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# Fabrication of Carbon Paste Electrode Modified with Bentonite Nanoparticles and Titanium Dioxide Nanoparticles for Analysis of Methyl Parabens by Cyclic Voltammetry

Ahmad Jihad Hizbullah, Pirim Setiarso*

Chemistry Study Program, Faculty of Mathematics and Natural Science, State University of Surabaya, Surabaya, Indonesia
*E-mail: pirimsetiarso@unesa.ac.id

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**Abstract:** Cosmetics are products of several substances or ingredients with a predetermined time limit. Efforts to extend the time limit of cosmetic use are made by adding preservatives. One preservative that is often used is methylparaben. Methylparaben has been tested using spectrophotometry, voltammetry, and HPLC. In this study, electrode modification was carried out in the voltammetry test to obtain a low detection limit. The purpose of this study was to determine the effect of the working electrode composition of carbon paste, bentonite nanoparticles, titanium dioxide nanoparticles, and paraffin on the best response in the analysis of methylparaben by cyclic voltammetry, knowing the optimum measurement conditions of pH with the best electrode composition in the analysis of methylparaben by cyclic voltammetry. FTIR characterized bentonite nanoparticles to determine vibrations and functional groups, and XRD was performed to determine the phase and particle size. The electrode was made from a mixture of carbon, bentonite nanoparticles, titanium dioxide nanoparticles, and paraffin. The best electrode composition was added with titanium dioxide nanoparticles to obtain a higher peak current. XRD characterization of bentonite nanoparticles showed an average particle size of 43.8155 nm. The result of determining the best electrode composition is 3:2:3:2 with an anodic peak current of 9.6.10-4 A. The best methylparaben measurement at pH seven solution conditions. The latest research shows that carbon paste electrodes modified with bentonite and titanium dioxide nanoparticles can be used for methylparaben analysis.

**Keywords:** Bentonite Nanoparticles; Cyclic Voltammetry; Electrode; Methylparaben; $TiO_2$ Nanoparticles.

## Introduction

Along with people's increasing desire to beautify their appearance, cosmetics have become ingrained in people's lives [1]. Cosmetics are substances used primarily to clean, perfume, and improve the appearance of the external parts of the human body (epidermis, hair, nails, lips, and external genitalia), as well as on mucous membranes, teeth, and skin [2]. Cosmetics that can be sold in the market must contain active ingredients that are safe and usable by customers [3]. Cosmetics require preservatives as antimicrobial agents. Commonly used preservatives are methyl paraben and propyl paraben [4].

Methyl parabens or p-hydroxy benzoic acid esters are used as food preservatives, cosmetics, and pharmaceuticals, as they have anti-bacterial properties [5]. Methyl parabens appear as colorless crystals or white crystalline powder and are odorless with a taste like topical preparations. Its solubility is easily soluble in methanol, ethanol, ether, and propylene glycol, slightly soluble in water, and practically insoluble in mineral oil [6]. The recommended use of parabens in cosmetics recommended by the FDA is 0.4% for single preservative and 0.8% for preservative mixed [3]. In paraben compounds, when exceeding predetermined limits and coming into contact with skin that is susceptible to it, harmful side effects such as dermatitis, allergic reactions, redness, and skin irritation can occur [7]; even the discovery of methyl parabens in the development of cancer cells [5].

Currently, several analytical methods can be used to detect parabens, including UV-Vis spectrophotometric methods [8] [9], electrochemistry (6], and HPLC [10].

One method that can be used to analyze methyl parabens is the voltammetry method with a modified working electrode. The voltammetric method is an electrical analysis technique that limits its potential as a function. Voltammetry is based on the measurement of current in the electrochemical section, where the oxidation-reduction speed of the analyte is determined based on the mass transfer of the analyte to the electrode section [11]. This method can be used to analyze organic and inorganic samples. Measurement of organic compounds is based on the presence of functional groups that can cause oxidation or reduction on the electrode surface [12]. Voltammetry can be used to detect parabens that are electroactive so that they can undergo oxidation and reduction reactions [6].

