# **Fabrication of Carbon Paste Electrode Modified with ZnO Nanoparticles and Nanobentonite for Analysis of Bisphenol A by Cyclic Voltammetric**

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# **Abstract**

The Bisphenol A (BPA) is a 2,2-bis(4-hydroxyphenyl) propane compound that is produced on a large scale for industrial applications, particularly in polycarbonate plastics. BPA molecules can migrate from plastics into food if stored at high temperatures and for extended periods. Various methods have been developed for BPA analysis, including cyclic voltammetry. This study focuses on the fabrication and application of a carbon paste electrode (CPE) modified with ZnO nanoparticles and nanobentonite for the analysis of BPA in polycarbonate-based bottled drinking water using cyclic voltammetry. The results showed that the optimal electrode conditions were: electrode composition 3:4:1:2 (carbon: nanobentonite: ZnO nanoparticles: paraffin), and pH 7. The BPA content obtained by cyclic voltammetry for brands A, B, and C was 0.2102; 0.1752; and 0.2210 mM. These results demonstrate that cyclic voltammetry with a ZnO nanoparticle and nanobentonite modified carbon paste electrode can be used for BPA analysis.

*Keywords: Cyclic Voltammetry, Carbon Paste Electrode, Bisphenol A, ZnO Nanoparticles, Nanobentonite*

# **INTRODUCTION**

Bisphenol A (BPA) is a 2,2-bis(4-hydroxyphenyl) compound produced on a large scale for industrial plastic needs. BPA is essential as a monomer in polycarbonate plastics, epoxy resins used as protective materials for metal cans, and other plastic products, such as dental fillings, medical devices, children's toys, pipes, and beverage bottles. Along with the various applications of BPA compounds, the production and use of BPA also continue to increase (Aulia & Mita, 2023).

Despite its various applications, using BPAcontaining plastics in food and beverage containers poses significant health risks. BPA molecules can migrate from the plastic into the food when products are stored in inadequate conditions. BPA compounds in polycarbonate (PC) polymers degrade more rapidly when exposed to heat. Heat exposure can occur during food packaging sterilization, storage, or distribution. BPA can enter the human body through contaminated food. BPA in the body can disrupt the function of endocrine glands, particularly estrogen and thyroid hormones, interfere with the reproductive system by

lowering testosterone levels, and disrupt insulin hormones (Puspita & Noviandri, 2021)

Given BPA's various harmful effects, a monitoring or analysis system is needed to detect BPA in food and beverage packaging to prevent its adverse effects. One of the analysis methods that can be used is cyclic voltammetry. Cyclic voltammetry is an alternative method that can be used for BPA analysis. This is because BPA has electroactive phenolic hydroxyl groups. BPA can undergo an oxidation reaction by releasing two electrons. Therefore, when BPA is oxidized at the electrode, the voltammetric equipment detects and records a current change (Hikma & Arpah, 2024).

Voltammetric methods employ three types of electrodes: a reference electrode (Ag/AgCl), an auxiliary electrode (platinum), and a working electrode. Carbon Paste Electrode (CPE) is a commonly used working electrode for electroanalysis. CPE offers several advantages, including a wide potential range, no background current, variable surface area, inertness, and suitability for identifying various organic compounds. Paraffin is a binder in CPE preparation, forming physical interactions with

carbon. However, paraffin's insulating properties hinder electron flow, impeding electron transfer. Consequently, CPE modification with conductive materials and a larger surface area is necessary to enhance performance in the f (Setiarso & Lukmana, 2018)

Nanobentonite possesses a complex surface structure with numerous pores and a large surface area. When incorporated into the electrode, nano bentonite expands the area, enhancing interactions with the target analyte. Consequently, electrode sensitivity improves due to increased electrolyte molecules interacting with the electrode (Putri & Setiarso, 2023). Additionally, zinc oxide (ZnO) is a semiconductor metal oxide with a wide band gap (3.37 eV). It has violet absorption in the ultraviolet (UV) at room temperature (Julita et al., 2022). ZnO nanoparticles exhibit good electrical conductivity. When dispersed within the electrode matrix, ZnO nanoparticles facilitate electron transport (Tehubijuluw et al., 2023). This study aims to analyze BPA in polycarbonate-based bottled drinking water using cyclic voltammetry with optimized pH conditions and an electrode modified with ZnO nanoparticles and nano bentonite.

