane are tested for performance with various parameters, ie optimum pH, optimum immersion time, working range, limit of detection (LOD), and limit of quantification (LOQ). The standard CTA optode membranes and synthesized worked at pH 3 and 4 with optimum immersion time for 15 min, respectively. The optode produced a linear response in detecting Cr(VI) ion in the concentration range of 0.02-1 mg/L for standard CTA with an R^2 of 0.9726 and 1-25 mg/L for synthesized CTA with an R^2 of 0.9764, The limit of detection (LOD) and limit of quantitation (LOQ) were 0.0015 mg/L and 0.0051 mg/L for standard CTA, while 0.0224 mg/L and 0.0749 mg/L for synthesis CTA respectively. Since both optode membranes' performance test results are adequate, the synthesis results of CTA optode membranes can be employed as one source of cellulose triacetate.

Keywords— *Cellulose triacetate; Degree of substitution; Hexavalent chromium; Optode; Membrane*

1. INTRODUCTION

Paper waste, a key raw material, is currently underutilized within the recycling sector, with only 70% being effectively reused or recycled. Addressing this issue requires a robust strategy to maximize its potential and enhance its value. Recycling paper waste can mitigate these adverse effects [1]. One promising approach involves repurposing it as a raw material for optical sensors (optodes), thereby increasing its utility value.

An optode is an active component placed in a matrix that will form color when it binds to an analyte ion [2,3]. Optode has several advantages, namely low cost, excellent flexibility, and easy operation. The advantages of the optode membrane allow it to be used as a test strip or kit so that it can be used for in-situ analysis. Optode membranes commonly used are polyvinyl chloride (PVC) and cellulose triacetate (CTA). PVC membranes can bind water from the liquid phase so that the resulting complex color becomes opaque, while membranes made from cellulose triacetate as a base material have the advantage of not absorbing water and the resulting complex color is better [4].

Paper waste serves as a cellulose source suitable for optode membranes. Recycling paper waste into these membranes starts with delignification, removing hemicellulose and lignin to counteract lignin's stiffening effect on paper. Following this, cellulose undergoes acetylation to produce cellulose triacetate [5]. The advantages of paper waste as a source of cellulose triacetate are that it reduces the production costs and has properties that are almost the same as commercial cellulose triacetate so that it can be a potential source as raw materials [6].

Cellulose triacetate from paper waste is applied to detect heavy metals using a simpler method, namely an optode membrane. The main function of the optode membrane is to detect heavy metals in water, one of which is chromium. Chromium contamination is form of two species, trivalent chromium species, (Cr(III)) and hexavalent chromium species (Cr(VI)). Chromium(III) is

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the most abundant form of chromium metal ion in the environment. Changing environmental conditions, such as pH, can cause trivalent chromium to oxidize to hexavalent chromium. Hexavalent chromium is carcinogenic and its toxicity level is 100 to 1000 times higher than that of trivalent chromium [7,8]. The maximum hexavalent chromium concentration permitted in drinking water according to the Ministry of Health, Republic of Indonesia is 0.05 mg/L. It is therefore envisaged that this research will enable the creation of an optode membrane based on cellulose triacetate.

2. EXPERIMENTAL SECTION

2.1. Materials

The materials used for this research were waste paper with a specification of 70 gsm used paper, glacial acetic acid (CAS 64-19-7), chloroform (CAS 67-66-3), acetophenone (CAS 98-86-2), oleic acid (CAS 112-80-1), 1,5-diphenylcarbazide (DPC) (CAS 140-22-7), trioctylmethylammonium chloride (aliquot 336) (CAS 63393-96-4), ethanol (CAS 64-17-5), nitric acid (CAS 7697-37-2), acetic anhydride (CAS 108-24-7), methanol (CAS 67-56-1), NaOH (CAS 1310-73-2), hydrochloric acid (CAS 7647-01-0), H_2SO_4 (CAS 7664-93-9), potassium dichromate (CAS 7778-50-9), and chloroform (CAS 67-66-3). Chemicals were pro analyst grade from Merck, Darmstadt, Germany.

