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Electrochemical investigation of 4-aminophenol at natural phosphate modified carbon paste electrode

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ABSTRACT

4-aminophenol is the main impurity present in preparations of paracetamol. Using the Cyclic voltammetry, the electrode behaviour of 4-aminophenol has been studied in 0.1 M Na₂SO₄ solutions at natural phosphate (NP) modified carbon paste electrode (CPE).

The optimal potential window of wide range from -1V to 1V was selected. The electron transfer kinetics of the NP-CPE in the detection of analyte was determined by the scan rate effect and concentration variation studies. The scan rate effect showed the electrode process is adsorption controlled. The oxidation peak currents represented a linear dependence on 4-aminophenol concentration from 0.45 mM to 2.29 mM with correlation coefficient $r^2=0.996$. The effect of cationic surfactant shows good high sensitivity and stability for the redox process of the 4-aminophenol.

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KEYWORDS

4-aminophenol;
Natural phosphate modified
carbon paste electrode;
Cyclic voltammetry.

INTRODUCTION

4-aminophenol has highly toxic and mutagenic effects and induces DNA cleavage in mouse and human lymphoma cells^[1,2]. Aminophenols are interesting electrochemical materials^[3,4,6]. This is because, unlike aniline^[7] and other substituted anilines^[8], they have two oxidizable groups (NH₂ and OH) providing more reactive sites. Therefore, in principle, they could show electrochemical behavior resembling anilines^[9] and phenols^[10]. This compound is an intermediate in the degradation of azo dyes^[11]. However, little is known

about the metabolism of 4-aminophenol by bacteria^[12]. 3-Nitrophenol-grown cells of *Ralstonia eutropha* JMP 134 convert nitrobenzene to hydroxylaminobenzene, 2-aminophenol and 4-aminophenol^[13]. Hydroxylaminobenzene is transformed by 3-nitrophenol-grown cells of *Pseudomonas putida* 2NP8 to 1, 4-benzenediol via 4-aminophenol^[14]. A number of reports indicated that 4-aminophenol might be a key intermediate in the biodegradation of nitrobenzenes and amines^[11,14]. 4-aminophenol is a well-known compound that has been used as a redox agent in photography^[6]. In neutral media, it is oxidized to a complex oligomeric dye that can

be used in enzymatic assays^[15].

Voltammetric studies^[16] showed that the first step of the oxidation of 4-aminophenol in organic and aqueous media on gold electrodes probably results in the uptake of one electron, producing an intermediate oxidation product (semiquinoneimine) in agreement with the literature^[17,18]. Heras et al.^[18] studied the electrochemical oxidation of 4-aminophenol on a mercury electrode in aqueous medium. They indicated that the electrooxidation of 4-aminophenol occurs by the loss of one proton and one electron. The next step is the loss of another electron and of a second proton to yield p-quinoneimine that is hydrolyzed to p-benzoquinone. Investigations of the modification of platinum^[19-21], graphite^[4,25,26] and gold^[22] by polymers derived from 4-aminophenol have been carried out. Graphite electrodes coated with poly (4-aminophenol) are efficient for the immobilization of purine bases^[4]. In the present work, it describes the electrochemical investigation of 4-aminophenol at Phosphate Modified Carbon Paste Electrode. Many of the analytes have been detected by cyclic voltammetric technique by our research group^[23,24]. The aim of the work reported here was to investigate the electrochemical properties of 4-aminophenol on Natural phosphate modified carbon paste electrode as well as the electrochemical characterization of electrodes by cyclic voltammetric technique. It can be applied to routine investigations of pharmaceutical preparations in the form of tablets by using the cyclic voltammetric technique.

EXPERIMENTAL

Instrument

Cyclic voltammetry were carried out with 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).

The electrochemical cell was configured to work with three electrodes; using NP-CPE as the working, platinum plate for counter and saturated Calomel (SCE) as reference electrodes. The pH-meter (Radiometer Copenhagen, PHM210, Tacussel and French) was used for adjusting pH values.

Procedure

The initial working procedure consisted of measuring the electrochemical response at NP-CPE at a fixed concentration of 4-Aminophénol. Standard solution of 4-Aminophénol 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 -1.0 V to 1 V.

Optimum conditions were established by measuring the peak currents in dependence on all parameters. All experiments were carried out under ambient temperature.