# **METHODOLOGY**

## **Materials and Instrumentals**

The materials used in this research are water in polycarbonate packaging (three brands), Loba Chemie BPA standard, 1 mm copper wire, carbon, bentonite, paraffin, Whatman No. 42 filter paper, H2SO4 pa 97%, Na2HPO4.2H2O p.a Supelco, NaH2PO4.H2O p.a Supelco, deionized water, ethanol p.a 99% (Merck), zinc acetate dihydrate 99%, NaOH p.a, and KCl p.a.

The instruments used in this research are 797 VA computrace voltammeter, XRD X'pert PRO PANalytical, FTIR Shimadzu IRPrestige 21, SEM FEI Inspect-S50, Ultrasonic bath Elsa S 0H, platinum electrode, Ag/AgCl electrode, Ohaus analytical balance, 50 mL Iwaki beaker, 100 mL Pyrex beaker, 300 mesh sieve, sandpaper, thermometer, Eutech Instruments pH meter, magnetic stirrer, Corsair Heating and Catering Etd oven, volume pipettes, 250 mL Iwaki volumetric flask, and Eppendorf 5810 centrifuge.

### **Synthesis of ZnO Nanoparticles**

ZnO nanoparticle synthesis was carried out using the sol-gel method (Utomo & Wihadi, 2022). 2 grams of zinc acetate dihydrate  $(Zn(CH_3COO)_2.2H_2O)$ crystals were dissolved in 10 mL of deionized water and stirred at 70 °C until homogeneous. The solution, which was then reacted with 2 M sodium hydroxide

(NaOH) solution until pH eight was reached and stirred. After obtaining a milky white solution, the solution was titrated with 100 mL of ethanol, resulting in a white ZnO solution. The impurities in the ZnO sediment were collected and centrifuged for 15 minutes at 5000 rpm. The residue was then rewashed with deionized water and centrifuged to remove the supernatant. Subsequently, it was washed twice with ethanol to remove any remaining contaminants. The ZnO residue was then dried in an oven at 100 °C for 30 minutes and calcined at 400 °C for 30 minutes (Vishwakarma & Singh, 2020).

#### **Synthesis of Nanobentonite**

Twenty grams of bentonite were dispersed in 50 mL of 2 M  $H_2SO_4$  and stirred for 6 hours at 70 $^{\circ}$ C. The mixture was then covered and allowed to stand for 24 hours. After that, the mixture was washed with hot deionized water and filtered. The bentonite was then heated in an oven at 100 °C for 3 hours, ground, and sieved through a 300 mesh sieve. Activated bentonite was obtained (Sari & Setiarso, 2020). The activated bentonite was then added to 50 mL of 99% ethanol. The mixture was sonicated using an ultrasonic bath for 4 hours at 60 °C. After that, it was dried in an oven at 100 °C for 30 minutes. The dry nano bentonite was then crushed with a mortar and pestle and oven-dried at 100 °C for 5 hours (Saputra & Setiarso, 2020).

### **Preparation of Carbon Paste Electrode Modified with ZnO Nanoparticles and Nanobentonite**

Fabrication of working electrode by cutting a 10 cm long copper wire. Then, peel the bottom end to a length of 0.5 cm and the top end to 1.5 cm. Both ends are polished (sanded) until shiny. The next step is to give the lower back a 1 cm insulator pipe. Then insert the electrode mixture into the insulator pipe with a ratio of carbon: nano bentonite: ZnO nanoparticles: paraffin as follows 3:2:3:2; 3:3:2:2; 3:1:4:2; 3:4:1:2 on the watch glass.

### **Determination of the Optimal Electrode Composition**

10 mL of 0.1 mM Bisphenol A standard solution was added to 10 ml of 10 mM KCl solution and 5 ml of 0.1 M phosphate buffer solution at pH 7 in a voltammetric cell. The next step was to insert a modified CPE (Carbon Paste Electrode) working electrode with nanoparticles of ZnO and nano bentonite with various compositions into the voltammeter cell. Then, measurements were carried out at a potential of  $-1.2$  V to  $+1$  V, deposition time of 5 seconds, and scan rate of 0.1 V/s (Puspita & Noviandri, 2021).

# **Determination of optimum pH**

Optimization pH was performed by varying the pH of a 0.1 M phosphate buffer solution from pH 3, 4, 5, 6, 7, and 8 containing 0.1 mM BPA analyte. Measurements were carried out using the electrode with the best composition inserted into a voltammetric cell containing 10 mL of 0.1 mM BPA standard solution, 10 mL of 10 mM KCl solution, and 5 mL of 0.1 M phosphate buffer solution with various pH values of 3, 4, 5, 6, and 7. Measurements were then performed at a potential of  $-1.2$  V to  $+1$  V, deposition time of 5 seconds, and scan rate of 0.1 V/s (Puspita  $\&$ Noviandri, 2021).

