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Electrochemical determination of phenol at natural phosphate modified carbon paste electrode

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ABSTRACT

A Cyclic voltammetry (VC) and Square Wave Voltammetry methods for the determination of trace amounts of phenol at carbon paste electrode modified with Natural Phosphate (NP-CPE) is proposed. The results showed that the NP-CPE exhibited excellent electro catalytic activity to phenol. The concentration of phenol and measuring solution pH was investigated.This electrochemical sensor shows an excellent performance for detecting phenol.The sensor was successfully applied to the determination of phenol in a real sample with satisfactory results.

KEYWORDS

Modified electrodes;
Cyclic voltammetry;
Natural Phosphate;
Phenol.

INTRODUCTION

Phenol and related compounds are used extensively in industry in the manufacture of a large variety of aromatic compounds including rubber, fertilizer, paints, drug preparations, petroleum, and agricultural industries[1-3]. Phenol is reported to be carcinogenic and exposure to phenol results in several symptoms such as convulsions, dizziness and irregular respiration[1,4].

The phenols are noted more as water pollutants than as air pollutants[5]. It is frequently pollutant in industrial waste and occurs in soil and drinking water supplies[6]. In the food industry, phenols are of interest because they are essential compounds of fruit juices, beer, and wines[7]. Since many phenolic compounds can cause bad taste and undesirable odor contamination and are highly toxic and hazardous to human health[8], their analysis at low concentrations is very important[9,10]. As the manufacture and use of phenols requires qualitative and quantitative control, a wide variety of methods have been developed to determine phenolic compounds. The range of available methods extends from distillation[11], membrane extraction[12], liquid-liquid extraction[13,14] and gas chromatography[15,16] to more sophisticated techniques such as microwave-assisted extraction[17,18], ultra sonication and supercritical fluid extraction[19, 20].

Recently, some achievements in the field of enzyme electrode[21,22] and biosensors[23,24] have been reported. Tyrosinase-based biosensors for the determination of phenolic compounds in the organic phase have been reported extensively[25-27]. Regarding electroanalytical techniques, procedures involving phenol oxidation at solid electrodes[28-29] have been reported. In addition, chemically-modified carbon paste electrodes have proven very useful for analytical applications[22,30]. In the previous works[31-35], the electrochemical oxidation of phenol was investigated we present a simple and sensitive method of determination of these compounds based on their reaction.

EXPERIMENTAL

Apparatus and software

Voltammetric experiments were performed using a voltalab potentiostat (model PGSTAT 100, Eco Chemie B.V., Utrecht, The Netherlands) driven by the general purpose electrochemical systems data processing software (voltalab master 4 software) run under windows 2007. The three electrode system consisted of a chemically modified carbon paste electrode as the working electrode a saturated calomel electrode (SCE) serving as reference electrode, and platinum as an auxiliary electrode.

Electrodes

Modified electrodes were prepared by mixing a carbon powder and the desired weight of Natural Phosphate (NP). The body of the working electrode for voltammetric experiments was a PTFE cylinder that was tightly packed with carbon paste. The geometric area of this electrode was 0.1256cm2. Electrical contact was made at the back by means of a bare carbon.

Procedure

The initial working procedure consisted of measuring the electrochemical response at NP-CPE at a fixed concentration of phenol. Standard solution of phenol was added into the electrochemical cell containing 100 mL of supporting electrolyte.

The mixture solution was kept for 20 s at open circuit and deoxygenated by bubbling pure nitrogen gas prior to each electrochemical measurement.

The cyclic voltammetry was recorded in the range from -1.8V to 1,8V.

Optimum conditions were established by measuring the peak currents in dependence on all parameters. The square wave voltammetry was recorded in the range from -1.8V to1.8V, for which the scan rate is 1 $mV.s^{-1}$, step potential 50 mv, amplitude 2 mV and duration 0.1 s. Optimum conditions were established by measuring the peak currents in dependence on all parameters. All experiments were carried out under ambient temperature. All experiments were carried out under ambient temperature.