2.2. Instrumentations

The instruments for conducting research were a analytical balance (0.0001 mg, OHAUS AX224/E), magnetic stirrer (MG-78-1), sonicator (AS ONE), oven (Memmert UM 400), pH meter (Hanna HI 2211), UV-Vis spectrophotometer (Ocean Optics Vis-NIR USB4000), and FTIR spectroscopy (ABR, 4000-400 cm^{-1}).

2.3. Preparation of Cellulose Triacetate from Paper Waste

The HVS paper waste was cut into small pieces and weighed as much as 4 g, mixed with 76 mL of distilled water and left for 24 hours. After that, the mixture was filtered and the paper sediment was taken. Then, 76 mL of 0.25 M NaOH was added to the paper and left for 18 hours. After that, the mixture was filtered again and the resulting precipitate was then refluxed with three portions of a 20% v/v mixture of nitric acid in ethanol which were replaced every hour. After refluxing, the mixture was filtered and washed with distilled water until the filtrate was colorless. The precipitate was dried at 105 °C for 180 minutes and allowed to stand. The precipitate that will be produced is a white powder.

Initially, 1 g of cellulose precipitate was added with 40 mL of glacial acetic acid, then the mixture was heated to 40 °C and stirred for 3 hours. The mixture was added with 45 mL of acetic anhydrous and 0.5 mL of H_2SO_4, then continued with heating at 50 °C and stirring for 1 hour. The mixture was then cooled to room temperature and added with distilled water. The mixture was neutralized with distilled water and filtered using vacuum, then the precipitate was dried in an oven at 105 °C until the weight was constant. The results of CTA were then analyzed with FTIR for identification.

2.4. Characterization, Fabrication, and Perfomance Test of Cellulose Triacetate Optode for Cr(VI) Detection

The CTA optode film was manufactured utilizing the taking after methods. CTA arrangement made by blending 0.1350 g of CTA into 10 mL of chloroform. The DPC arrangement was arranged by blending 5 mg DPC into 5 mL acetone. The homogenous cellulose triacetate arrangement was included with a 0.30 mL plasticizer made from 0.03 mL of oleic corrosive and 0.27 mL of acetophenone. Aliquot 336 as much 0.07 mL of was included to the cellulose triacetate arrangement and mixed with a attractive stirrer for 5 min. The DPC arrangement was included into cellulose triacetate arrangement blend and the mixed once more for 5 min. The arrangement blend was homogenized with a sonicator for 5 min. The homogenized blend was poured into a petri dish and cleared out at discuss temperature for 48 h. The optode layer that has been created was at that point cut to a estimate of 1×3 cm. The same strategy was done utilizing the synthesized CTA.

The Optode film testing carried out included deciding the ideal pH for color arrangement, deciding the ideal contact time, and the optode performance (linearity test, LOD, and LOQ). Permformance test were carried out utilizing UV-Vis spectrophotometer of solid materials at the maximum wavelength.

3. RESULT AND DISCUSSION

3.1. Cellulose Extract and Characterization of Cellulose Triacetate

Cellulose is a polymer with a large molecular weight and is formed from linear polysaccharides linked to β-1,4-D-glucopyranose. The cellulose used in this research comes from the colorless part of HVS paper waste. HVS paper is cut first into smaller sizes so that the cellulose is easier to extract. The paper is soaked for 24 hours to form pulp, 0.5 M NaOH is added, and soaked for 18 hours to remove some of the lignin in the paper fibers [5]. The paper pulp will expand after the application of NaOH and undergo a mercerization reaction in the cellulose fibers which can reduce the number of hydroxyl groups in the cellulose, thereby reducing its polarizability and making it more hydrophobic. Heating with ethanol-nitric acid to completely remove lignin and activate cellulose for the acetylation reaction [5].