### **Measurement of BPA Standard Linearity**

BPA standard linearity was used to construct a BPA standard curve. The electrode with the best composition was inserted into a voltammetric cell containing 10 mL of BPA standard solution with varying concentrations of 0.1, 0.3; 0.5, 0.7, and 1 mM, 10 mL of KCl solution with a concentration 100 times the concentration of bisphenol A (10, 30, 50, 70, and 100 mM) and 5 mL of phosphate buffer solution with optimum pH conditions. Measurements were then carried out at a potential of  $-1.2$  V to  $+1$  V, deposition time of 5 seconds, and scan rate of 0.1 V/s (Puspita  $\&$ Noviandri, 2021b).

# **Testing for BPA in Polycarbonate-Based Drinking Water Samples**

The electrode with the best composition was tested by inserting it into a voltammetric cell containing a mixture of 10 mL sample, 10 mL 100 mM KCl, and 5 mL pH optimum phosphate buffer. Measurements were performed at a potential of -1.2 V to  $+1$  V (Puspita & Noviandri, 2021), deposition time of 5 seconds, and scan rate of 0.1 V/s.

## **RESULTS AND DISCUSSION**

#### **Synthesis of ZnO Nanoparticles**

Zinc oxide (ZnO) nanoparticles were synthesized in this study using the sol-gel method (Utomo  $\&$ Wihadi, 2022). The sol-gel method was chosen due to its several advantages, including ease of composition modification, the ability to be synthesized at a relatively low heating temperature, and the ease of particle size modification (Afrilia et al., 2019). This synthesis used zinc acetate dihydrate  $(Zn(CH_3COO)_2.2H_2O)$  as the precursor. This precursor was chosen because of its advantages, namely that it is more cost-effective than other precursors, such as zinc nitrate and zinc sulfate, has higher purity, is easily soluble in organic solvents such as ethanol, methanol and 2-propanol, and uses zinc acetate for better control over the size and morphology of the resulting particles (Wimarsela et al., 2021). The reactions occur during the synthesis of ZnO nanoparticles are (1) hydrolysis and (2) condensation.

#### $Zn(CH_3COO)_2.2H_2O_{(s)}$  + NaO $H_{(aq)} \rightarrow Zn(OH)_{2(aq)}$  + CH<sub>3</sub>COONa<sub>(aq).</sub> (1)  $Zn(OH)_{2(aq)} \rightarrow ZnO_{(s)} + H_2O_{(l)}$

FTIR, XRD, and SEM further characterized the synthesized ZnO nanoparticles. For FTIR, the synthesized ZnO nanoparticles were scanned at a wavenumber of  $4000 \text{ cm}^{-1}$  to  $450 \text{ cm}^{-1}$ . The results of FTIR of ZnO nanoparticles in this study are shown in Figure 1 and Table 1.



Figure 1. FTIR Results of ZnO Nanoparticles

Table 1. Functional Groups and FTIR Wavenumbers of ZnO Nanoparticles

| Functional   | Wavenumbers $(cm^{-1})$ |           |                       |
|--------------|-------------------------|-----------|-----------------------|
| Groups       | Research                | Reference | Source                |
|              | data                    |           |                       |
| O-H          | 3476.3                  | 3506.9    | (Patel et al.,        |
|              |                         |           | 2022)                 |
| $C=\Omega=C$ | 2345.2                  | 2334      | (Srujana $&$          |
|              |                         |           | <b>Bhagat</b> , 2022) |
| $C = C$      | 1518.4                  | 1569.5    | (Rhamdiyah &          |
|              |                         |           | Maharani,             |
|              |                         |           | 2022)                 |
| $C=\Omega$   | 1326.7                  | 134.6     | (Ramadanti &          |
|              |                         |           | Maharani,             |
|              |                         |           | 2022)                 |
| $Z_{n}$      | 907.8                   | 875       | (Rohmawati            |
|              |                         |           | et al., 2024)         |
| $Zn-O$       | 554.6                   | 594.6     | (Patel et al.,        |
|              |                         |           | 2022)                 |

The FTIR spectrum analysis of ZnO nanoparticles reveals several peaks corresponding to different vibrational frequencies. The peak at 554.6 cm-1 indicates the presence of Zn-O stretching vibrations. The peak at  $3476.3$  cm<sup>-1</sup> is characteristic of O-H stretching vibrations due to water adsorption on the

ZnO nanoparticles. C=C stretching vibrations are also observed at  $1518.4$  cm<sup>-1</sup>. The peak at  $1326.7$  cm<sup>-1</sup> is attributed to C=O stretching vibrations. The peak at 907.8 cm-1 corresponds to the tetrahedral coordination conformation of Zn.