Electrodes

Modified electrodes were prepared by mixing a carbon powder and the desired weight of natural phosphate. 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.

RESULTS AND DISCUSSION

Surface characteristics

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

Preliminary voltammetric characterization

Preliminary voltammetric characterization the performance of the newly developed phosphate modified carbon paste electrode is based on the preconcentration of 4-Aminophenol from aqueous solution onto the surface of the modified electrode by adsorption onto the modifier surfaces.

The probable electrochemical reactions of 4-aminophenol has shown in the scheme 1

Figure 2 Shows a cyclic voltammograms (CV) in the potential range -1 V to 1 V recorded, respectively, for carbon paste and phosphate modified carbon paste electrode at 100 mV.s⁻¹. The voltammograms take

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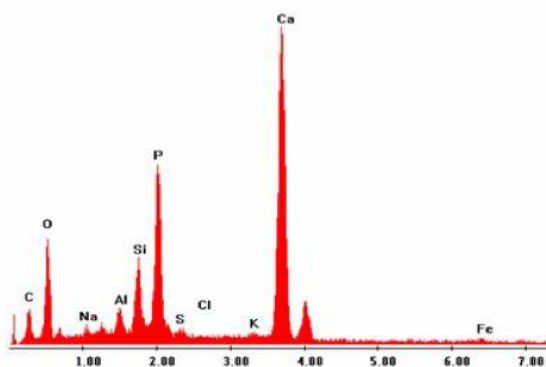
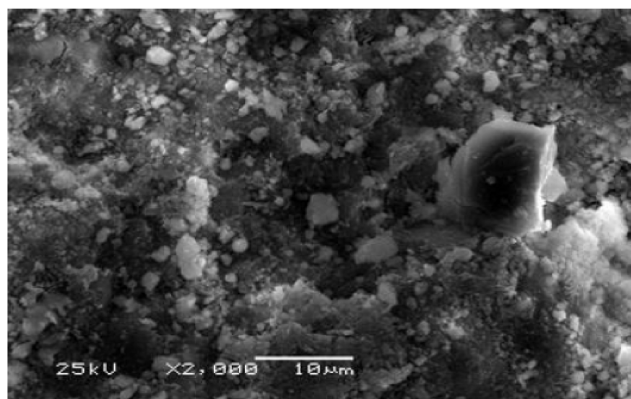
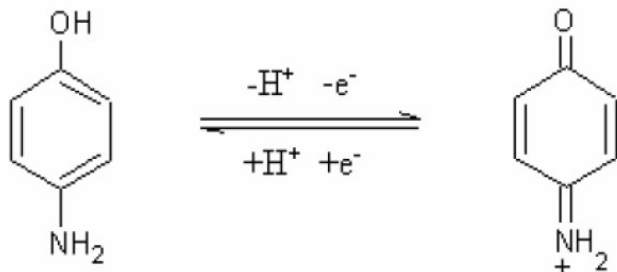


Figure 1 : Scanning electron microscopy for Natural Phosphate



Scheme 1 : Mechanism of electrochemical redox reaction of 4-aminophenol at NP-CPE

different forms. No peak is observed in the case of NP-CPE, it is recognized that carbon surface was effectively modified by phosphate.

A CV was used to investigate the electrochemical behaviour of 4-Aminophenol on a NP-CPE in the buffer solution $0.1 \text{ M Na}_2\text{SO}_4$ ($\text{pH}=7$) at scan rate of $100 \text{ mV}\cdot\text{s}^{-1}$. The figure 3 shows, 4-Aminophenol exhibits a pair of redox waves on the NP-CPE with E_{pa} (anodic peak potential) $= -69.3 \text{ mV}$ and E_{pc} (cathodic peak potential) $= -208 \text{ mV}$.