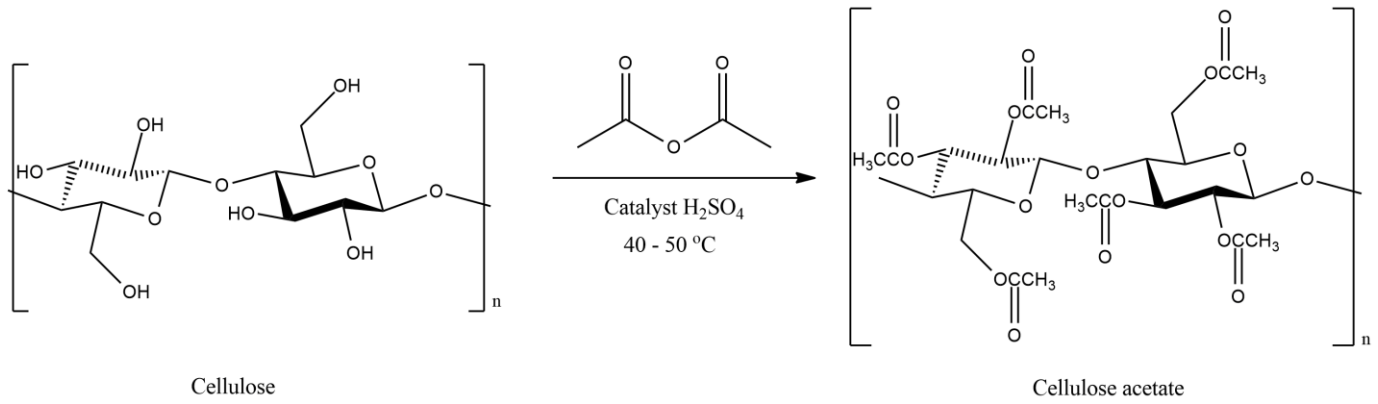

Fig. 1 Acetylation reaction between cellulose and acetic anhydride

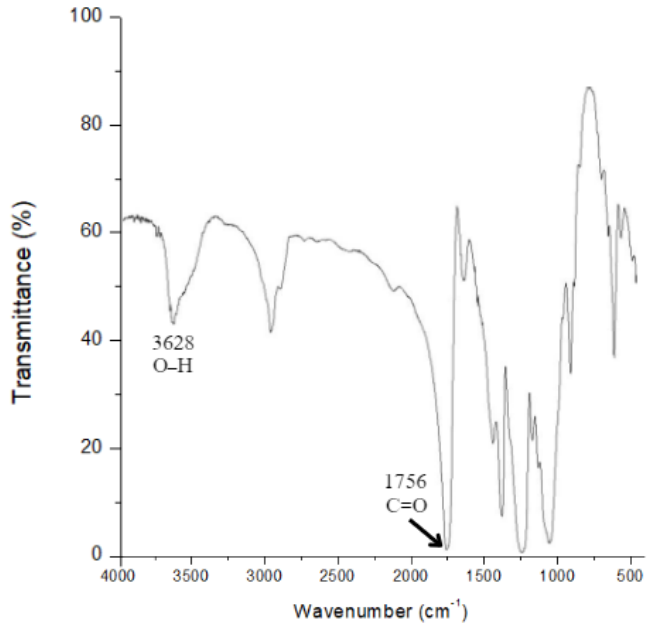

Fig. 2. FTIR spectra of synthesized CTA

The resulting cellulose is further acetylated to create cellulose triacetate. The acetylation process begins by dissolving cellulose with glacial acetic acid which functions as a swelling agent which can increase the accessibility of acetyl groups to hydroxyl groups on cellulose. Sulfuric acid is used as a catalyst to speed up the acetylation reaction. In the acetylization process, the temperature used 40–50 °C which can increase the rate of cellulose development. Acetic anhydrous is used as a source of acetyl groups [9]. The cellulose acetylation reaction is written in **Fig. 1.**

The percent value of acetyl groups (%AG) obtained from the reaction was 43.64 and the degree of substitution (DS) value was 2.84. Cellulose triacetate has a %AG value of 43.5–44.8% and a DS of 2.8–3.9 [10]. The results of the FTIR spectrum of synthesized CTA are shown in **Fig.2**, the greatest intensity is at a wavenumber of 1756 cm^{-1}, this indicates the presence of carbonyl groups in synthesized CTA. The large intensity of the carbonyl group causes a decrease in the intensity of the OH group at the wavenumber 3628 cm^{-1}. The obtained spectrum results were compared with the spectral results of Li et al. These results show that there is no significant difference in wavenumber and the OH group was successfully acetylated and substituted by the acetyl group [11].

