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RESEARCH ARTICLE

MAKING OF GRAPHENE OXIDE-NANOZEOLITE COMPOSITE AS A WORKING ELECTRODE FOR SALICYLIC ACID ANALYSIS USING CYCLIC VOLTAMMETRY

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ABSTRACT

In this study, graphene oxide was made by using improved hummer method and nanozeolite was made by using a top down method with a ball mill as a working electrode for the analysis of salicylic acid by cyclic voltammetry. Graphene oxide needs to be modified to increase its sensitivity to the analyte so that the graphene oxide working electrode is modified with a modifier, namely nanozeolite. In this study, analysis of salicylic acid using graphene oxide-nanozeolite working electrodes has the best composition with a ratio of graphene oxide: paraffin: nanozeolite which is 3: 2: 5, the optimum solution pH is 2, the optimum deposition time is 5 seconds and the optimum scan rate is 100 mV/second. In the analysis of salicylic acid by cyclic voltammetry, graphene oxide-nanozeolite working electrodeshave a detection limit of up to 0.467 ppm with a percent recovery of 99.292%.

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INTRODUCTION

Face powder is one of the cosmetics that is often used by the public. In face powder preparations often added salicylic acid which serves to treat skin problems, such as acne, itching and others [1]. The maximum salicylic acid level determined is 2%. Salicylic acid with the right dosage can provide the desired therapeutic effect, but in its continued use it can cause damage to the skin. The use of topical salicylic acid with high concentrations, in large areas of the skin, damaged skin and in the long term can cause acute systemic poisoning, therefore it is necessary to analyze the detection of salicylic acid levels in the powder to avoid the danger of salicylic acid. So far, various techniques have been used to detect levels of salicylic acid, including alkalimetric methods [2], UV-Vis spectrophotometry [3], and High Performance Liquid Chromatography (KCKT) [4]. Voltammetry is an electroanalytic method that is based on the oxidation-reduction reaction process on the electrode surface [5]. The resulting current is proportional to the concentration of the chemical species in the solution. All elements that can undergo oxidation-reduction on the electrode surface can be analyzed by voltammetry [6]. Voltametri has several methods. One of them is cyclic voltammetry. Cyclic voltammetry is an electrochemical analysis method that is based on measuring the value of an electric current as a function of the potential flow that is given back and forth (reduction-oxidation) to electrochemical cells [7]. Information that can be obtained from this technique are: interpretation of reaction reversibility, study of reaction mechanisms and; study of adsorption processes [5]. A set of voltammetry instruments consists of several electrodes, namely the working electrode, the comparative electrode and the assistive electrode. In this research, the electrodes to be modified are the working electrodes. Working electrodes that are often used so far include carbon, platinum, gold, graphite, and carbon paste. The latest working electrode in voltammetry is graphene oxide. Graphene oxide is a sheet of carbon allotrope. Graphene oxide has a conductivity value of 5000 W / mK[8] with a surface area of 2630 m^2 / g [9]. the difference in conductivity values between graphene / parafin and graphene oxide / parafin each with a value of 0.488 (W / mK) and 0.506 (W / mK) [10]. This shows that Graphene oxide material is a good material for the manufacture of working electrodes on voltammetry. However, graphene oxide has a slow transfer of electrons so it needs to be modified [11]. Modifications are made by composing graphene oxide with a material that can help speed up the process of electron transfer to the electrode surface. The material is nanozeolite where zeolite has a hollow surface. In this research, graphene oxide-nanozeolite electrodes have a sharp oxidation peak compared to graphene oxide electrodes alone. This shows that graphene oxide-nanozeolite electrodes have sensitivity in the process of analysis of salicylic acid. The electrode has a low detection limit for the analysis of salicylic acid, so it is recommended to be used in the analysis of salicylic acid levels in a sample.

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MATERIAL AND METHODS

Equipment and material: The tools used include glass beaker, a unit of voltammetry, analytical balance, copper wire, sandpaper, magnetic stirer, pH meter, thermometer, centrifuge, oven, ultrasonic, planetary ball milling and HPLC instrument . Materials used include fabercastel pencil graphite, paraffin, natural zeolite, H_2SO_4 solution pa, 85% H_3PO_4 solution, $KMnO_4$ powder, 30% H_2O_2 solution, 37% paLHCl solution, 1M HCl, Zn powder, aquademineral, salicylic acid, 96% ethanol % pa, 10 M NaOH, KCl 5000 ppm, citric acid powder and sodium citrate pa).

