Modification of Carbon Paste Electrode with Ag Nanoparticle for Voltammetric Determination of Phenol

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Abstract. Phenol is an aromatic derivative of hydrocarbons from coal which used as a base for making plastic bottles, cans of packaged food, and pesticides. However, this compound is emerging as a pollutant in the environment. This work, the carbon paste electrode based on Ag nanoparticle was developed for the detection of phenol. Carbon paste electrode modified Ag nanoparticles which were previously synthesized first and then mixed with graphite and paraffin. The best composition of CPE-nAg is 5:70:25 for Ag nanoparticles, graphite, and paraffin, respectively. After measurement using CPE-nAg, it is necessary to remove phenol on the electrode surface with 6 cycles. Measurement was carried out using square wave voltammetry techniques range with 0 V to 1.2 V, a frequency of 10 Hz, and a scan rate of 75 mV/s. The result showed the presence of an oxidation peak of phenol is 0.475 V in 1 M of sodium hydroxide solution.

Keywords: CPE, Ag nanoparticles, Voltammetric, Phenol

1 Introduction

Phenols are pollutants in industrial waste that have low degradability and in low concentrations, phenols can cause toxicity and bioaccumulation problems. Phenolic compounds can be found in water that is the result of waste from the food industry and the chemical industry such as in the production of resins, pesticides, and oil refineries [1]. Based on the Minister of Health Decree No.907/MENKES/SK/VII/2002, the maximum concentration of phenol that declared safe in the water for aquatic ecosystem life is 0.5 – 1.0 mg/L [2]. A large amount of phenol in industrial fields cause phenol easily found in water. This has quite an impact on the environment because phenols are also known to be very reactive to human body tissues if absorbed through contact with the skin, breathing, and digestion. Contact with phenols can cause irritation, dermatitis, and burn [3].

Several studies have explained how to detect phenols accurately and sensitively such as adsorption using eggshell [4], HPLC-UV [5], UV-VIS spectrophotometers [6], and high-performance liquid chromatography [7]. However, these techniques need expensive instrumentation, so we need another analytical method for the determination of phenols in the sample. One method that can be used is electrochemistry which has several advantages such as high sensitivity and selectivity, simple modification, and economical [8],[9],[10],[11],[12]. In voltammetric techniques, usually using electrodes that the reactivity of an electrode depends on

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the composition of its constituent materials, so that optimization of the composition is needed to obtain a good electrode. The electrodes used are carbon paste electrodes (CPE) which have several advantages such as easy modification processes, renewable surfaces, and economical. Carbon paste electrodes modified by adding a certain substance can detect samples in very small levels so high selectivity can be obtained [13]. The use of nanomaterials in CPE has been widely used because it can increase sensitivity and selectivity in electrochemical. Nanomaterials that commonly used are nickel, gold, and silver.

Silver nanoparticles (nAg) are widely used because easily obtained, inexpensive, and produce good catalytic properties [14]. Synthesis of Ag nanoparticles which is widely used is by reducing silver ions in various stabilizers such as surfactants and polymers [15],[16]. In this study, the synthesis of Ag nanoparticles was carried out using polyvinylpyrrolidone (PVP) which is quite interesting because of its excellent physical and chemical properties as a coating [17]. PVP is a biocompatible polymer that is one of the water-soluble polymers and PVP works as a stabilizer of metal nanoparticles but also has an impact on the control level of the reduction of silver ions and aggregation process of the silver atom [18].

In this paper, phenol measurements were carried out by carbon paste modified Ag nanoparticles (CPE-nAg). The parameters studied were the optimum composition of Ag nanoparticles, the number of phenol removal cycles, and anodic peak analysis of phenols.

2 Experimental

2.1 Reagents, Solution, and Samples

The chemicals used in this study were graphite powder, paraffin oil, silver nitrate/$AgNO_3$, phenol/C_6H_5OH, potassium hexacyanoferrate (II)/$K_4[Fe(CN)_6]$, potassium hexacyanoferrate (III)/$K_3[Fe(CN)_6]$, sodium borohydride/$NaBH_4$, sodium chloride/NaCl, L-glutamic acid, Polyvynilpyrrolidone/PVP, sodium hydrogen phosphate/Na_2HPO_4, sodium hydroxide/NaOH, and sodium dihydrogen phosphate/$NaH_2PO_4.H_2O$. These reagents are available in the chemistry department laboratory. Electrolyte solution used is phosphate buffers for removing phenol from the electrode surface while sodium hydroxide was used as the supporting electrolyte to dissolve phenol.

2.2 Preparation of Reference Electrode

In the making reference electrode (Ag/AgCl electrode), the first silver wire is sanded then electrolyzed with 0.1 M NaCl solution at the potential of 0.223 V for 2 minutes until a black AgCl layer will be formed on the surface of the Ag wire. In this process, Ag wire functions as a working electrode and Pt wire has functioned as a reference electrode. Furthermore, the electrolyzed Ag wire is inserted into the electrode body which has been filled with 3 M NaCl solution and characterized in a 0.01 M $K_3[Fe(CN)_6]$ and $K_4[Fe(CN)_6]$ solution in 0,1 M NaCl. Characterization was performed using the cyclic voltammetry (CV) method in the potential range of -200 mV to 800 mV with a scan rate of 100 mV/s for 1 cycle. The characterization results compared with BAS commercial reference electrode.

