

## Modification of Screen Printed Carbon Electrode (SPCE) with Polypyrrole (Ppy)-SiO<sub>2</sub> for Phenol Determination

Erasti Pratiwi<sup>1</sup>, Ani Mulyasuryani<sup>1\*</sup>, and Akhmad Sabarudin<sup>1</sup>

<sup>1</sup>Department of Chemistry, Faculty of Mathematics and Natural Science, Brawijaya University

\*Corresponding email : mulyasuryani@ub.ac.id

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### ABSTRACT

Modification of electrodes on a screen printed carbon electrode (SPCE) using polypyrrole (Ppy)-SiO<sub>2</sub> has been successfully conducted for phenol determination. Modification has been undertaken with electropolymerization-wise using cyclic voltammetry. Electrode resulted are used to determine phenol using cyclic voltammetry and differential pulse voltammetry. A cyclic voltammetry analysis using potential range of -1 to 1 V versus Ag/AgCl at scan rate of 100 mV/sec. Meanwhile, analysis using differential pulse voltammetry method applied potential range of 0 to 1 V versus Ag/AgCl, scan rate of 50 mV/sec, pulse rate of 0.2 V, and pulse width of 50 ms. The results provide the increase of pH and decrease of Epa potential peak. It may increase in the current of phenol. Modified SPCE Ppy-SiO<sub>2</sub> can be applied for phenol determination at a concentration of 10<sup>3</sup> -10<sup>-5</sup> mM with sensitivity of 7.93 µA/mM.

Key word: Phenol, Polypyrrole-SiO<sub>2</sub>, Cyclic Voltammetry, Differential Pulse Voltammetry

### INTRODUCTION

Phenol is a dangerous pollutant that is commonly found in water, canned food, air, and chemical products [1]. Excessive phenol contain in water reservoir can be dangerous and causes death to water organisms [2]. The Regulation of State Minister of Environment number 03 of 2010 regulates the maximum concentration of phenol allowed in waters is 1 mg/L [3]. Phenol has a high toxicity and dissolves easily in water. It harms to human's health [1]. Therefore, this is due to will be useful to establish a sensitive and accurate analysis.

Phenol is an electroactive compound that can undergo oxidation reaction, which can be analyzed using electrochemical method. The developed method using a modified electrode has been attracting a great deal of attentions. This technique has several advantages, such as does not require a complicated preparation, fast, and only requires very few samples [1]. Screen-printed electrode is an electrode device of working electrodes, comparative electrodes, and printed supporting electrodes, filled and coated on the surface of the substrate [4]. The surface modification of the electrode can be accomplished by addition various substances such as metal oxides, polymers, and enzymes [5]. Various electrodes such as PbO<sub>2</sub>-paste carbon electrodes, enzyme-modified electrodes, and nafion-modified glassy carbon electrodes, have been extensively investigated for the determination of phenol oxidation [1].

Determination of phenol using cyclic voltammetry method has been widely studied on various modifications of working electrodes. In 2014, the modification of working electrode using Np-CPE, Ag/AgCl as the compare electrode and Pt as the supporting electrode was

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applied for the determination of phenol using cyclic voltammetry method [6]. Alemu, et.al. reported the electrode modification has been conducted using single-wall carbon nanotube (SWCNT)/GCE. The modified electrode was applied for the determination of phenol using cyclic voltammetry and differential pulse voltammetry (DPV) [7]. The modification of working electrode using poly(3,4-ethylenedioxythiophene) immobilized in a single-wall carbon nanotube (SWCNT) had been previously reported by Negash, et. al. The result was applied for the determination of phenol using cyclic voltammetry and amperometry. The cyclic voltammetry method can provide a better way for controlling the growth of film polymer and avoiding over oxidation of phenol [8]. The other method for phenol detection had also been reported by Sakti, et.al. which applied using bacterial biosensor through *Pseudomonas putida* and *Pseudomonas fluorescens* as a biological sensitive material. The sensor was made from glass micro electrode using Ag/AgCl electrode as reference electrode, silver electrode and cellulose ester [9].