3.2. Standard and Synthesized CTA Optode Membrane

The main ingredients in this optode membrane are CTA, plasticizers (acetophenone and oleic acid), aliquot 336, and 1,5-diphenylcarbazide (DPC). Aliquot 336 (trioctylmethylammonium chloride) is a quaternary ammonium salt which functions as a carrier for chromium ions from the membrane surface into the membrane to react with DPC. Aliquot 336 when reacting with anions will exchange Cl^- ions. The reaction is explained in Equation (1).

$$R_3(CH_3)N^+Cl^- + HCrO_4^- \rightarrow (R_3(CH_3)N^+)HCrO_4^- + Cl^- \quad (1)$$

Chromium will react with DPC to produce a reddish purple color. The DPC-Cr color complex formation involves two stages. First, oxidation of DPC by Cr(VI) to form diphenyl carbazone (DPCO) and reduction of Cr(VI) to Cr(III). The second stage is complex formation between Cr(III) and DPCO to produce a purple color [12]. This reaction stages is shown in **Fig. 3.**

Table 1. Standard CTA optode membrane formulation

Mem-brane	CTA Weight (g)	Plasticizer (mL)		Aliquat 336 (mL)	DPC (mg)
		Oleic	Aceto-phenone		
A	0.1367	0.10	0.30	0.10	2
B	0.1369	0.03	0.27	0.07	8
C	0.1369	0.03	0.27	0.07	5

The best composition of standard and synthesized CTA optode membranes is first sought to obtain an optode membrane that is transparent, sensitive to chromium ions, and does not experience discoloration when placed in a Cr(VI) solution. In **Table 1**, the best standard CTA optode membrane is membrane C because it has a transparent, flexible and non-brittle physical appearance. Meanwhile, membrane A was unable to change color when immersed in a Cr(VI) solution. This is likely a lack of DPC concentration

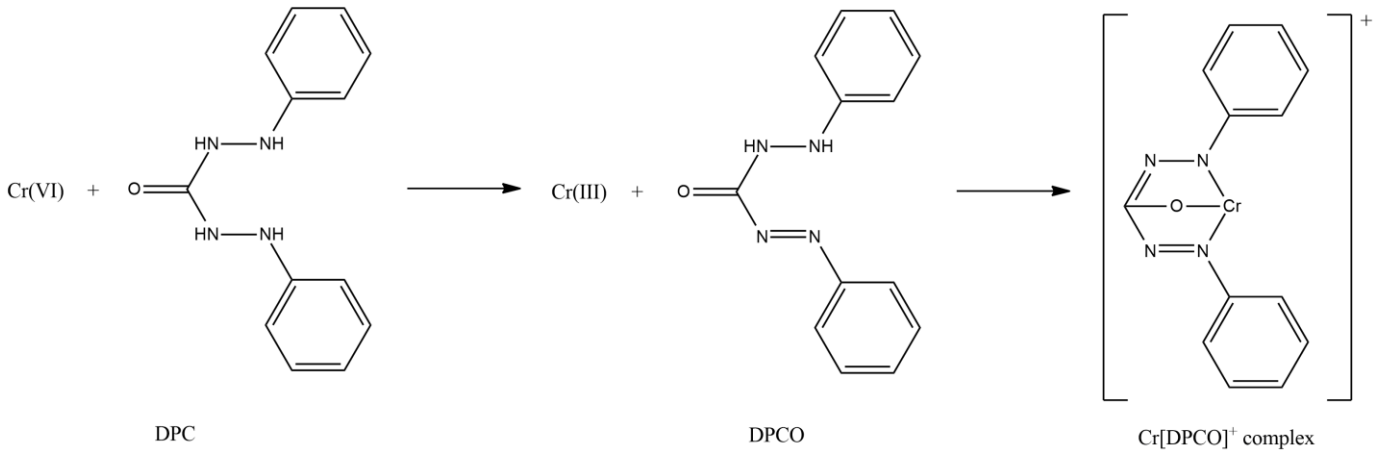

Fig. 3 Reaction of Cr(VI) with DPC to form DPCO

added to the optode membrane. Membrane B is also not good for use as an optode membrane because it is less transparent and the color of the membrane is dark red because the DPC concentration added to the optode membrane is greater.