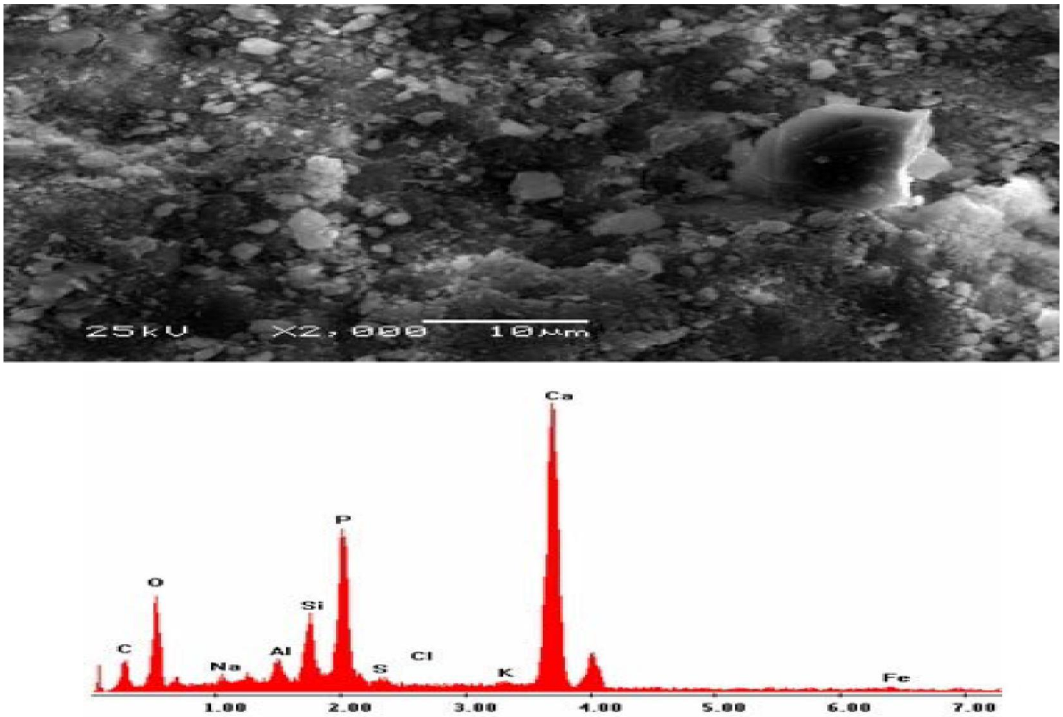


Figure 1 : Scanning electron micrograph of natural phosphate

RESULTS AND DISCUSSION

Surface characteristics

The surface structure of natural phosphate (NP) electrode was observed using scanning electron microscopy Figure 1.

Phenol oxidation

Cyclic voltammetry at a scan rate of 100mV/s was the electrochemical technique applied to study the oxidation behavior of phenol. Figure 2 shows the oxidation peak of the phosphate modified electrode paste appeared at approximately 1 V in a phenol concentration of 0.004 M. No reduction peak was observed. Scheme 1 shows the phenol undergone oxidation with the loss of one electron and hydrogen transfer. The presence of only anodic oxidation peak year, Suggests that the electrochemical process of phenol is totally irreversible.

Optimization of experimental conditions

Optimum conditions for the electrochemical response were established by measuring the peak current in dependence on all parameters.

Influence of accumulation time

The effect of the accumulation time is investigated Figure 3; this significantly affects the oxidation peak current of phenol. The peak current of 3 mmol L^{-1} phenol increases greatly within the first 3min. Further increase in accumulation time does not increase the amount of phenol at the electrode surface owing to surface saturation, and the peak current remains constant. This phenomenon is due to the cavity structure of phosphate-CPE that improves the ability of the electrode to adsorb electroactive phenol. Maybe this is attributed to the saturated adsorption of phenol on the NP-CPE surface. Taking account of sensitivity and efficiency, accumulation time was 4 min in the following experiments.