In this study, modification of electrode was undertaken on screen printed carbon electrode (SPCE) using polypyrrole (Ppy)-SiO<sub>2</sub> for phenol determination. Electrode modification using polypyrrole (Ppy) has been widely applied in chemical sensors due to its high conductivity of  $10^2 - 7.5 \times 10^3$  S/cm[10], its electrically conductive properties, its good mechanical properties[11], its easiness to be synthesized in water solvents, and its film thickness that can be controlled using electropolymerization process [12]. This study performed both polymers and oxide nanoparticles; one of them is silicon oxide (SiO<sub>2</sub>), have a role as the supporting material and oxidation catalyst in the process of phenol determination. SiO<sub>2</sub> was utilized in this research due to its ability to cover a large surface area and its high adsorption power [13].

In this study, Ppy-SiO<sub>2</sub> synthesis was conducted through direct electropolymerization on SPCE working electrode using the cyclic voltammetry method. Electropolymerization using cyclic voltammetry is preferable because it can deposit the monomer of a Ppy film in the electrolyte solution on the electrode surface at the peak potential[11]. Therefore, the use of modified electrodes using Ppy-SiO<sub>2</sub> is expected to increase phenol and electrode surface interaction, and also the oxidation peak using cyclic voltammetry method and differential pulse voltammetry.

## EXPERIMENT

### Chemicals and instrumentation

The apparatus were used in this study are analytical balance (Mettler Toledo AL204), pH meter (Trans Instruments Senz pH) with an accuracy of  $\pm 0.2$  pH, magnetic stirrer (IKAMAG®RH), oven (Memmert), glassware, micropipette (Accumax pro), Screen Printed Carbon Electrode (SPCE) BI 1302 (Quasense Inc.) consisting of carbon as the working electrode and auxiliary electrode, Ag/AgCl as the reference electrode, and potentiostat/galvanostat (Uniscan PG581) connected with computer and Scanning Electron Microscopy (SEM) FEI Inspect S50 and EDAX AMETEK.

The materials applied in this study are ethanol, concentrated ammonia 25% (Merck), tetraethylorthosilicate (TEOS) 99% (Sigma Aldrich), pyrrole 98% (Sigma-Aldrich), potassium chloride 99.5% (Merck), phenol 99% (Merck), acetic acid 99% (Merck), phosphoric acid 85% (Merck), sodium acetate 99% (Sigma-Aldrich), disodium hydrogen phosphate 99% (Merck), sodium dihydrogen phosphate 99% (Merck), sodium hydroxide 99% (Merck), and aquadem (Hydrobatt). All chemicals had labeled analytical purity grade.

### Preparation of SiO<sub>2</sub> solution

A mixture consisting of 5 mL of ethanol, 0.125 mL of tetraethylorthosilicate (TEOS), 0.125 mL of concentrated ammonium, and 0.125 mL of ion-free distilled water in a container stirred for 4 hours. Thus, a modified suspension was ready to be applied on the surface of the screen printed carbon electrodes.