Influence of accumulation time

The dependence of peak current on the

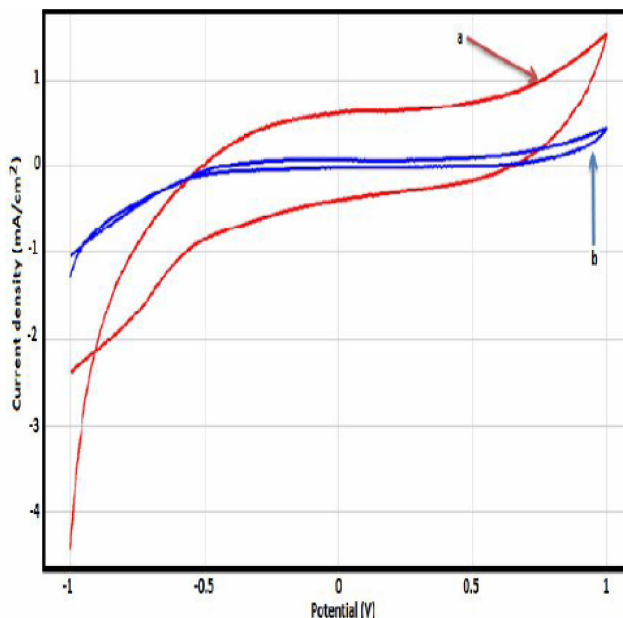


Figure 2 : Cyclic voltammograms recorded for bare CPE (a) and NP-CPE (b), in $0.1 \text{ M Na}_2\text{SO}_4$ at 100 mV/s

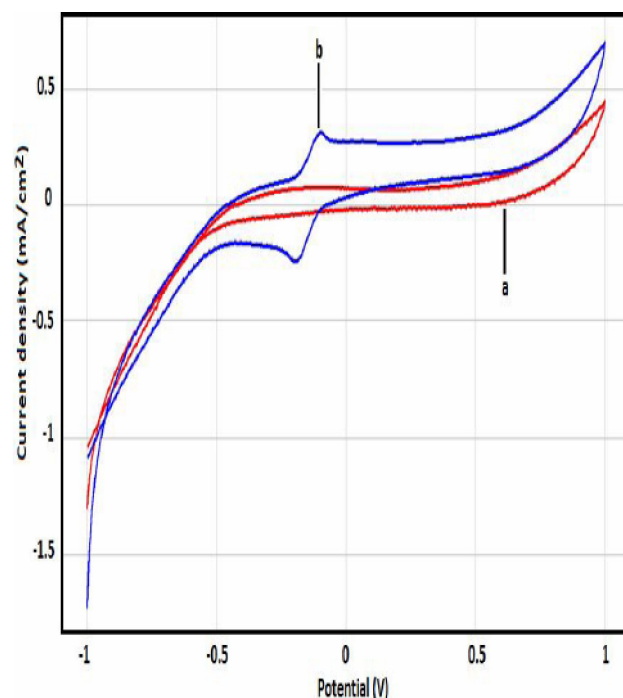


Figure 3 : CVs recorded for 0.45 mM 4-Aminophenol at $\text{pH} 7$ at bare NP-CPE (a) and NP-CPE/4-Aminophenol (b), scan rate 100 mV/s

preconcentration time for 0.91 mmol L^{-1}

4-Aminophenol was also investigated (Figure 4). The peak current increases with the increasing in the preconcentration time between 0 and 45 min above which it became nearly constant due to the surface saturation. Hence, a 10 min preconcentration time was used