Effect of scan rate

The influences of scan rate on the oxidation peak potential (Ep) and, peak current (Ip) of phenol, (0.1M Na_2SO_4, pH=5) were studied by cyclic voltammetry. The Figure 4 shows both the anodic currents linearly increase with the scan rate over the range of 40 to 140mVs^{-1}, suggesting that the electron transfers for phenol at the phosphate modified CPE is adsorption controlled reaction. The Figure 5 shows the linear relationship between the scan rate anodic peak currents of phenol at NP/CPE.

Calibration graph

In order to obtain an analytical curve for the de-

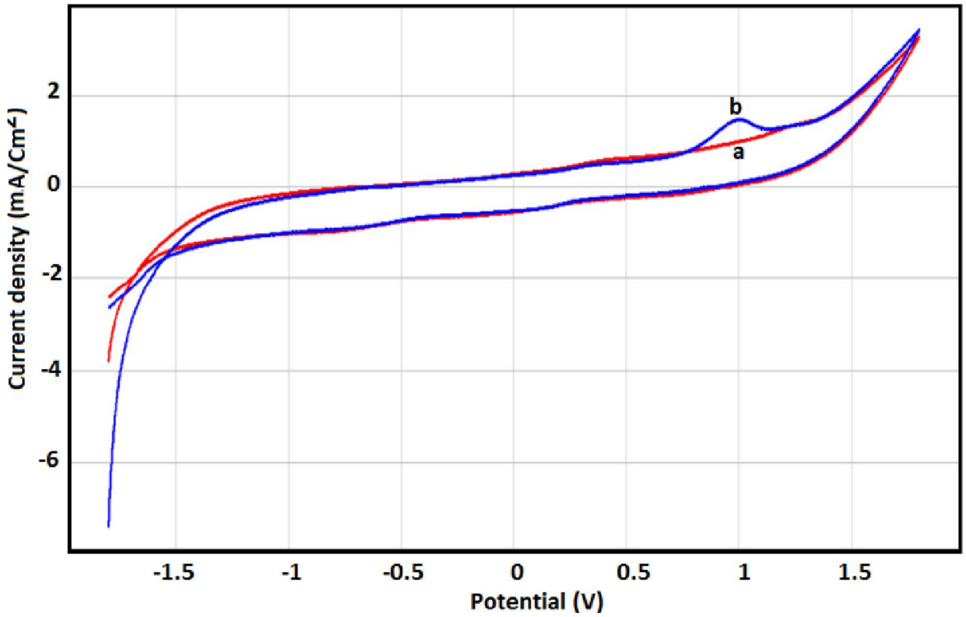
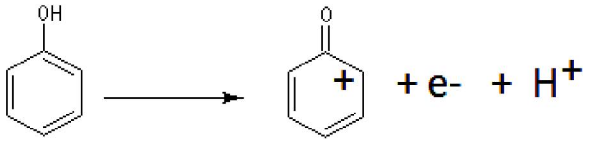


Figure 2 : CVs recorded for 4 mM phenol at pH=5 at bare NP-CPE (a) and NP-CPE/phenol (b), scan rate 100 mV/s, preconcentration time (tp)= 4min



Scheme 1 : mechanism of electrochemical oxidation reaction of phenol at NP/CPE

veloped sensor, we carried out cyclic voltammograms for oxidation an phenol at different concentrations in 0.1mol L^{-1} Na$_2$SO$_4$ (pH=5) at a sweep rate of 100mVs^{-1}.