### Modification of SPCE with Ppy-SiO<sub>2</sub> by Electropolymerization

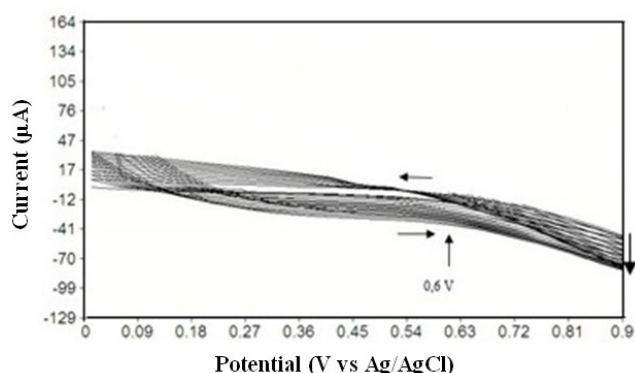
In this study, the electropolymerization of pyrrole was carried out using cyclic voltammetry method on the SPCE surface using a working potential of 0 to 0.9 V and a scan rate of 100 mV/sec in 10 cycles [14]. The electropolymerization of the pyrrole was conducted in a 75 mM pyrrole solution, KCl 0.1 M in a water solvent, and 2.5  $\mu$ L of SiO<sub>2</sub> suspension was added. SPCE using modified Ppy-SiO<sub>2</sub> was activated in 0.1 M NaOH solution through cyclic voltammetry at a potential of 0 to 1.2 V in 10 cycles[15], and then it was washed by using aqua demineralization (aqua DM) and dried at room temperature. Scanning Electron Microscopy (SEM) FEI Inspect S50 and EDAX AMETEK are used to determine the surface morphology of SPCE using modified Ppy-SiO<sub>2</sub>.

### Effect of pH

The effect of pH was determined using phenol solution in 1 mM acetate buffer solution (pH 3-5). Measurements were carried out using cyclic voltammetry in the potential range of -1 to 1 V toward Ag/AgCl, a scan rate of 100 mV/sec, and a current range of 100  $\mu$ A/V.

### Determination of phenol with *Differential Pulse Voltammetry (DPV) Method*

SPCE with Ppy-SiO<sub>2</sub> modified by using electropolymerization was applied for the measurement of phenol solution in acetate buffer as the supporting electrolyte solution. Measurements was performed using DPV method with the potential range of 0 to 1 V, pulse height of 0.2 V, scan rate of 50 mV/sec, and pulse width of 50 ms. Phenol measurements were undertaken at phenol concentration range of 10<sup>-3</sup> -10<sup>-5</sup> M.



**Figure 1.** Ppy-SiO<sub>2</sub> cyclic voltammogram of 10 cycles of Ppy 0.075 M in KCl 0.1 M

## RESULTS AND DISCUSSION

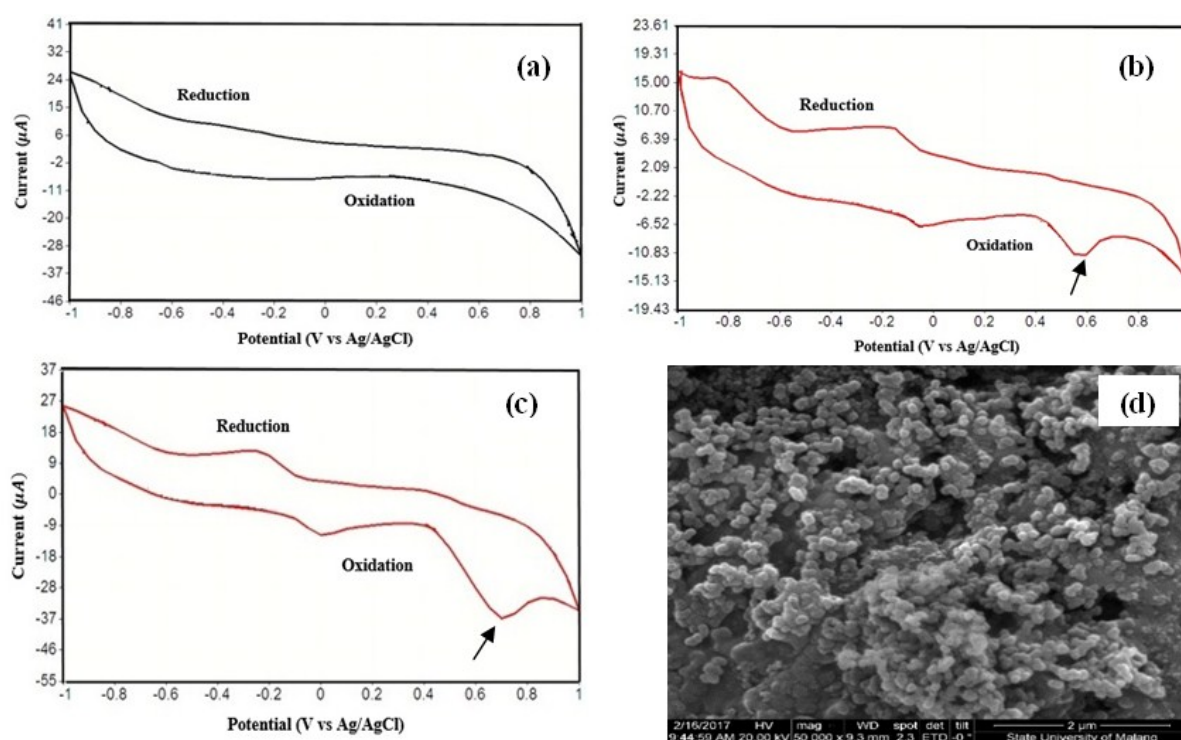
### Electrode Modification Method with Ppy-SiO<sub>2</sub>