2.3 Synthesis of Ag Nanoparticles

Ag nanoparticles were synthesized with polyvinylpyrrolidone (PVP). Synthesis of nAg was carried out by dissolving 0.025 grams of $AgNO_3$ in 500 µL distilled water. Then this solution is dropped into 20 mL PVP and also added with a 5 mL $NaBH_4$ solution. The mixture of this solution is stirred for 1 hour. After one hour, a dark brown solution will be produced which indicates the formation of the Ag nanoparticles. This solution kept in room temperature and stable in 90 days.

2.4 Preparation of Carbon Paste Electrode Modified Ag Nanoparticles

Carbon paste electrode modified Ag nanoparticles (nAg) was prepared by adding graphite, paraffin oil, and Ag nanoparticles. The amount of Ag nanoparticles given was varied to 5, 15, 25, and 35%. From the measurement results, the maximum yield is obtained when nAg are in the amount of 5% with a ratio of 70: 25: 5 (%w/w) for graphite, paraffin oil, and nAg, respectively. Then the mixture is heated until 70^0C to form a homogeneous paste. Then the paste is inserted into the body of the electrode that containing copper wire while being pressed until it is solid. The final step is rubbing the surface of the carbon paste on a clean paper.

3 Results and Discussion

3.1 Characterization of Reference Electrodes

In this study, phenol measurements were carried out using 3 electrodes that are Ag/AgCl electrode as a reference electrode, CPE-nAg as a working electrode, and Pt wire as an auxiliary electrode. Ag/AgCl reference electrode was characterized by cyclic voltammetry method in the potential range of -200 V to 800 V for 1 cycle using the mixture of K4Fe(CN)6 and K3Fe(CN)6 in 0,1 M NaCl solution. Furthermore, the results of the Ag/AgCl electrode's characterization compared with the BAS electrodes. The results of the characterization of these electrodes must resemble (coincide) in order to show the same quality. This is important to ensure there are no errors in the measurements that can be caused due to the poor quality of the comparison electrodes. The cyclic voltammogram of these electrodes is presented in **Figure 1**.

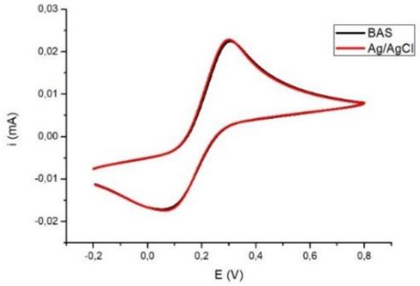

Fig. 1. Cyclic voltammogram of Ag/AgCl electrode and BAS electrode in solution mixture of K4Fe(CN)6 and K3Fe(CN)6 in 0,1 M NaCl solution.

Based on the voltammogram in **Figure 1**, it can be seen that the Ag/AgCl electrode and BAS electrode are very coinciding. Anodic and cathodic peak current values resulting from Ag/AgCl electrode characterization are shown in Table 1.

Table 1. Characteristic value of Ag/AgCl and BAS electrode.

Electrode	Ipa (μA)	Ipc (μA)	Epa (V)	Epc (V)	E^0 (V)
BAS	22.24	17.19	0.290	0.089	0.1895
Ag/AgCl	22.67	17.58	0.285	0.093	0.1890

3.2 Determination of Composition Carbon Paste Electrode Modified Ag Nanoparticles

Variation of Ag nanoparticle composition needs to be done in order for the best composition of Ag nanoparticles is known so the sensitivity will be getting better. Variation composition of Ag nanoparticles is done by making 4 variants with the ratio of graphite, paraffin, and Ag nanoparticles respectively (70:25:5), (70:20:10), (70:15:15) and (70:10:20). Measurements were made using a square wave voltammetry technique with a scan rate of 75 mV/s, frequency of 10 Hz, in the potential range of 0 V to 1,4 V in a 10 mM phenol solution. Results of measurement of 10 mM phenol solution using CPE-nAg with various composition comparisons are shown in **Figure 2**.

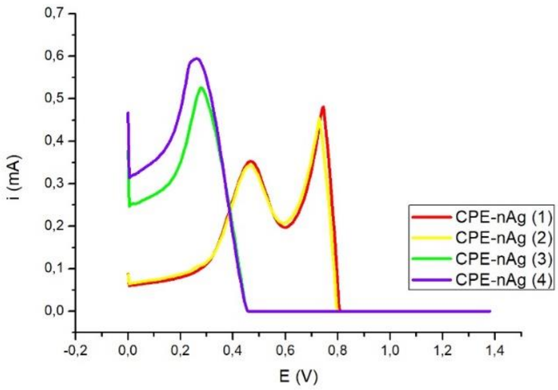

Fig. 2. Effect of variations in the composition of Ag nanoparticles on anodic peak current of 10 mM phenol in 1 M NaOH solution using SWV techniques.