Figure 6 shows the CV curves of different concentration of phenol at NP/CPE was increased from

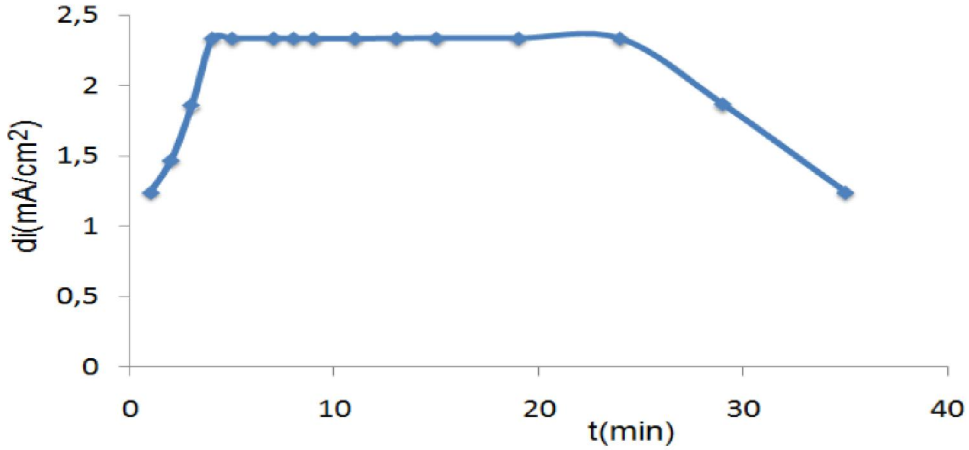


Figure 3 : Effects of accumulation time on oxidation peak currents of 3 mmol L^{-1} phenol (pH=5) at NP-CPE, supporting electrolyte is Na$_2$SO$_4$ 0.1M

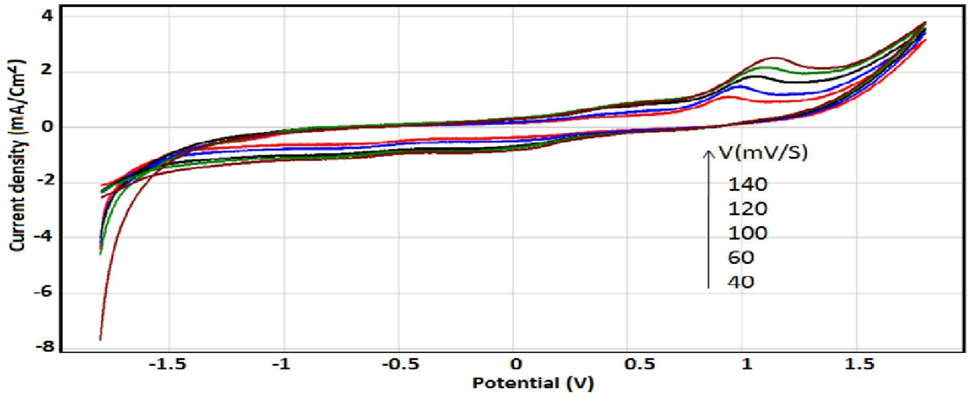


Figure 4 : CVs acquired on NP-CPE with 8 mM phenol in the buffer solution at different scan rates from 40 to 140mV.s^{-1}. Inset is the plot of the peak current of phenol versus scan rate