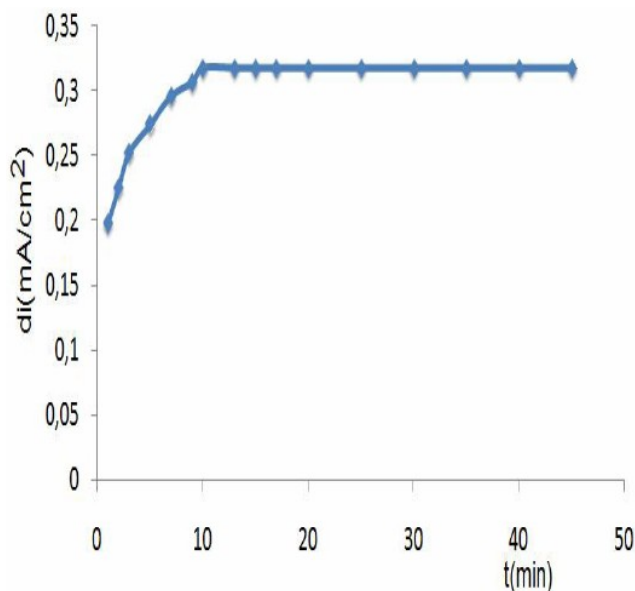


Figure 4 : Effects of accumulation time on 4-Aminophenol oxidation peak currents

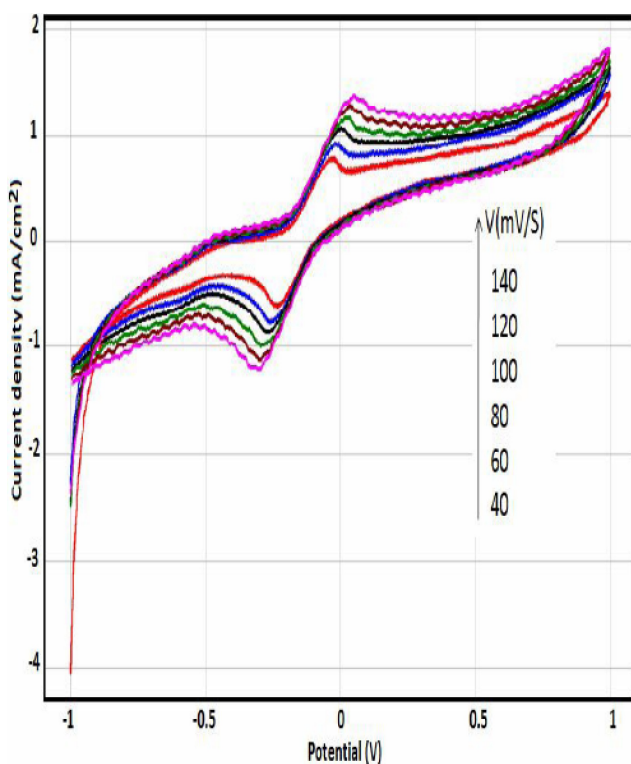


Figure 5 : CVs acquired on NP-CPE with 1.83 mM 4-Aminophenol in the buffer solution at different scan rates from 40 to 140 mV.s⁻¹. Inset is the plot of the peak current of 4-Aminophenol versus scan rate

in all subsequent experiments.

Effect of scan rate

The effect of scan rate on the redox of 4-aminophenol was examined in 0.1 M Na₂SO₄ buffer

solution of pH7 as a supporting electrode. The figure 5 shows both the anodic and the cathodic peak currents linearly increase with the scan rate over the range of 40 to 140 mV.s⁻¹, suggesting that the electron transfers for 4-aminophenol at the phosphate modified CPE is adsorption controlled reaction. The cathodic peak shifted towards negative potential with increased in scan rate, the anodic peak shifted towards positive potential with increased in scan rate. The Figure 6 shows the linear