Ppy-SiO<sub>2</sub> electropolymerization process using cyclic voltammetry was shown in Figure 1. In the redox process during electropolymerization, three phases take place. The early phase was during the half-cycle at the beginning of polymerization, in which the potential starts from 0.6 to 0 V, which leads to neutral by releasing anion charge. In the second phase, the polymer reaches the top of oxidation with a re-diffusing anion to maintain its charge

neutrality. The final phase was when it reaches the reduction potential and the anion is released. Usually, the second oxidation potential was higher than the monomer oxidation of Ppy layer on the electrode surface, but its density decreases [15]. In the pyro-electropolymerization process, the addition of SiO<sub>2</sub> works as a support material to absorb phenol and to expand the effective surface of the electrode. Polypyrrole (Ppy) on the SPCE surface can increase the conductivity of the electrode due to its characteristic of electric current conductor [11].

### Phenol Characteristics of Ppy-SiO<sub>2</sub> Modified Electrodes

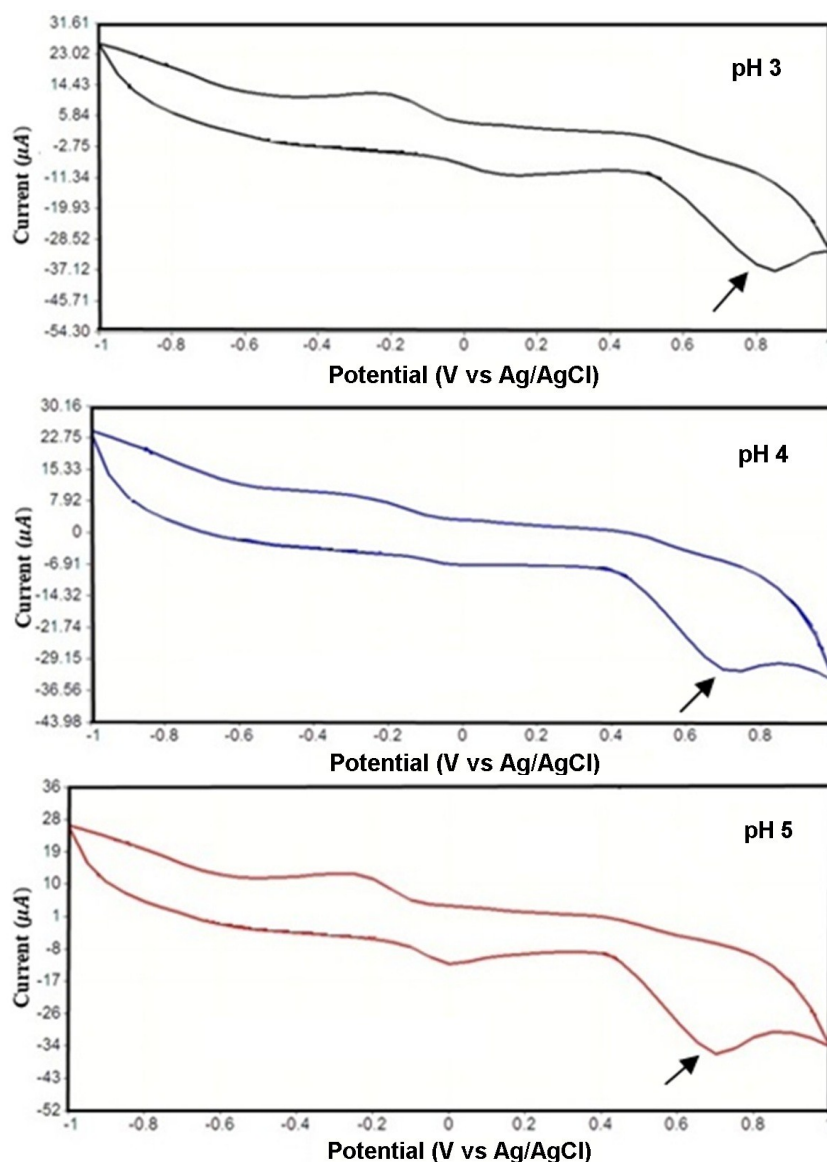
The electrode-modified test was performed using cyclic voltammetry in a pH 5 acetate buffer solution and 1 mM phenol in a pH 5 acetate buffer in the potential range of -1 to 1 V and scan rate of 0.1 V/s. The test results of the modified electrodes were shown in Figure 2. The success of the modified electrode was identified from the electroactive properties which were shown by the phenol E<sub>pa</sub> value.