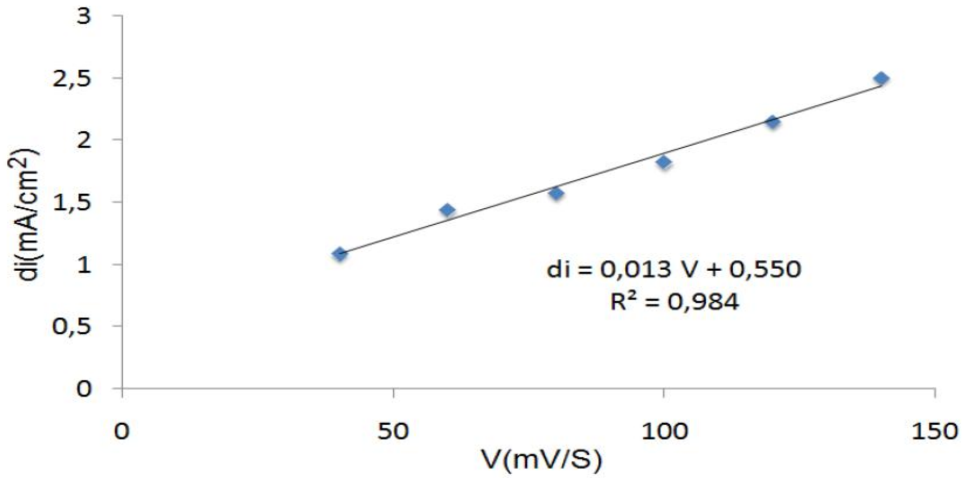


Figure 5 : Plot of peaks area versus scan rate

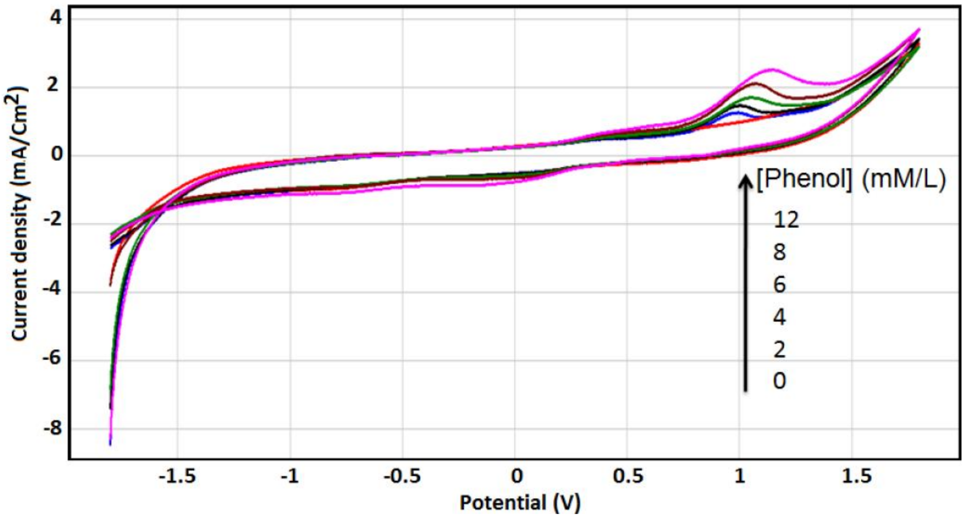


Figure 6 : Cyclic voltammograms of different concentration of phenol (2mM to 12mM) at NP/CPE in 0.1 M Na_2SO_4 PH=5, Scan rate 100 mV/s