Cyclic voltammetry has fast analysis time, high sensitivity and selectivity, and low detection limit [13]. The electrodes used in voltammetry instruments are auxiliary, working, and comparison. The working electrode is where the oxidation-reduction reaction occurs. One of the working electrodes often used is the carbon paste electrode. This is because carbon electrodes have a fairly wide potential range of good electrical conductivity, are chemically inert, easy to obtain, relatively cheap, and can be used as sensor applications [14]. The performance of carbon paste electrodes can be improved by chemical modification [15].

Modified carbon paste electrodes increase the current generated during the absorption of electrolyte ions

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from an analyte. In previous research by Setiarso and Sari [16], the composition of the electrode used was carbon-paraffin-nanoparticle bentonite with parameters of composition variation, pH, deposition time, and scan rate; the best variation results were obtained in the composition of 3: 4: 3, and pH 5 affected the current produced, and the research of Bukkitgar et al. [17] and Cahyatomo, et al. [6] had shortcomings in the form of the current produced was quite low, namely in Bukkitgar, et al [17] of $4.2.10^{-5}$ A and Cahyatomo, et al [6] of $9.5.10^{-5}$ A.

Adding two nanoparticle components to carbon paste electrodes can be a solution to increasing the current because it can produce different electrochemical characters on the electrode to increase the current in the working electrode of cyclic voltammetry. Using bentonite nanoparticles on carbon paste electrodes can increase the conductivity of the working electrode [18], while other nanoparticles added are titanium dioxide nanoparticles. The addition of titanium dioxide nanoparticles is based on the non-toxic nature of TiO2, high electron transfer, good focatalytic ability, and microelectronics [19].

This study aims to determine the effect of carbon paste electrodes on cyclic voltammetry modified by the addition of bentonite nanoparticles and titanium dioxide nanoparticles as an alternative method in measuring methylparaben concentrations at a lower cost and more efficient analysis time compared to UV-Vis Spectrophotometry and HPLC methods. In addition, research was conducted on the effect of solution pH that produced optimum current in measuring methyl parabens as a form of optimum conditioning during the analysis process.

## Research Methods

### Materials and Tools

The materials used in this research are copper wire, carbon, bentonite, paraffin, and Whatman filter paper no. 42, HCl p.a 37%, $Na_2HPO_4.H_2O$ p.a, $NaH_2PO_4.2H_2O$ p.a, distilled water, methanol p.a 99% (Merck), $TiO_2$ nanoparticles anatase 99%, NaOH p.a, ethanol p.a 96%, KCl p.a [20].

The tools used in this research are platinum electrode, Ag/AgCl electrode, analytical balance, beaker, 300 mesh sieve, sandpaper, thermometer, pH meter, spray bottle, ultrasonic bath S 30 H Elmasonic, hotplate, magnetic stirrer, oven, desiccator, volume pipette, volumetric flask. The instruments used were Voltammetry 797 VA *computrace*, XRD X'pert PRO PANalytical, FTIR thermos scientific Nicolet iS10, and UV-Vis Spectrophotometry Shimadzu 1800.

### Synthesis of Bentonite Nanoparticles

Bentonite synthesis was carried out by the sonochemical method [20]. A total of 20 grams of bentonite was added to 100 mL of 5M HCl solution and stirred using a stirrer at 70℃ for 4 hours at 400 rpm. Separated bentonite with HCl, then bentonite was washed with hot distilled water until the pH was neutral. Oven at 100℃ for 2 hours. Sifted using 300 mesh sieve and activated bentonite was produced. Activated bentonite was put into a beaker. Added 50 mL of 96% ethanol. Sonicated using an ultrasonic bath for 2 hours and in the oven at 100℃ until ethanol evaporates. The resulting bentonite nanoparticles were characterized using XRD and FTIR. As for $TiO_2$, no nanoparticle synthesis was carried out because the $TiO_2$ obtained was already in the form of nanoparticles with a 99% anatase phase.

### Preparation of Methyl Paraben Standard Solution

Methylparaben was weighed as much as 0.1 gram and measured using methanol (MERCK) with a 100 mL volumetric flask. A mother liquor of 0.1M methylparaben was obtained. Standard solutions of 10, 20, 30, 40, and 50 mg/L methylparaben were prepared from 100 mg/L mother liquor.