Synthesis of graphene oxide: Graphene oxide were prepared by improved hummer method [12, 13] and characterized (FTIR, PSA and XRD). To reduce graphene oxide, 0.6 grams of Zn powder is added with 20 mL 37% HCl. Then stir for 1 hour, the solution is cooled. Next centrifuged and sediment washed using aqua DM, then dried at 60^0C in the oven for 24 hours.

Synthesis of nanozeolite: Nanozeolite was synthesized by the top down method by using planetary ball milling and characterized (FTIR, PSA and XRD). Natural zeolites are prepared by mashing, sifting and then washing with aqua DM. Then do the chemical and physical activation. Chemical activation is carried out acidically by adding HCl with a zeolite: aqua dm: HCl ratio of 1: 4: 2, and alkaline by adding NaOH with a zeolite: aqua dm: NaOH ratio of 1: 4: 2. Decanted and dried in an oven with a temperature of 80^0C to dry (gray). For physical activation, zeolites resulting from chemical activation are calcined at 600^0C for 3 hours. Then the calcination results from zeolite, carried out the milling process on a planetary ball milling for 4 hours at a speed of 500 rpm.

Electrode preparation: The process of preparing graphene oxide-nanozeolite electrodes is to make variations in the composition consisting of graphene oxide: paraffin oil: nanozeolite (3:2:5; 3:3:4; 3:4:3; 3:5:2). Making variations of the composition aims to determine the best composition of the electrodes in the analysis of salicylic acid. The best composition of the electrodes can be determined by the presence of a maximum peak current intensity. Graphene oxide-nanozeolite composite electrodes are made by mixing graphene oxide, paraffin oil and nanozeolite using a watch glass and spatula until they become a paste. Then the paste is inserted into the end of the copper wire (about 15 cm and 2.5 mm) which has been coated with an insulating pipe to prevent the paste from slipping.

RESULTS AND DISCUSSION

The best composition of electrodes: Composition of graphene oxide-nanozeolite composite electrodes made with several variations between grapheneoxide: paraffin oil: nanozeolite which aims to determine the best electrode composition in the analysis of salicylic acid by cyclic voltammetry. The best electrode composition is obtained by comparing the voltammogram result from several variations of the composition, the best electrode has the peak of the oxidation current and the highest reduction of the peak current. Salicylic acid measurements at pH 2 with a concentration of 50 ppm were carried out in the range of potential difference of -2 to 1 Volt with a scan rate of 0.1 V/sec. Based on the results of the study, the Ipa and Ipc values of each electrode composition increased in each comparison. This increase is in accordance with the nature of the material used in the manufacture of electrodes, graphene oxide is a conductor, paraffin oil is an insulator and nanozolite is an adsorbent that helps the process of electron transfer to the electrode surface, so the more composition of nanozeolite in electrode the result is much better. In this study, the optimal electrode composition is a composition at a ratio of 3: 2: 5 30% graphene oxide, 20% paraffin oil and 50% nanozeolite. The composition is the best because it has the largest Ipc value compared to other electrode compositions. The working electrode of graphene oxide-nanozeolite in the analysis of salicylic acid has an Ipc value of -0.00242 A and a potential difference of -0.7713 Volt. The best electrode composition is used in subsequent measurements. The voltamogram of the graphene oxide-nanozeolite working electrodes of various compositions is shown in Fig. 1.Processed in origin 7.0.

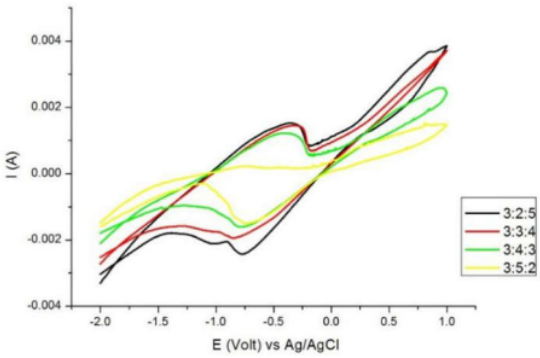

Fig. 1. Salicylic acid voltammogram of 50 ppm with pH 2, deposition time of 5 seconds and scan rate of 0.1 V / sec with variations in the composition of the graphene oxide-nanozeolite working electrodes