Table 2. Synthesized CTA optode membrane formulation

Mem-brane	CTA Weight (g)	Plasticizer (mL)		Aliquat 336 (mL)	DPC (mg)
		Oleic	Aceto-phenone		
A	0.1356	-	-	0.07	5
B	0.1356	0.03	0.27	0.07	5
C	0.6099	-	-	0.07	5
D	0.6106	0.18	1.62	0.07	5
E	0.6052	0.03	0.27	0.07	5
F	0.4505	0.07	0.20	0.07	5

Synthesized CTA optode membrane were made in six different compositions to obtain the best optode membranes (**Table 2**). Membranes A and B produce membranes that are fragile and poorly fused, so they tear easily when touched. Membrane C produces a membrane that is stronger than the previous membrane, but forms a membrane that is brittle and very fragile. Then membranes D and E were given the addition of plasticizer to reduce brittleness and increase flexibility, but still had the drawback of the membrane being a little fragile when held. Membrane F produces a membrane that is much better than the previous membrane and has physical characteristics that are more flexible, stronger and not easily torn.

3.3. Optimization of pH and Contact Time

To determine the effective performance of the optode membrane in absorbing Cr(VI), the optimum pH was assessed (**Fig. 4**). The research found that the λ_{max} for standard CTA membranes was 541.59 nm at pH 3, 537.28 nm at pH 4, 542.18 nm at pH 6, and 543.94 nm at pH 8. The highest absorbance at pH 3 was 0.049. For the synthesized CTA membrane, the λmax values were 520.75 nm at pH 3, 511.26 nm at pH 4, and 503.53 nm at pH 6, with the highest absorbance at pH 4 being 0.357. The $HCrO_4^-$ species forms at pH 2-4 and decreases above pH 4. This species ionically bonds with aliquot 336, serving as an anion carrier medium into the optode membrane [13].

The optode membrane was immersed for different durations to ascertain the optimal contact time for absorbing Cr(VI) from the solution. The HCrO4- species, which is ionically bonded to aliquot, diffuses into the optode membrane. According to **Fig. 4**, both standard and synthesized CTA membranes exhibit optimal contact times of 15 minutes.

The uptake of Cr(VI) into the membrane increases linearly with immersion time. The synthesized CTA optode membrane showed superior results after soaking for 15 minutes, producing a more vivid and intense purple color compared to the standard CTA optode membrane under the same conditions. However, prolonged soaking led to the standard CTA optode membrane's color fading into the solution, potentially allowing re-entry of Cr(VI) into the solution and altering its color [16]. Meanwhile, the synthesized CTA optode membrane did not experience discoloration when immersed in a Cr(VI) solution.

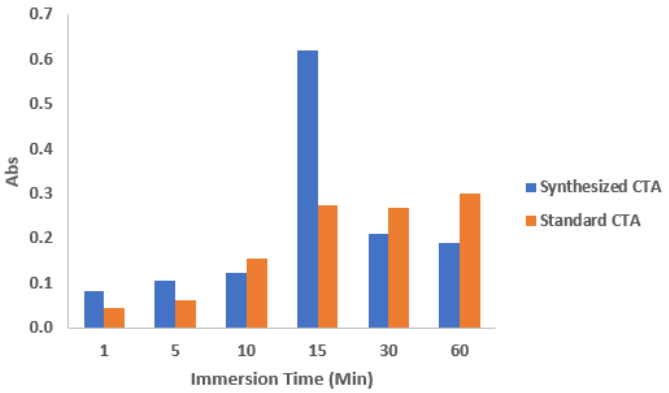

Fig. 4. Effect of immersion time on standard and synthesized CTA membrane absorption values

3.4. Limits of Detection (LOD) and Quantitation (LOQ)

Analyte concentration estimation with standard and synthesized CTA film optodes combines chemical

responses with spectroscopic estimations. The optode film changes color when association with the analyte. The flag reaction within the frame of retention coming about from this estimation gives greatest conditions at the greatest wavelength. λ_{max} is obtained by measuring absorpions within the wavelength extend 400–700 nm .