## Results and Discussion

### Synthesis of Bentonite Nanoparticles

Bentonite synthesis begins with bentonite activation using acidic compounds. Activation of bentonite using acidic compounds aims to exchange cations contained in bentonite pores with H + and remove metal oxides such as $Al^{3+}$, $Mg^{2+}$, and $Fe^{3+}$ to obtain later active bentonite [21]. Acidic compounds commonly used for activation are $H_2SO_4$ [20] and HCl [22]. Bentonite activation in this study uses a 5M HCl solution because when compared to H2SO4, the lower the *pka*, the more acid dissociates, so the stronger the acid. HCl has pKa = -6, while $H_2SO_4$ has pKa = -3.
Activation is expected to give bentonite a stronger adsorption ability because the bentonite pores are empty so that they can be filled by the analyzed analyte ions [22].

$$Al^{3+}_{(s)} + HCl_{(aq)} \rightarrow AlCl_{3(aq)}$$
$$Mg^{2+}_{(s)} + HCl_{(aq)} \rightarrow MgCl_{2(aq)}$$
$$Fe^{3+}_{(s)} + HCl_{(aq)} \rightarrow FeCl_{3(aq)}$$

Bentonite-HCl [22]

Bentonite was washed with distilled water to remove the HCl solution in bentonite. Bentonite was oven to 100 ℃ for 2 hours and sieved using mesh 300. Then bentonite was sonicated for 4 hours. Nanoparticle-sized bentonite was obtained.

### FTIR and XRD Characterization of Bentonite Nanoparticles

In this study, the chemical characteristics of bentonite nanoparticles used an FTIR instrument to determine the groups contained in bentonite nanoparticles. The FTIR results are shown in Figure 1.

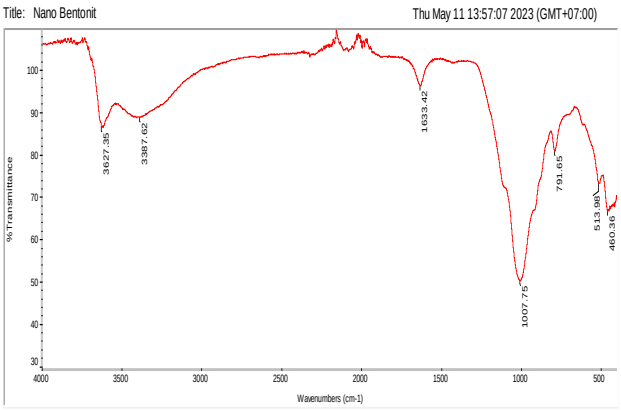


**Figure 1.** FTIR Spectrum Results of Bentonite Nanoparticles

**Table 1.** Results of Infra-Red Absorption Frequency and Tentative Vibrational Determination of Bentonite Nanoparticles

| Wavenumber ($cm^{-1}$) | Vibrations and Functional Groups |
|---|---|
| 3627.35 | Stretching Vibrations O-H |
| 3387.62 | Stretching Vibrations O-H |
| 1633.42 | O-H from water |
| 1007.75 | Si-O |
| 791.65 | Al-O-Si |
| 513.98 | Al-O-Si |
| 460.36 | Si-O-Si |

The FTIR spectrum of bentonite nanoparticles synthesized by the sonochemical method is shown in Figure 1. A weak absorption indicates symmetrical O-H stretching that can be identified at wave numbers 3627.35 $cm^{-1}$ and 3387 $cm^{-1,}$ presented in Table 1. The wave number region 1633.42 $cm^{-1}$ shows the bending of the O-H group, indicating the presence of water molecules in the bentonite nanostructure. The strong absorption at 1007.75 $cm^{-1}$ shows the stretching of the Si-O group. The wavelengths of 791.65 $cm^{-1}$ and 513.98 $cm^{-1}$ indicate the Al-O-Si strain. The wavelength of 460 $cm^{-1}$ shows the Si-O-Si stretch [20].