XRD analysis of ZnO nanoparticles was performed using a diffraction angle range of 5-90° and a wavelength of 1.54060 Å. The XRD results are shown in Figure 2. The analysis revealed several diffraction peaks, including those at 2θ angles of 31.889°, 34.442°, 36.236°, 47.536°, 56.636°, 62.898°, 67.933°, and 69.159°. These diffraction angles indicate the hexagonal wurtzite structure of ZnO crystals, in agreement with the reference code 00-036-1451.



Figure 2. XRD Results of ZnO Nanoparticles

X-ray diffraction (XRD) analysis can be employed to determine the crystal size of a specific phase using the Debye-Scherrer equation, as presented in Equation (3), which relates crystal size to the width of the XRD peak.

$$
D = \frac{K\lambda}{\beta \cos \theta} \tag{3}
$$

For:

 $D =$  Crystal size (nm)

- $K =$ Shape factor of the crystal  $(0.89)$
- $\lambda$  = X-ray wavelength (1.5406 Å/0.15406 nm)

 $β = FWHM$  (radians)

 $\theta$  = Diffraction angle (radians)

Table 2. XRD Diffraction Peak List of ZnO Nanoparticles with Crystal Size

| Pos.          | <b>FWHM</b>   | d-spacing | Crystal Size |
|---------------|---------------|-----------|--------------|
| [ $2\theta$ ] | [ $2\theta$ ] | [Å]       | (nm)         |
| 31.889        | 0.216         | 2.80644   | 37.82568     |
| 34.442        | 0.177         | 2.60398   | 46.46743     |
| 36.236        | 0.079         | 2.47907   | 104.63109    |
| 47.536        | 0.276         | 1.91283   | 31.10173     |
| 56.636        | 0.394         | 1.62519   | 22.64966     |
| 62.898        | 0.315         | 1.47763   | 29.23409     |
| 66.427        | 0.394         | 1.40744   | 23.83253     |
| 69.159        | 0.197         | 1.35837   | 48.43478     |
| 72.606        | 0.236         | 1.30213   | 41.30578     |
| 76.905        | 0.472         | 1.23971   | 21.25348     |
| 81.552        | 0.472         | 1.18078   | 21.97913     |

Based on data in Table 2, the average crystal size of the ZnO nanoparticles synthesized in this study was 38.97413 nm.

SEM also characterized ZnO nanoparticles, which can provide insights into their surface morphology. Figure 3 presents an SEM image of ZnO nanoparticles. It exhibits a porous and textured structure. The image was processed using ImageJ software, and the smallest particle size was determined to be 54 nm.



Figure 3. SEM Results of ZnO Nanoparticles

#### **Synthesis of Nanobentonite**

The synthesis of nano bentonite material in this study employed the sonochemical method using processed natural bentonite powder, an ultrasonic bath instrument for the sonochemical method, and ultrasonic sound waves to accelerate chemical reactions. When a solution is irradiated with ultrasonic waves, its molecules oscillate (change periodically) relative to their average position, causing the solution

to experience compression and rarefaction. Ultrasonic waves generate substantial energy, leading to the stretching of the solution and breaking of intermolecular bonds within the solution. When the solution recompresses, it traps dissolved gases.

These gases form bubbles that grow larger by merging and eventually burst. The bursting bubbles trigger incredibly high heat and pressure, reaching 5000 °C and 1000 atm. The influence of high pressure and temperature can trigger chemical reactions that alter surface morphology and composition, resulting in nano-sized structure impurities such as Al, Fe, Ca, and Mg that cover the pores of bentonite. The reactions that occur during bentonite activation at equations (4), (5), (6), and (7):

 $Fe<sub>2</sub>O<sub>3(s)</sub> + 3H<sub>2</sub>SO<sub>4(aq)</sub> \rightleftharpoons Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3(aq)</sub> + 3H<sub>2</sub>O<sub>(l)</sub>$  (4)  $\text{Al}_2\text{O}_{3(s)} + 3\text{H}_2\text{SO}_{4(aq)} \rightleftharpoons \text{Al}_2(\text{SO}_4)_{3(aq)} + 3\text{H}_2\text{O}_{(1)}$  (5)  $CaO_{(s)} + H_2SO_{4(aq)} \rightleftharpoons CaSO_{4(aq)} + H_2O_{(l)}$  (6)  $MgO_{(s)} + H_2SO_{4(aq)} \rightleftharpoons MgSO_{4(aq)} + H_2O_{(1)}$  (7)

FTIR, XRD, and SEM further characterized the synthesized nano bentonite. For FTIR, the synthesized

nano bentonite was scanned at a wavenumber of 4000 cm-1 to 500 cm-1 . The results of FTIR of ZnO nanoparticles in this study are shown in Figure 4 and Table 3.