Based on **Figure 2**, measurements using CPE-nAg 1 give a higher current compared to CPE-nAg 2 which is 0.3526 mA with a potential value of 0,465 V. But on measurements using CPE-nAg 3 and CPE-nAg 4, the potential given becomes more negative compared to the supposed value of 0.280 V. The existence of this potential value shift, can be caused by the influence of the composition of Ag nanoparticles given in the carbon paste mixture. In the measurement of phenol using CPE-nAg 3 and CPE-nAg 4 the composition of each electrode was (70:15:15) and (70:10:20) where the amount of Ag nanoparticles used were 0.075 grams and 0.100 grams. The amount of Ag nanoparticles is more than the liquid paraffin used, causing the paste to be less homogeneous. The measured phenolic anodic peak current value is shown in Table 2.

Table 2. Measurement anodic peak current of 10 mM phenol in 1 M NaOH using CPE-nAg with various comparisons.

nAg	Graphite (g)	Paraffin oil (g)	Ag Nanoparticles (g)	i (mA)	E (V)
1	0.35	0.125	0.025	0.3526	0.465
2	0.35	0.100	0.050	0.3422	0.480
3	0.35	0.075	0.075	0.5259	0.280
4	0.35	0.050	0.100	0.5880	0.275

After knowing the right electrode composition, it is necessary to remove the analyte (phenol) from the electrode surface. Phenol removal is carried out using cyclic voltammetry in the potential range of 0 V to 1,4 V with a scan rate of 100 mV/s. After phenol removal, CPE-nAg was measured in 10 mM phenol solution using the SWV technique with a scan rate of 75 mV/s, frequency of 10 Hz, in the potential range of 0 V to 1,4 V. Effect of the number of phenol removal cycles is shown in **Figure 3**.

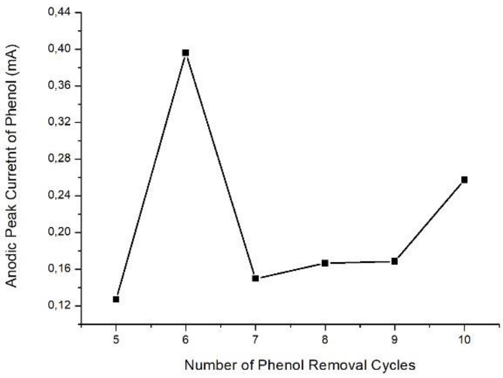

Fig. 3. Effect of the number of phenol removal cycles on the phenolic anodic peak current in 10 mM phenol solution.

Figure 3 shows that the removal of phenol from CPE-nAg with 6 cycles gives the highest anodic peak current in 0.3960 mA with a potential value of 0.470 V.

3.3 Evaluation of Phenol Anodic Peak Current

Evaluation peak of phenol is done by comparing the peak of phenol using unmodified CPE and CPE-nAg. Measurements were made using square wave voltammetry techniques in the potential range of 0 V to 1.4 V with a scan rate of 75 mV/s in a 10 mM phenol solution. The results of the measurement of two electrodes are compared to determine the good electrode performance. Square wave voltammograms in measurements of phenol peak by different electrodes are shown in **Figure 4**.

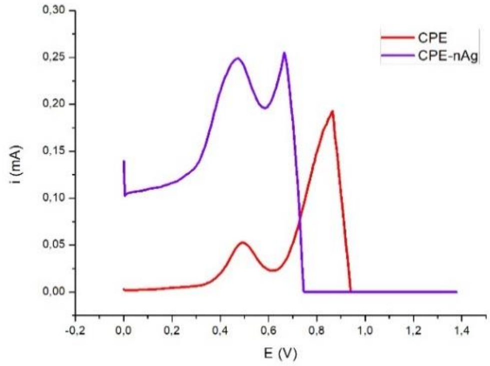

Fig. 4. Voltammogram measurement of 10 mM phenol in 1 M NaOH solution using unmodified CPE and CPE-nAg.

Based on **Figure 4**, seen that the phenolic anodic peak currents measured using CPE-nAg are higher than unmodified CPE. CPE gives a very small current because the electron transfer kinetics of CPE is slow due to the buildup of oxidation products that pollute the surface of the working electrode. While CPE-nAg provides higher anodic peak currents compared to others due to the presence of Ag nanoparticles in carbon paste mixture used so it can increase the interactions with phenols. A comparison of the phenolic anodic peak current values is shown in Table 3**.**

Table 3. Comparison of anodic peak current value and potential oxidation of phenol 10 mM using different electrodes.

Electrode	i (mA)	E (V)
CPE	0.0524	0.490
CPE-nAg	0.2481	0.475

4 Conclusions

Modification of carbon paste electrodes using Ag nanoparticles is successfully carried out using a square wave voltammetry technique by giving a high current value compared to unmodified CPE. The best composition of CPE-nAg is 70:25:5 (%w/w) for graphite, paraffin, and Ag nanoparticles. Measurements of phenol were made using square wave voltammetry techniques with a scan rate of 75 mV/s in the potential range of 0 V – 1.4 V in a 10 mM phenol solution. The result showed a phenol oxidation peak in 0.475 V in 1 M of sodium hydroxide solution.

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