Raw bentonite has cations with weak bonds between layers. It will be easily exchanged if activated by acid, so when bentonite is activated using HCl, it will cause loss of structural hydroxyl groups, or in other words, dehydroxylation is observed due to the weakening of structural hydroxyl vibrational bands followed by leaching of impurity ions like $Al^{3+}$, $Mg^{2+}$ and $Fe^{3+}$ [21]. It can also be indicated by the swelling of structures such as OH [23]. HCl causes damage to the tetrahedral layer in bentonite, which makes the material contain more amorphous silica than before; this confirms the presence of quartz particles, indicating that activation of bentonite nanoparticles was successful.

**Physical Characterization of Bentonite Nanoparticles**

XRD testing of bentonite nanoparticles uses an angle length of 5-90°. The crystal size can be determined using the Debye-Scherrer equation. The test results can be seen in Figure 2.

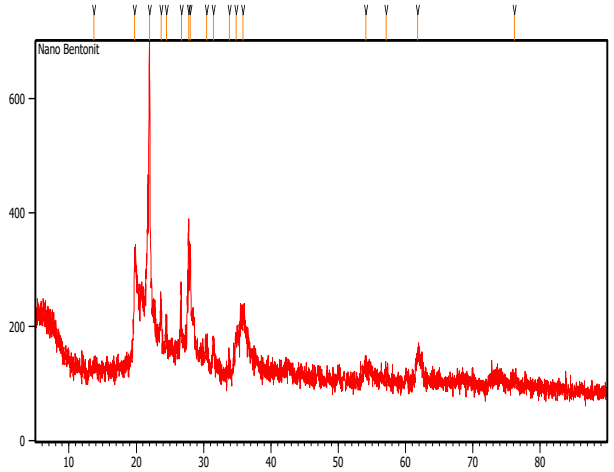


Figure 2. XRD Diffraction Pattern Results of Bentonite Nanoparticles

**Table 2.** Crystal Size of Bentonite Nanoparticles using Debye Scherrer Method

| Pos. [°2Th.] | Height [cts] | FWHM Left [°2Th.] | Particle Size (nm) |
|---|---|---|---|
| 19.7401 | 184.49 | 0.1338 | 60.26636 |
| 23.7182 | 101.07 | 0.1673 | 48.52092 |
| 24.4588 | 73.63 | 0.1673 | 48.58788 |
| 26.6866 | 139.65 | 0.1004 | 81.32168 |
| 27.7723 | 247.98 | 0.1338 | 61.16184 |
| 35.8079 | 83.75 | 0.6691 | 12.47733 |
| 54.0896 | 25.06 | 0.3346 | 26.65762 |
| 61.7883 | 45.66 | 0.8029 | 11.53047 |

From the XRD graph of bentonite nanoparticles in Figure 2 and the data in Table 2, the particle size of bentonite nanoparticles can be determined using the Debye Scherrer equation [23].

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

D = crystal size
K = shape factor of the crystal (0.89)
λ = wavelength of X-ray (1.5406Å)
β = value of Full Width at Half Maximum (FWHM) (rad)
θ = angle of diffraction (degree)

In Figure 2, the maximum peaks of diffraction intensity produced by bentonite nanoparticles, which are at 26.68°, 24.45°, and 19.74°, have been verified using the d values of the minerals found in bentonite. These findings are in agreement with bentonite where DHKL (101), (011), (100), and (112). The main peak, which is the peak at 2 = 26.68° and is the defining peak of the quartz field (101), indicates that bentonite nanoparticles are montmorillonite. The diffraction peak at 21.971° is silica mineral ($SiO_2$) in tridymite. The 26.670° peak marks quartz ($SiO_2$) with a hexagonal crystal form with reference code 01-085-0335. The patterns confirm the presence of most of the bentonite. At the same time, some peaks indicate the presence of impurities such as kaolinite, quartz and gypsum [25].

Based on Table 2, the average bentonite nanoparticle size is 43.8155 nm. Nanoparticles are particles with nanometers of size, which are about 1-100 nm [26]. Smaller crystal sizes can lead to a larger surface area, increasing the photocatalytic activity of the material [27].