Figure 4. FTIR Results of Nanobentonite

The IR spectroscopy result revealed the presence of Si-OH and O-H vibrations at wavenumbers of 3619 cm<sup>-1</sup> and 3389 cm-1 , respectively. The IR peak at 2112 cm-1 indicates the presence of C-C bonds. The IR peak at 1883 cm-1 is attributed to the bending vibration of aromatic C=C groups. The presence of water molecules in nano bentonite is confirmed by the O-H bending vibration at 1637 cm-1 . The IR peak at 1014 cm-1 is associated with the asymmetric stretching mode of Si-O. Stretching vibrations of Al-O-Si are also observed in the IR peak at  $787 \text{ cm}^{-1}$ . As shown in Table 3, the presence of Si-O and Al-O-Si groups, the primary constituents of nano bentonite material, confirms this study's successful synthesis of nano bentonite (Bukit, Frida, Bukit, & Bukit, 2021).

Table 3. Functional Groups and FTIR Wavenumbers of Nanobentonite

| Functional   | Wavenumbers $(cm-1)$ |           |                |
|--------------|----------------------|-----------|----------------|
| Group        | Research             | Reference | Source         |
|              | data                 |           |                |
|              |                      |           |                |
| O-H          | 3389 and             | 3387 and  | (Putri $\&$    |
|              | 3619                 | 3627      | Setiarso,      |
|              |                      |           | 2023)          |
| $C \equiv C$ | 2112                 | 2104      | (Raturandang   |
|              |                      |           | et al., 2022)  |
| $C = C$      | 1883                 | 1872      | (Bukit et al., |
|              |                      |           | 2021)          |
| $O-H$        | 1637                 | 1633      | (Putri &       |
|              |                      |           | Setiarso,      |
|              |                      |           | 2023)          |
| $Si-O$       | 1014                 | 1008      | (Hizbullah &   |
|              |                      |           | Setiarso,      |
|              |                      |           | 2024)          |
| $Al-O-Si$    | 787                  | 790       | (Putri &       |
|              |                      |           | Setiarso,      |
|              |                      |           | 2023)          |
|              |                      |           |                |

XRD analysis of nano bentonite was performed using a diffraction angle range of 5-90° and a wavelength of 1.54060 Å. The XRD results are shown in Figure 5.

Bentonite's primary constituents are montmorillonite and quartz. The presence of montmorillonite in bentonite is confirmed by diffraction peaks at 19.920°, 34.874°, and 61.983° corresponding to d-spacings of 4.45730 Å, 3.34783 Å, and 1.49722 Å, respectively, by reference code 00- 002-0227. Another diffraction peak at 21.966° identifies the presence of quartz  $(SiO<sub>2</sub>)$  with an intensity of 100%, categorized as an impurity with reference code 00-029-0085. Diffraction peaks at 26.627°, 68.072°, and 73.602° indicate the presence of hexagonal quartz crystals with reference code 01-085- 0796 (Utubira et al., 2020). Quartz's thermal stability up to 400°C contributes to its high peak intensity. However, the quartz crystal structure deteriorates when calcinated above 1000 °C.



Figure 5. XRD Results of Nanobentonite

Equation (3) presents the Debye-Scherrer equation, which can be employed to determine the crystal size of a specific phase using X-ray diffraction (XRD) analysis. According to Table 4, the average crystal size of the nano bentonite synthesized in this study was determined to be 28.08155 nm.

Table 4. XRD Diffraction Peak List of Nanobentonite with Crystal Size

| Pos.   | <b>FWHM</b> | d-spacing | <b>Crystal Size</b> |
|--------|-------------|-----------|---------------------|
| 201    | 20]         | `Å]       | (nm)                |
| 19.920 | 0.276       | 4.45730   | 28.89939            |
| 21.966 | 0.157       | 4.04660   | 50.97195            |
| 26.627 | 0.138       | 3.34783   | 58.49988            |
| 34.874 | 0.315       | 2.57276   | 26.14100            |
| 61.983 | 0.787       | 1.49722   | 11.64457            |
| 68.072 | 0.945       | 1.37737   | 10.03184            |
| 73.602 | 0.945       | 1.28696   | 10.38220            |