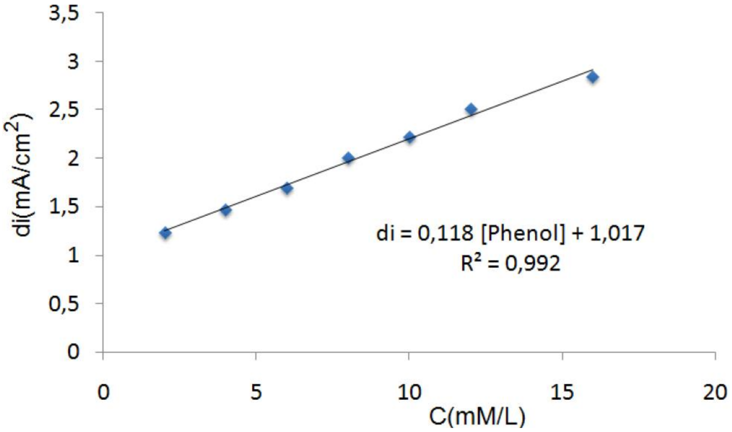


Figure 7 : Plot of peaks area versus added concentration of phenol

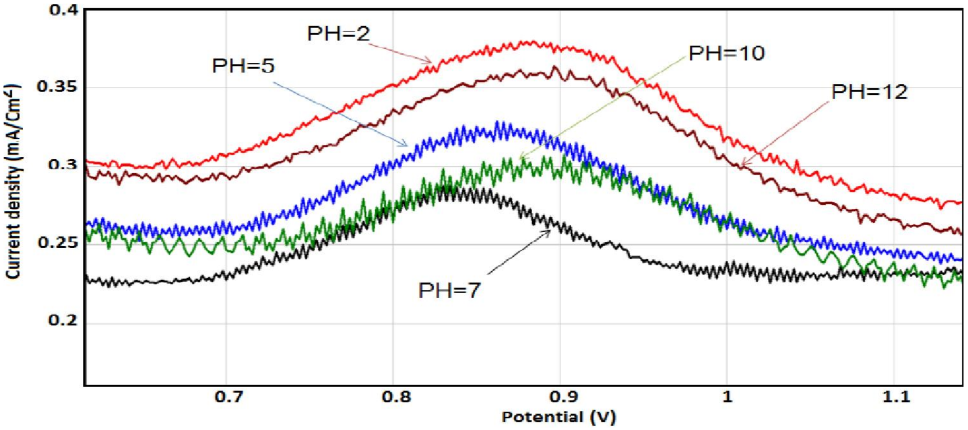


Figure 8 : Effect of pH on the oxidation of phenol at the phosphate modified CPE

2 mM to 12 mM. The anodic peak current increases linearly with the concentration of phenol and the plot of current versus concentration obeys Randles-Sevic equation, which implies that the electrode process is adsorption controlled reaction.

Influences of pH

The effect of varying pH on the current response of NP/CPE at constant phenol concentration (16 mM) is shown in Figures 8 and 9. As can be seen, the peak current, gradually reduce with the increase of pH and

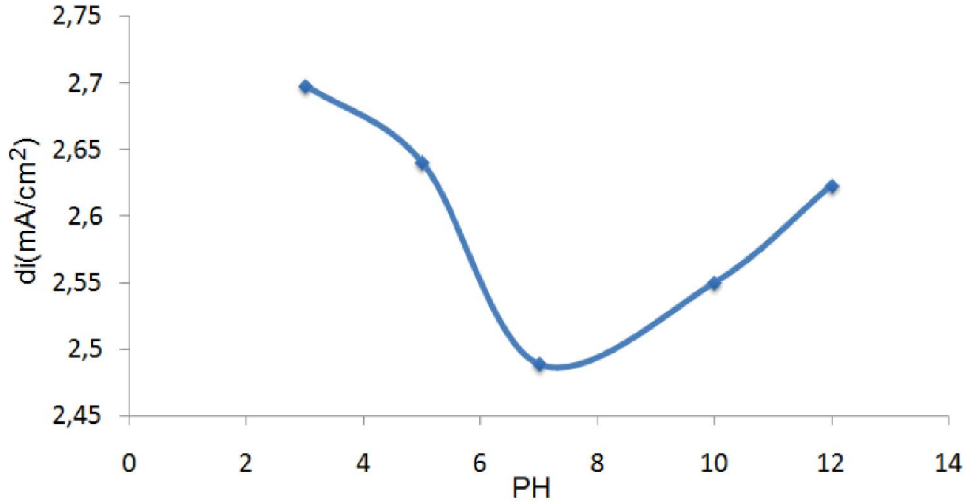


Figure 9 : Plot of the relationship between solution pH and the oxidation peak current