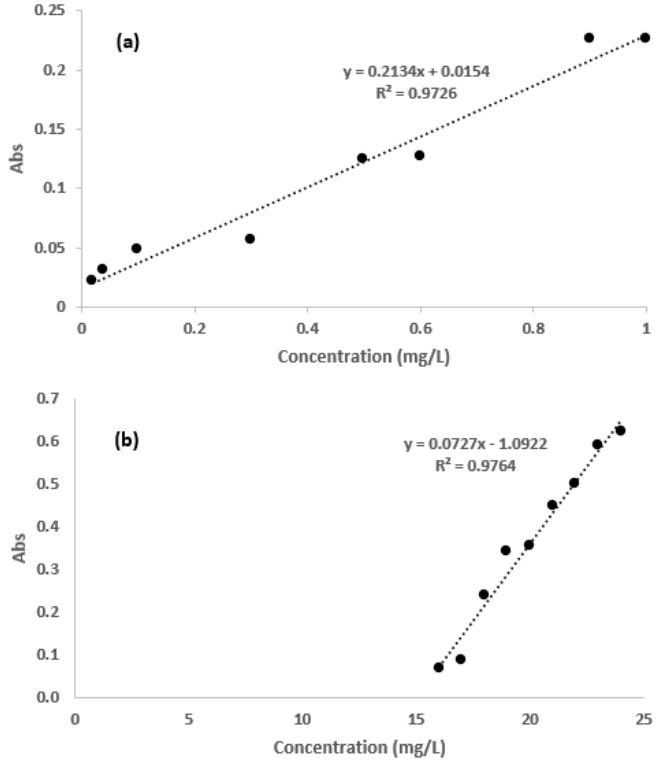

Fig. 5. Standard curve of standard CTA (a) and synthesized CTA (b) optode membrane

The working range of both standard and synthesized CTA optode membranes can be observed from the graph depicting the relationship between Cr(VI) concentration and absorbance value, which also shows their linearity (Figure 5). This linearity in concentration indicates the optimal working area for the optode membrane. For standard CTA, the working range was measured at analyte concentrations of 0.02-1 mg/L, while for synthesized CTA, it was 1-25 mg/L. The optode membrane color intensifies with increasing analyte concentration, correlating directly with the absorbance value. The measurement results showed poor linearity, with coefficients of determination (R^2) values of 0.9726 and 0.9764. An R^2 value is considered to have better linearity if it is close to 1 or greater than 0.99 [14].

The detection limit (LOD) and quantification limit (LOQ) were calculated using the standard deviation and slope of the standard curve, with three repetitions. The LOD represents the lowest level of analyte that the optode membrane can detect. The LOQ indicates the smallest amount of analyte that can be reliably quantified [15].

The LOD and LOQ for the CTA standard-based optode membrane as a Cr(VI) detector are 0.0015 mg/L and 0.0051 mg/L, respectively. For the CTA synthesis-based membrane, the LOD and LOQ are 0.0224 mg/L and 0.0749 mg/L. This indicates that both the CTA standard and CTA synthesis membrane optodes can detect Cr(VI) concentrations below the maximum threshold of 0.05 mg/L, as regulated by the Republic of Indonesia for drinking water, raw drinking water materials, water used in fisheries, and animal husbandry [17]. If the Cr(VI) concentration in a sample is lower than the LOD value, the sample's signal response becomes indistinguishable from the blank signal and noise. Errors in detecting and quantifying an analyte can arise from matrix effects, sample concentration, and reagent purity. The detection of hexavalent chromium aligns well with previous research by Arif et al. In their study, a commercial CTA-based membrane was used, yielding detection and quantification limits of 0.0055 mg/L and 0.0165 mg/L, respectively [16]. Although the results appear slightly higher, they remain within the regulatory limits set by the Republic of Indonesia [17,18]. This research offers valuable data and insights that contribute to the effective management and diversification of paper waste. Additionally, this data provides a new perspective on CTA derived from different cellulose sources, allowing for comparisons with our work [19].

CONCLUSION

CTA optode membranes made from waste paper can detect Cr(VI) similarly to standard CTA optode membranes. The synthesized CTA optode membrane from paper waste has a quicker contact time and higher absorption compared to standard membranes. Additionally, the synthesized membrane does not discolor in the Cr(VI) solution, which is a significant advantage. This membrane operates effectively at concentrations of 16-25 mg/L, with detection and quantification limits of 0.0224 mg/L and 0.0749 mg/L, respectively. Therefore, the performance of the synthesized CTA optode membrane is considered good and acceptable.