# **Preparation of Carbon Paste Electrode Modified with ZnO Nanoparticles and Nanobentonite.**

In this research, CPE was modified with nano bentonite and ZnO nanoparticles. The composition of carbon: nano bentonite: ZnO nanoparticles: paraffin with the following ratios: 3:2:3:2; 3:3:2:2; 3:1:4:2; 3:4:1:2 w/w were mixed on a watch glass and inserted into an insulator pipe on the electrode body with a spatula and compacted evenly until there were no voids. This composition ratio refers to research showing that the carbon: modifier: paraffin 3:5:2 ratio can increase the anodic peak current better than other electrode composition ratios (Putri & Setiarso, 2023). Carbon in CPE serves as a conductor and matrix that supports other materials in electrochemical applications. Nanobentonite has a large surface area, so it can expand the analyte area to adsorbed on CPE. ZnO nanoparticles have good conductivity and can conduct electric current on CPE. Paraffin is a binder for all components of the CPE material.

## **Determination of the Optimal Electrode Composition**

In this determination of optimal conditions, the best electrode composition is determined by measuring each composition ratio using the voltammetry method. The voltammograms of the best electrode composition measurements are shown in Figure 6.



### Figure 6. Voltammogram of the Best Electrode Composition

BPA is easily oxidized, producing a high oxidation current peak, but is not easily reduced, resulting in a slight reduction current. This is due to slow charge transfer or rapid homogeneous reaction of the oxidation products during the oxidation process so that the reduction process does not occur. In other words, the reaction that occurs in BPA is irreversible. BPA can undergo oxidation because it has two hydroxyl (-OH) groups attached to the aromatic ring. These hydroxyl groups readily lose electrons, making them susceptible to oxidation. The oxidation reaction of BPA is shown in Figure 7.

Table 5 shows that adding nano bentonite and ZnO nanoparticles produces a higher oxidation current peak than unmodified. In the composition 3:4:1:2 w/w, the addition of nano bentonite is higher than the others. Thus, nano bentonite significantly influences the effectiveness of the working electrode. Nanobentonite has a complex surface structure with many pores and a large surface area. Additionally, bentonite has a layered plate structure composed of silicate and alumina. This structure provides high mechanical strength and crack resistance, strengthening the carbon paste electrode (Putri & Setiarso, 2023). When added to the electrode, nano bentonite expands the area,

which results in more reactions when the analyte is measured.



Figure 7. Reaction Oxidation BPA

Table 5. Peak Current of Unmodified and Modified Carbon Paste Electrode Composition with Nanobentonite and ZnO Nanoparticles



### **Determination of optimum pH**

Acidity (pH) can affect electrochemical response. Changes in pH value affect the oxidation and reduction potential of a compound. In this study, a pH range of 3 to 8 was used. To stabilize the pH in this study, a 0.1 M phosphate buffer was used. This pH range was chosen because BPA has pH stability in the range of 3- 7 for the occurrence of the oxidation reaction (Puspita & Noviandri, 2021). The results of the optimum pH voltammogram are shown in Figure 8 below.



Figure 8. The Voltammogram of the Optimum pH

Based on Figure 8, the measurement results show that the current values at pH 3, 4, 5, 6, and 7 increase steadily. pH 7 is the optimum pH for BPA measurement, as this is when the ionic distribution reaches its peak, allowing for optimal ion exchange in the electrochemical process.

The highest peak current shown in Table 6 for BPA analysis is pH 7 with an Ipa value of  $6.94 \times 10^{-4}$ A. This indicates that the BPA solution at pH 7 undergoes many oxidation reactions. At pH 8, it decreases because, at a basic pH, BPA will become a

phenolic anion (BPA-OH-), which occurs in resonance in its aromatic ring, where the electrons are pretty stable, and little is oxidized.



### **Measurement of BPA Standard Linearity**

Measuring the linearity of BPA standards aims to help ensure that the instrument or method used (cyclic voltammetry) to measure BPA concentration in samples can provide consistent and accurate results, significantly when BPA concentration varies within a specific linear range.

The standard BPA solution testing uses the best electrode composition and optimum pH. The voltammogram results of various concentrations of the standard BPA solution are shown in Figure 9.