**Figure 2.** Cyclic Voltammogram on SPCE using (a) 0.1 M acetate buffer solution pH 5.(b) 1mM phenol solution in 0.1 M acetate buffer pH 5 without modification. (c) 1mM phenol solution in 0.1 M acetate buffer pH 5 modified by Ppy-SiO<sub>2</sub>. (d) SEM image of SPCE modified by Ppy-SiO<sub>2</sub>

According to Figure 2, the test voltammogram result using the acetate buffer solution shows that there is no oxidation or reduction peak, while the voltammogram test of 1 mM phenol solution in acetate buffer on SPCE and SPCE pPy-SiO<sub>2</sub> modified produces a phenol peak current response in a modified SPCE pPy-SiO<sub>2</sub> is higher than SPCE without modification. This indicates that the electrode modified by Ppy-SiO<sub>2</sub> can increase the effective surface area of the coated electrode and can detect phenol. Moreover, the addition of Ppy-SiO<sub>2</sub> on the electrode surface will lead to high sensitivity of the working electrode and

tend to enhance the resulting current. This result is accordance with the SEM image which depicted the spherical surface morphology that shows the morphology of Ppy-SiO<sub>2</sub> [16].



**Figure 3.** Cyclic Voltammetry of 1 mM phenol in 0.1 M acetate buffer solution with pH variation

### Effect of pH

Based on cyclic voltammogram in Figure 3, it can be seen that the pH has an effect on  $E_{pa}$  and  $I_{pa}$ . The effect of pH on peak current indicates that the increase of pH causes the equilibrium to shift toward the formation of phenolic ions, so the number of phenol molecules in the solution decreases. A potential shift to negative indicates that the increase in pH will induce an oxidation reaction. The  $E_{pa}$  and  $I_{pa}$  data are shown in Table 1, and, based on the data, it can be seen that the increase in  $I_{pa}$  can cause  $E_{pa}$  shift, which progressively shifts towards negative as the pH rises.