Optimal pH: Every analyte analyzed using voltammetry must be kept in pH. Preservation of the pH of the analyte can produce a good peak current during measurement, therefore a citrate buffer solution is used to maintain the pH of the analyte. Measurements were made at a potential difference of -2 to 1 volt with a deposition time of 5 seconds, a scan rate of 0.1 V/s and with a variation of pH of 2; 3; 4; 5; 6 and 7. The results obtained from the measurement of cyclic voltammetry are processed using Origin 7.0, resulting in a voltammogram (Fig. 2). In the voltammogram, Fig. 2 shows that the graphene oxide-nanozeolite composite working electrode can work well at pH 2, because at pH 2 it produces the highest peak of oxidation and reduction current compared to other pH. The oxidation peak current is 0.00262 A and the potential difference is -0.2664 Volts.

Optimum deposition time: Deposition time is the time required for the analyte to settle to the electrode surface. The amount of deposition time applied during the measurement will affect the stability of the analyte collected on the electrode surface. Based on the Ipc value, the results of the analysis show that salicylic acid deposition time is 5 seconds, because at 5 seconds deposition time it has a higher Ipc value than other deposition times. The Ipc value of deposition time of 5

seconds in the analysis of salicylic acid by cyclic voltammetry is -0.002218 A (Fig. 4).

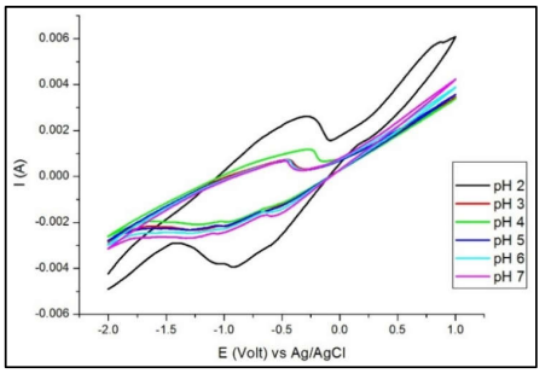

Fig. 2. Salicylic acid voltammogram of 50 ppm at 5 seconds deposition time, scan rate of 0.1 V/sec with pH variations

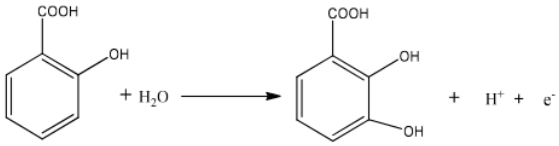

Fig. 3. Salicylic acid oxidation reaction

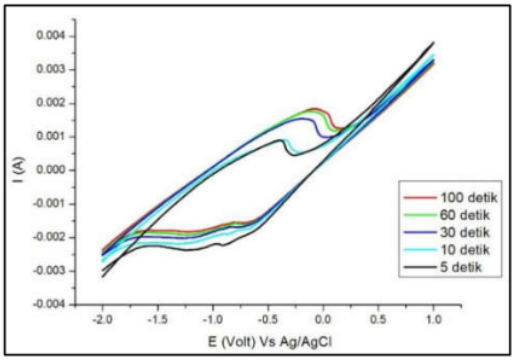

Fig. 4. Salicylic acid voltammogram with a concentration of 50 ppm, pH 2, a scan rate of 0.1V/s with variations in deposition time

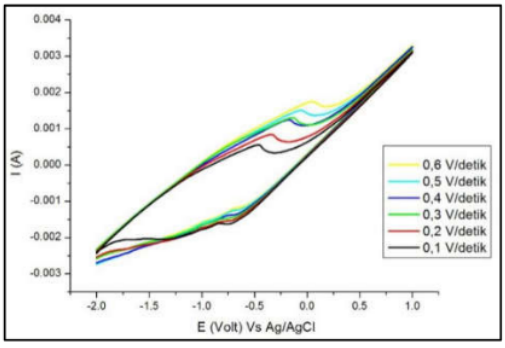

Fig. 5. Salicylic acid voltammogram with various scan rates with pH 2 and deposition time of 5 seconds

Optimum scan rate: In cyclic voltammetry measurements, the scan rate also affects the peak current height. To determine the effect of the scan rate on the peak current of an analyte can be measured cyclic voltammetry with variations in the scan rate. Measurements were made using 50 ppm salicylic acid, pH 2 (optimum pH) and deposition time of 5 seconds (optimum deposition time) with a scan rate variation of 0.1; 0.2; 0.3; 0.4; 0.5 and 0.6 V / sec. Based on the voltammogram (Fig. 5), seen from the Ipc value, the scan rate of 0.1 V/s has the highest Ipc value of -0.00163 A.