### Figure 9. The Voltammogram of the Standard BPA Solution

As illustrated in Figure 9, the relationship between solution concentration and peak current demonstrates that higher concentrations lead to correspondingly higher peak currents. This phenomenon can be attributed to the increased accumulation of BPA molecules on the surface of the working electrode at higher concentrations, resulting in a more substantial current flow. Table 7 presents the peak anodic current (Ipa) values for standard BPA solutions of varying concentrations.

| Consentration (mM) | Ipa $(A)$             |
|--------------------|-----------------------|
| 0.1                | $4.59 \times 10^{-4}$ |
| 0.3                | $5.37 \times 10^{-4}$ |
| 0.5                | 6.11 x $10^{-4}$      |
| 0.7                | $7.00 \times 10^{-4}$ |
| 1.0                | $7.88 \times 10^{-4}$ |

Table 7. Peak Current of Standard BPA Solutions



Figure 10. Standard BPA Linearity Curve

Figure 10 shows a linear relationship between solution concentration and the oxidation peak current of BPA. The linear curve can be represented by the equation  $y = ax + b$ , where  $y = 0.000371x + 0.000426$ and  $R^2 = 0.9955$ . This equation is a calibration tool for determining unknown BPA concentrations in polycarbonate-based samples using cyclic voltammetry.

# **Testing for BPA in Polycarbonate-Based Drinking Water Samples**

Bisphenol A (BPA) concentration was determined in three widely available polycarbonatebased drinking water samples. Before analysis, the samples were exposed to sunlight for 20 days. This simulated real-world conditions where products may be exposed to sunlight during storage or distribution. The voltammogram results of the sample solution are shown in Figure 11.

The BPA concentration in the samples can be determined by substituting the peak current (Ipa) values obtained from cyclic voltammetry measurements into the linear equation of the standard curve:  $y = 0.000371x + 0.000426$ .

Based on data in Table 8, the polycarbonate-based drinking water samples exhibited relatively high BPA concentrations. This elevated BPA content can be attributed to improper storage practices, particularly prolonged exposure to high temperatures and direct sunlight. Such conditions can accelerate the degradation of polycarbonate packaging, leading to increased BPA migration into the contained beverage.



Figure 11. Voltammogram of the Sample Solution Table 8. Peak Current and Sample Concentration



# **CONCLUSION**

The optimal composition for the paste working electrode for BPA analysis was determined to be 3:4:1:2 for carbon: nano bentonite: ZnO nanoparticles: paraffin. The optimum measurement conditions were found to be at pH 7. The BPA content obtained by cyclic voltammetry for polycarbonate-based drinking water samples brands A, B, and C was 0.2102, 0.1752, and 0.2210 mM. These results demonstrate that cyclic voltammetry with a ZnO nanoparticle and nano bentonite-modified carbon paste electrode can be used for BPA analysis.

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# **REFERENCES**

- Afrilia, C. G., Hanavi, D. P., Aprilia, A., Safriani, L., & Bahtiar, A. (2019). Studi proses sintesis serbuk nano ZnO beserta karakterisasi. *Jurnal Ilmu dan Inovasi Fisika*, *3*(2), 105–113.
- Aulia, G., & Mita, S. R. (2023). Review Artikel: Pengaruh Bisphenol-a (bpa) Dalam Kemasan

Pangan Terhadap Kesehatan. *Farmaka*, *21*(1), 43–49.