**Preparation of carbon paste electrodes modified with bentonite nanoparticles and titanium dioxide nanoparticles:**

Several compositions were used to compare modified carbon paste working electrodes. Carbon paste electrodes were made from a mixture of carbon, bentonite nanoparticles, $TiO_2$ nanoparticles and paraffin with various composition ratios; the composition of carbon paste electrodes used respectively in order are 3:2:3:2, 3:3:2:2; 3:1:4:2; 3:4:1:2. The variation of composition was to obtain the best electrode for methylparaben analysis.

Carbon, bentonite, and titanium dioxide nanoparticles function as conductors that conduct electricity in the composite. Paraffin is a binder used to bond the composite (filler material) electrode and as a hydrophobic agent that prevents further penetration of the solution into the electrode, thus minimizing electrode damage.

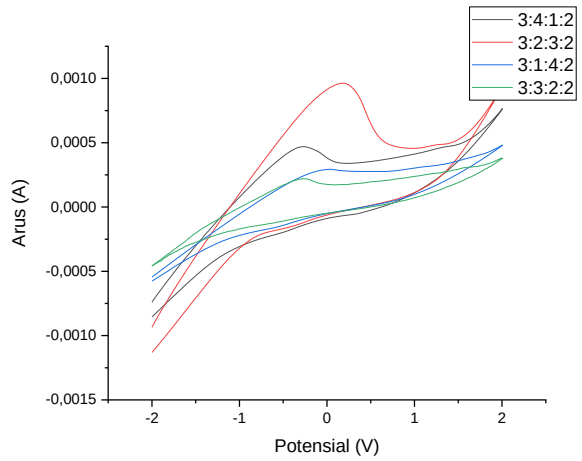


**Figure 3.** Voltammograms of Test Results Comparison of Carbon Paste Working Electrode Composition (Carbon: Bentonite Nanoparticles: Titanium Dioxide Nanoparticles: Paraffin) on Methyl Paraben Solution Concentration of 50 ppm and pH 7 with Deposition Time of 10 s and Scan Rate of 200 mV/s

Methylparaben produces a high oxidation peak current and almost does not form a reduction peak current. This can occur due to slow charge transfer or products that quickly react homogeneously in the oxidation process so that the reduction reaction is not formed [28]. In Figure 3, it can be seen that the peak current formed in each electrode composition is different. The higher the peak current on the working electrode, the better the conductivity of the electrode due to the easy transfer of electrons for the oxidation reaction process [29].

**Table 3.** Peak Current Measurement of 50 ppm Methyl Paraben Solution with Variation of Working Electrode Composition (Carbon: Bentonite Nanoparticles: Titanium Dioxide Nanoparticles: Paraffin)

| Composition (carbon: bentonite nanoparticles: titanium dioxide nanoparticles: paraffin) | $Ip_a$ (A) |
|---|---|
| 3 : 4 : 1 : 2 | $4.69x10^{-4}$ |
| 3 : 3 : 2 : 2 | $2.20x10^{-4}$ |
| 3 : 2 : 3 : 2 | $9.62x10^{-4}$ |
| 3 : 1 : 4 : 2 | $2.94x10^{-4}$ |

Bentonite nanoparticles and titanium dioxide nanoparticles greatly influence the effectiveness of the working electrode, because they have a large surface area, fairly good thermal stability, high absorption properties, and abundant adsorption sites for organic compounds [26]. The 3:2:3:2 composition has the highest anodic peak current of the compositions made, with a value of $9.62x10^{-4}$ A.

**Determination of the Best pH for Methyl Paraben Analysis**

Optimum pH measurement conditions can affect the selectivity and sensitivity of electrodes that affect the deposition stage and scan speed in voltammetric measurements. Besides that, under optimum pH conditions, the solution will reach the stability of the analyte, in which case the ions in the solution at a certain pH will turn into molecules and cannot be analyzed using voltammetry [27].