**Table 1.** Measurements of modified electrode of 1mM phenol using cyclic voltammetry with pH variation

pH	Average of $E_{pa}$ (V)	Average of $I_{pa}$ ( $\mu A$ )
3	0.75	10.13
4	0.70	11.33
5	0.68	13.16

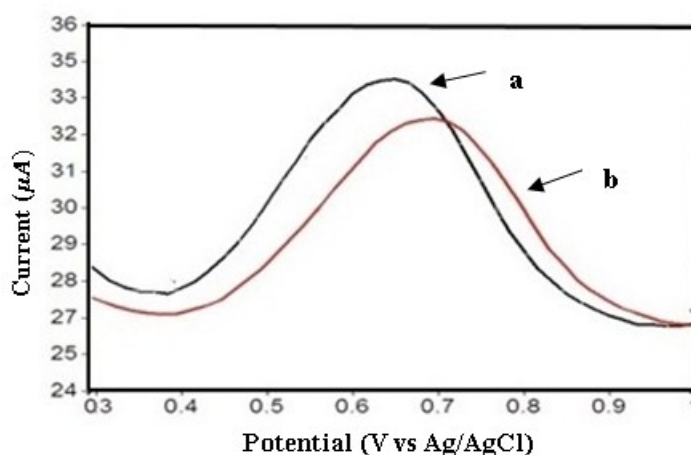
The comparison is done using DPV method. The DPV signal comparison shows the peak current response of the 1 mM phenol that uses SPCE modified polypyrrole-SiO<sub>2</sub>. The DPV method can increase the sensitivity and measurement limits detection by minimizing non-faraday currents. In this technique, the potential remains applied on the electrode surface. Table 2 shows that increasing pH makes the peak current increase as well. Thus, modification of SPCE with polypyrrole-SiO<sub>2</sub> can decrease the potential and increase the oxidation current of phenol.

**Table 2.** Measurements of modified electrodes to the 1 Mm phenol using DPV with pH variation

pH	Average of $E_{pa}$ (V)	Average of $I_{pa}$ ( $\mu A$ )
3	0.75	2.49
4	0.69	2.95
5	0.65	3.47

#### Determination of Phenol using DPV Method

Measurements were carried out in acetate buffer and phosphate buffer 0.1 M pH 5 under potential range of 0 to 1 V, scan rate of 50 mV/sec, pulse height of 0.2 V, and pulse width of 50 ms.



**Figure 4.** DPV voltammogram using 1 mM phenol in (a) 0.1 M acetate buffer pH 5, (b) phosphate buffer 0.1 M pH 5

Based on Figure 4, both of voltammograms showed peak potential at 0.6 V range. The resulted peak current has a difference, in which the acetate buffer produces a peak of 3.34  $\mu A$ , while the phosphate buffer yields a lower peak current of 2.9  $\mu A$ . This difference indicated the effect of supporting electrolyte on phenol measurement. This is due to the differences in conductivity based on the electrolyte composition of the supporting electrolyte solution. The conductivity of acetate buffer is 0.111 S-cm<sup>2</sup>/mole, while that of the phosphate

buffer is 0.03 S-cm<sup>2</sup>/mole. Thus, the modification of SPCE with polypyrrole-SiO<sub>2</sub> in acetate buffer can increase the oxidation current of phenol.

Based on the result of phenol measurement in acetate buffer, the greater the concentration of phenol contained in the solution, the larger the current occurred. This is because the phenol concentration is directly proportional to the resulting phenol peak current. The determination of phenol is performed using DPV method in the potential range of 0 to 1 V, scan rate of 50 mV/sec, pulse height of 0.2 V, and pulse width of 50 ms. Based on Figure 5, the linear regression equation of phenol concentration to phenol peak height can be expressed as follows :

$$I_p (\text{phenol}) = 7.93[\text{phenol}] + 1.41$$

Based on the above equation, the sensitivity of phenol sensor is 7.93  $\mu\text{A}/\text{mM}$ .

## CONCLUSION

Modification of screen printed electrode (SPCE) with Ppy-SiO<sub>2</sub> can be accomplished using electropolymerization method. The effect of pH on a modified electrode can produce a peak current, along with the increase of pH. Electrode modification results that can be used for the determination of phenol using cyclic voltammetry as well as differential pulse voltammetry. The result of phenol measurement in pH 5 acetate buffer has a sensitivity value of 7.93  $\mu\text{A}/\text{mM}$ .

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