- Bukit, F. R. A., Frida, E., & Bukit, N. (2021). Karakterisasi Dan Analisis Bentonit Alam Sebagai Bahan Pengisi Komposit. *Juitech*, *5*(2), 54–62.
- Bukit, F. R. A., Frida, E., Bukit, N., & Bukit, B. (2021). Karakterisasi dan Analisis Bentonit Alam sebagai Bahan Pengisi Komposit. *Juitech*, *5*(2), 54–63.
- Hikma, N., & Arpah, M. (2024). Perbandingan Migrasi Monomer Bisfenol A (BPA) Pada Kemasan Air Minum Plastik Polikarbonat (PC) dan Polietilena Tereftalat (PET): Kajian Meta-Analisis. *Syntax Idea*, *6*(5), 2417–2435.
- Hizbullah, A. J., & Setiarso, P. (2024). Fabrication of Carbon Paste Electrode Modified with Bentonite Nanoparticles and Titanium Dioxide Nanoparticles for Analysis of Methyl Parabens by Cyclic Voltammetry. *Jurnal Pijar Mipa*, *19*(1), 119–124.
- Julita, M., Shiddiq, M., & Khair, M. (2022). Determination of Band Gap Energy of ZnO/Au Nanoparticles Resulting in Laser Ablation in Liquid. *Indonesian Journal of Chemical Research*, *10*(2), 83–87.
- Patel, M., Mishra, S., Verma, R., & Shikha, D. (2022). Synthesis of ZnO and CuO nanoparticles via Sol gel method and its characterization by using various technique. *Discover Materials*, *2*(1), 1.
- Puspita, F., & Noviandri, I. (2021). Optimasi Pembuatan Elektroda Pasta Karbon Termodifikasi Poli(Metil Jingga) untuk Penentuan Bisphenol A SecaraVoltammetri. *Warta Akab*, *44*(2).
- Putri, D. A., & Setiarso, P. (2023). Fabrication of carbon pasta elektroda composition modified with nanobentonite and nano TiO2 for niacinamide detection sensor. *Jurnal Pijar Mipa*, *18*(6), 923–928.
- Ramadanti, A. H., & Maharani, D. K. (2022). *Green Synthesis of ZnO Nanoparticles with Papaya Leaf Extract (Carica papaya L.) as a Reductor and its Application on Cotton Fabrics*.
- Raturandang, R., Wenas, D. R., Mongan, S., & Bujung, C. (2022). Analisis Spektroskopi Ftir Untuk Karakterisasi Kimia Fisik Fluida Mata Air Panas Di Kawasan Wisata Hutan Pinus Tomohon Sulawesi Utara. *Jurnal FisTa : Fisika dan Terapannya*, *3*(1), 28–33.
- Rhamdiyah, F. K., & Maharani, D. K. (2022). Biosynthesis of ZnO Nanoparticles from Aqueous Extract of Moringa Oleifera L.: Its Application as Antibacterial and Photocatalyst. *Indonesian Journal of Chemical Science*, *11*(2), 91–102.
- Rohmawati, L., Lailia, L., Putri, N., Nasir, M., & Darminto, D. (2024). Characterization of ZnO Nanoparticles Pineapple Skin Extract Ananas comosus L.) as Photocatalytic Activity. *Journal of Water and Environmental Nanotechnology*, *9*(1).
- Saputra, E. C., & Setiarso, P. (2020). Pengaruh Variasi Ph Terhadap Pengukuran Asam Oksalat Dengan Elektroda Graphene Oxide Termodifikasi Nanobentonit Secara Siklik Voltametri. *UNESA Journal of Chemistry*, *9*(3), 197–202.
- Sari, N. P., & Setiarso, P. (2020). Pembuatan Elektroda Kerja Graphene Oxide Termodifikasi Nano Bentonit Untuk Analisis Asam Nikotinat Secara Voltametri Siklik Making of Graphene Oxide Nano Bentonite Modified Working Electrode for Analysis Nicotinic Acid Using Cyclic Voltammetry. *Unesa Journal of Chemistry*, *9*(3), 170–178.
- Setiarso, P., & Lukmana, K. M. (2018). Synthesis of Graphene Oxide Electrode for Paracetamol Analysis by Cyclic Voltammetry. *Asian Journal of Chemistry*, *30*(10), 2289–2293.
- Srujana, S., & Bhagat, D. (2022). Chemical-based synthesis of ZnO nanoparticles and their applications in agriculture. *Nanotechnology for Environmental Engineering*, *7*(1), 269– 275.
- Tehubijuluw, H., Souhoka, F., Kusumawati, Y., Prasetyoko, D., Subagyo, R., Nugraha, R. E., & Jalil, A. A. (2023). Characterization and Kinetic Study of Methylene Blue

Photocatalytic on ZnO/ZSM-5. *Indonesian Journal of Chemical Research*, *11*(2), 156– 162.

- Utomo, A. D. C., & Wihadi, Muh. N. K. (2022). Preparation of ZnO/TiO2 Nanocomposite Sensitized Mangosteen Rind (Garcinia mangostana L) Dye for Light Harvesting Efficiency in Solar Cell. *Indonesian Journal of Chemical Research*, *10*(2), 68–73.
- Utubira, Y., Onaola, B. M., & Manuhutu, J. B. (2020). Pilarisasi Lempung Alam Desa Ouw Dengan Al2o3 Sebagai Adsorben Zat Warna Metil

Orange. *Molluca Journal of Chemistry Education (MJoCE)*, *10*(1), 63–71.

- Vishwakarma, A., & Singh, S. P. (2020). Synthesis of Zinc Oxide Nanoparticle by Sol-Gel Method and Study its Characterization. *International Journal for Research in Applied Science and Engineering Technology*, *8*(4), 1625–1627.
- Wimarsela, S., Junaidi, R., & Silviyati, I. (2021). Sintesis Silika Gel dari Abu Cangkang dan Serabut Kelapa Sawit Terimobilisasi Difenilkarbazon dengan Metode Sol-Gel. *Jurnal Penelitian Inovatif*, *1*(2), 165–174.