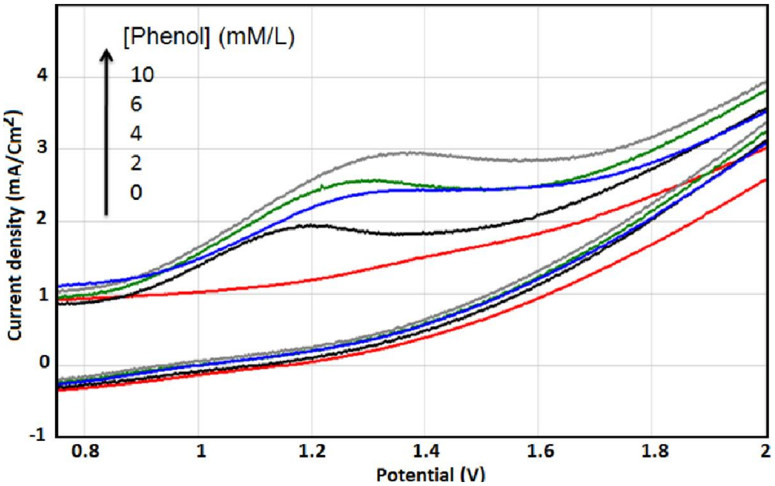


Figure 10 : Cyclic voltammograms of different concentration of phenol (2mM to 10mM) at NP/CPE in 100ml tap water, Scan rate 100 mV/s

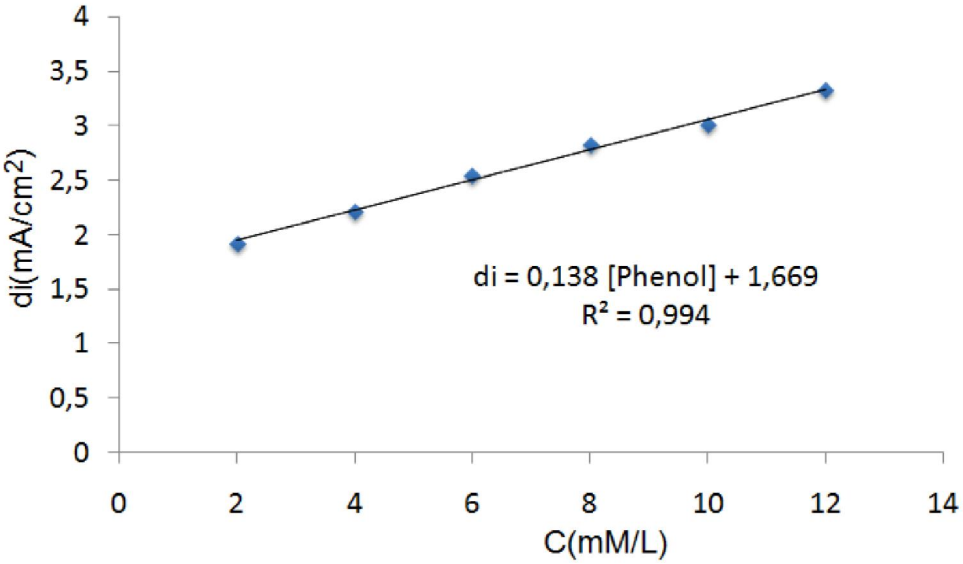


Figure 11 : Plot of peaks area versus added concentration of phenol

reach a minimum value when the pH is 7.0. Further increase in the solution pH yields a gradual increase in the phenol peak current.

PRACTICAL APPLICATION

In order to evaluate the performance of NP modified carbon paste electrode by practical analytical applications, the determination of phenol was carried out in tap water without any pretreatment. No phenol traces were found when the proposed procedure was used. The analytical curves were obtained by CV experiments in supporting electrode (Figure 9). It was founded that the peaks currents increase linearly versus phenol added into the tap water (Figure 10).

CONCLUSION

Cyclic voltammogram of phenol detection using phosphate modified carbon paste electrode showed an irreversible response. Phenol in solution was only oxidized and not reduced.

The fact that the modified electrode worked best at pH=3.

Since only the modified electrode was able to detect the presence of phenol, this lead to a conclusion that phosphate modified carbon paste provided a suitable surface for electron transfer. Due to contamination of electrolyzed component on the electrode surface, it is highly discouraged to reuse the electrode. Emphasis on environmental applications of this sensor can be expounded upon as an in-class exercise.

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