Electrocalalytic oxidation of salicylic acid using graphene oxide-nanozeolite working electrodes: The standard solutions used for calibration are 10, 20, 30, 40 and 50 ppm. Measurements on standard calibration with a deposition time of 5 s, a scan speed of 0.1 V/s with a potential difference of -2 to 1 volt by cyclic voltammetry. The voltammetry cell was filled with a mixture of 10 mL of a standard solution of salicylic acid each of 10, 20, 30, 40 and 50 ppm, 10 mL of KCl 50-100 times the sample concentration and 5 ml of pH citrate buffer 2. The voltammetry yield was processed using Origin 7.0, which shown in Fig. 6.

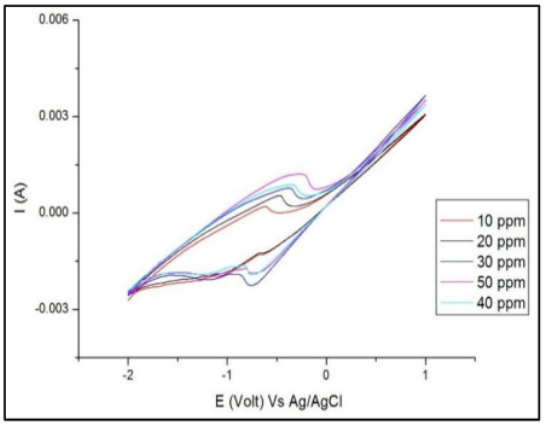

Fig. 6. Salicylic acid voltammograms of various concentrations with pH 2 buffer solution, deposition time of 5 seconds and a scan rate of 0.1 V/s

The graph of the relationship between concentration and peak oxidation current (Fig. 5) gives equation.1 with regression R^2 = 0.99276.

$$y = 2.30902 \times 10^{-5}x + 3{,}39045 \times 10^{-5} \quad (1)$$

Liner equation. 1 is used to determine the concentration of salicylic acid in the powder.

Recovery and detection limits: Data recovery is performed to determine the accuracy in the process of identifying salicylic acid using graphene oxide-nanozeolite composite working electrodes. Determination of percent recovery by comparing the concentration obtained (measured) when analysis with the actual concentration. To obtain the concentration obtained is to substitute the standard solution current in y in the linear equation 1. The resulting concentration is compared with the actual salicylic acid concentration, with equation 2.

$$\%\ recovery = \frac{concentrationobtained}{realconcentration} x\ 100 \quad (2)$$

The recovery results for the analysis of salicylic acid with graphene oxide-nanozeolite composite working electrodes with a composition of 3: 2: 5 is 99.292%. Good recovery results show that graphene oxide-nanozeolite composites are sensitive to salicylic acid samples.

Detection Limits: The limit of detection (LoD) is the smallest value limit of a tool in determining the results of quantitative analysis obtained based on a standard curve. In this study, the detection limit is the smallest limit of salicylic acid concentration that can be detected by graphene oxide-nanozeolite composite working electrodes on cyclic voltammetry, so the detection limit can also indicate the level of sensitivity of graphene oxide-nanozeolite working electrodes. The lower the detection limit the better the sensitivity to the sample. Based on the calculation results, the detection limit is 0.467 ppm.

Analysis of real samples: To determine the feasibility of the electrodes made, salicylic acid selectivity was tested on powder samples. The results of the analysis by voltammetry were compared with HPLC. HPLC analysis obtained a concentration of 54.61 ppm while based on the results of voltammetry analysis, salicylic acid concentration was obtained in Table 1.

Table 1. Concentrations of salicylic acid in powder based on voltammetry analysis

Sample	Ipc (A)	Measurable concentration (ppm)
1	-0.0012464372	55
2	-0.00113346118	50.55
3	-0.00135941322	60.34

Conclusion

Graphene oxide-nanozeolitecomposite electrodes show a good linear relationship with salicylic acid concentration in the range of 10-50 ppm and the detection limit is 0.467 ppm. Graphene oxide-nanozeolite composite working electrodes have good sensitivity in cyclic voltammetric analysis.

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