The best electrode was used to determine the optimum pH using phosphate buffer with pH 5, 6, 7; and 8 variations. The optimum pH of the analyte is the condition of the analyte that has the highest current peak in voltammetry. The analysis was performed with 10 mL of 50 ppm methylparaben solution, 10 mL of 5000 ppm KCl solution (100x sample concentration), and 5 mL of phosphate buffer solution pH 5. Measurements were carried out in the potential range of 0 V to +1.5 V with a deposition time of 10 seconds and a scan rate of 0.2 V/s. The same was done at pH variations 6, 7, and 8. The measurement results were processed using Origin 2018, and the resulting voltammogram is in Figure 4.

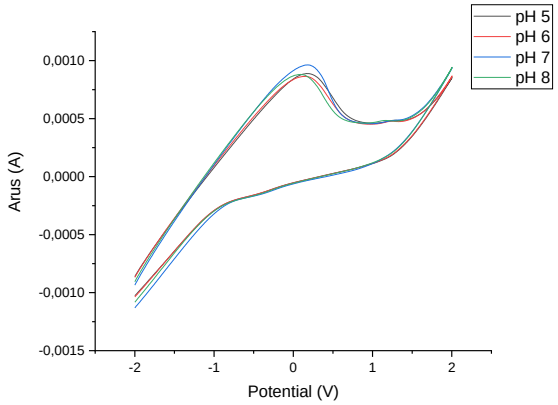


**Figure 4.** Voltammogram of Carbon Paste Electrode 3:2:3:2 50 ppm Methyl Paraben Solution with Comparison of pH Variations 5-8

Table 4. Peak Current Measurement of 50 ppm Methyl Paraben Solution with Various pH Variations

| pH | $Ip_a$ (A) |
|---|---|
| 5 | $8.97x10^{-4}$ |
| 6 | $8.64x10^{-4}$ |
| 7 | $9.63x10^{-4}$ |
| 8 | $8.82x10^{-4}$ |

The measurement results show that at pH 7, the methylparaben solution oxidizes. The amount of oxidation can be proven from the value of oxidation current (Ipa). Based on Table 4, pH 7 is the optimum pH for measuring methylparaben because, in these conditions, the methylparaben species is stable and can ionize optimally at pH 7. The effect of pH variation affects the peak current formed. The higher peak current value produced in the analysis of methylparaben at different pH variations indicates high electron transfer [32]. The higher the peak current, the more the concentration analysis of the test solution can be done because the measured concentration is linear with the measured current.

This study is the research conducted by Cahyatomo et al. [6]. The bentonite synthesis aims to obtain bentonite at nanoparticle size and clean from impurity elements. FTIR aims to determine the functional groups in bentonite nanoparticles so that it can be known that the bentonite used is in a state without impurities and is ready for analysis. XRD aims to determine the size of bentonite nanoparticles so that the bentonite used follows the size of the nanoparticles. Nanoparticle size is 1-100 nm [24]. In the

composition of carbon paste electrodes, it can be seen that the best-modified carbon paste electrodes are shown in carbon paste electrodes with the largest number of $TiO_2$ nanoparticles compared to bentonite nanoparticles because the addition of nano titanium dioxide has a great influence on the effectiveness of the working electrode, because it has a large surface area, fairly good thermal stability, high absorption properties, and has abundant adsorption sites for organic compounds [26].

This study follows research conducted by Cahyatomo et al. [6]. The best methylparaben analysis using cyclic voltammetry is shown at pH 7. The potential range of 0.0 V - +1.5 V produces a current indicating that the current is a methylparaben compound. This study has a higher current value compared to the research of Cahyatomo et al [6]. The sensitivity of the modified carbon paste electrode bentonite and titanium dioxide nanoparticles produced is better.

## Conclusion

Bentonite and titanium dioxide nanoparticles modified carbon paste electrode at composition 3:2:3:2 (carbon: bentonite nanoparticles: titanium dioxide nanoparticles: paraffin) gives the best peak current in identifying and measuring methylparaben solution. The best measurement conditions in the analysis of methyl parabens using cyclic voltammetry at pH 7 with a current value of 9.63x10-4. Bentonite and $TiO_2$ nanoparticles modified carbon paste electrodes can be used for methylparaben analysis.

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