SUPPORTING INFORMATION

There is no supporting information in this paper. The data that support the findings of this study 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

AAA performed the experiment, ZA carried out the experiment and data calculations. ZA, F, DS, and ER collaborated on writing and revising the manuscript. All authors approved the final version of the manuscript.

REFERENCES

[1] Sanchez, B., Wirosoedarmo, R., & Suharto, B. 2014. Analisis finansial sampah kertas di Universitas Brawijaya. *J. Sumberdaya Alam dan Lingkungan*. 1(2). 1–8.

[2] Suah, F.B.M. 2017. Preparation and characterization of a novel Co(II) optode based on polymer inclusion membrane. *Anal. Chem. Res*. 12. 40–46. doi: 10.1016/j.ancr.2017.02.001.

[3] Baezzat, M.R., & Karimi, M. 2013. Design and evaluation of a new optode based on immobilization of indophenol on triacetylcellulose membrane for determination of nickel. *Int. J. Chem Tech Res*. 5(5). 2503–2507.

[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. *Anal. Chim. Acta*. 515. 311–321. doi: 10.1016/j.aca.2004.03.074.

[5] Filho, G.R., Monteiro, D.S., Meireles, C.S., Assuncao, R., Cerqueira, D.A., Barud, H.S., Ribeiro, S., & Messadeq, Y. 2008. Synthesis and characterization of cellulose triacetate produced from recycled newspaper. *Carbohydrate Polymer*. 73(1). 74–78. doi: 10.1016/j.carbpol.2007.11.010.

[6] Beraich, F.Z., Arouch, M., Bakasse, M., & Nasrella, H. 2016. From waste to an ecological material : a new way to value the waste paper. *IJISR*. 20(2). 343–348.

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

[8] 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. *Int. J. Chem Tech Res*. 11 (01). 391–406.

[9] Bello, A., Isa, M.T., Aderemi, B.O., Mukhtar, B. 2016. Acetylation of cotton stalk for cellulose triacetate production. *ASRJET*. 15(1). 137–150.

[10] Fengel, D., Wegener, G, 1995. *Wood Chemistry, Ultrastructure, Reactions*. Berlin: Walter de gruyter & Co.

[11] 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/20166.

[12] 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.

[13] Kong, F., Ni, Y. 2009. Determination of Cr(VI) concentration in diluted samples based on the paper test strip method. *Water Sci. Tech*. 60(12). 3083–3089. doi: 10.2166/wst.2009.741.

[14] Association of Official Analytical Chemist. 2016. *Official Method of Analysis of AOAC International 20th Ed*. Washington: AOAC Pr.

[15] Chikanbanjar, N., Semwal, N., Jyakhwa, U. 2020. A review article on analytical method validation. *J. Pharm. Innov*. 1(1). 48–58.

[16] Arif, Z., Munandar, R., Rohaeti, E., Rafi, M. 2023. Detection of hexavalent chromium ion in water by optode membrane. *Indones. J. Chem. Stud*. 2(2). 76–82. doi: 10.5749/ijcs.v2i2.39.

[17] Regulation of the Minister of Health of the Republic of Indonesia Number 492/MENKES/PER/IV/2010 about drinking water quality requirements in Indonesia, including maximum levels of various contaminants. Jakarta: Ministry of Health.

[18] Regulation of Minister of Enviroment and Forestry of the Republic of Indonesia Number P.68/Menlhk.Setjen/Kum.1/8/2016 about Domestic Wastewater Quality Standards. Jakarta: Ministry of Environment and Forestry of the Republic of Indonesia.

[19] Shaikh, H.M., Anis, A., Poulose, A.M., Al-Zahrani, S.M., Madhar, N.A., Alhamidi, A., Aldeligan, S.H., Alsubaie, F.S., 2022. Synthesis and characterization of cellulose triacetate obtained from date palm (*Phoenix dactylifera* L.) trunk mesh-derived cellulose. *Molecules*. 27(4). 1434. doi: 10.3390/molecules27041434.