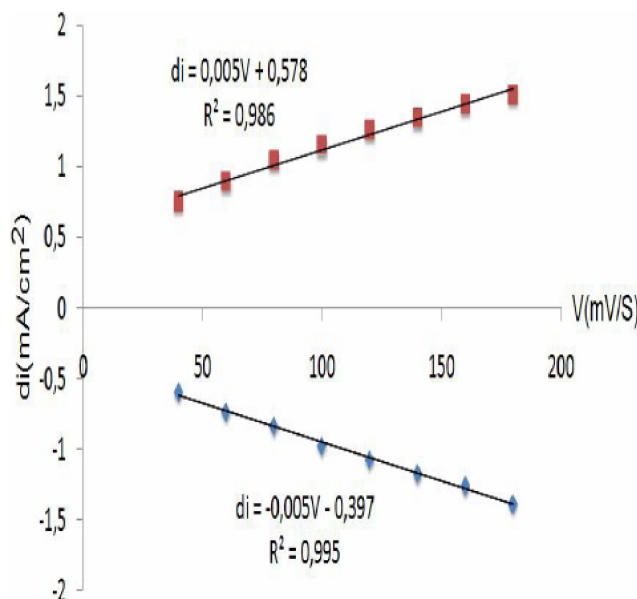


Figure 6 : Plot of peaks area versus scan rate

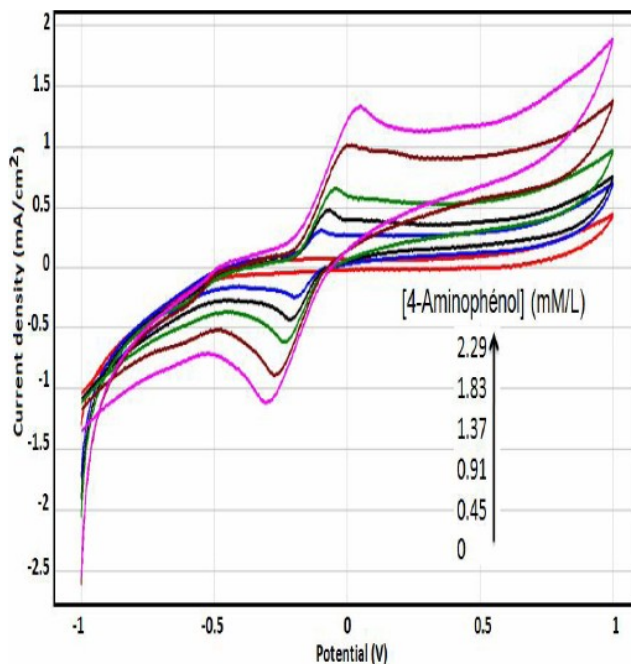


Figure 7 : Cyclic Voltammograms of different concentration of 4-aminophenol (0.45mM to 2.29mM) at NP-CPE in 0.1 M Na₂SO₄, Scan rate 100 mV/s

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relationship between the scan rate anodic peak and cathodic peak currents of 4-amino phenol at NP-CPE.

Effect of concentration of 4-aminophenol

Figure 7 shows the CV curves of different concentration of 4-aminophenol at NP/CPE was increased from 0.45 mM to 2.29 mM in 0.1 M Na_2SO_4 buffer solution at pH=7 at a sweep rate of 100 mVs^{-1} . Both the anodic and cathodic peak current increases linearly with the concentration of 4-aminophenol and the plot of current versus concentration obeys Randles-Sevcik equation, which implies that the electrode process is adsorption controlled reaction. It was also observed that

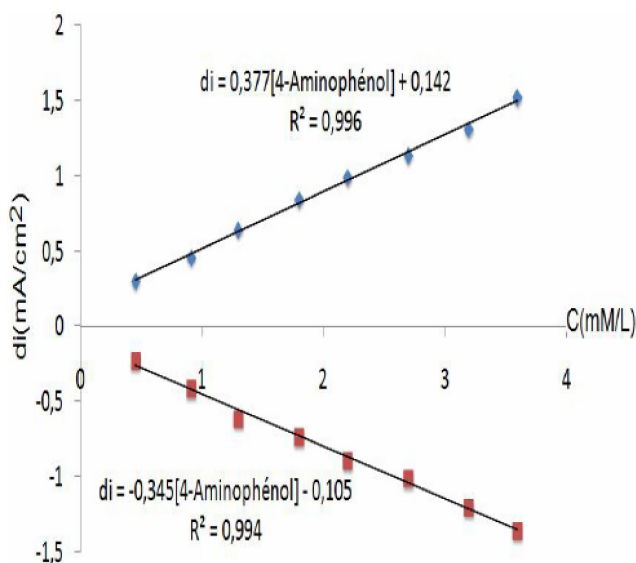


Figure 8 : Plot of peaks area versus added concentration of 4-Aminophénol

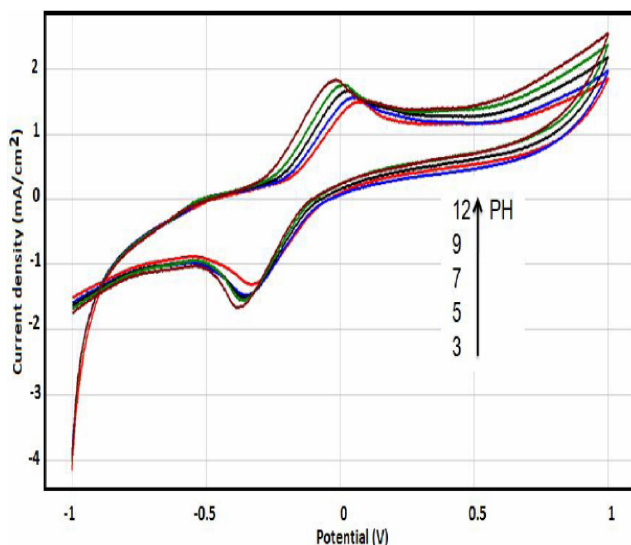


Figure 9 : Effect of pH on the oxidation and the reduction of 4-aminophénol at the NP modified CPE

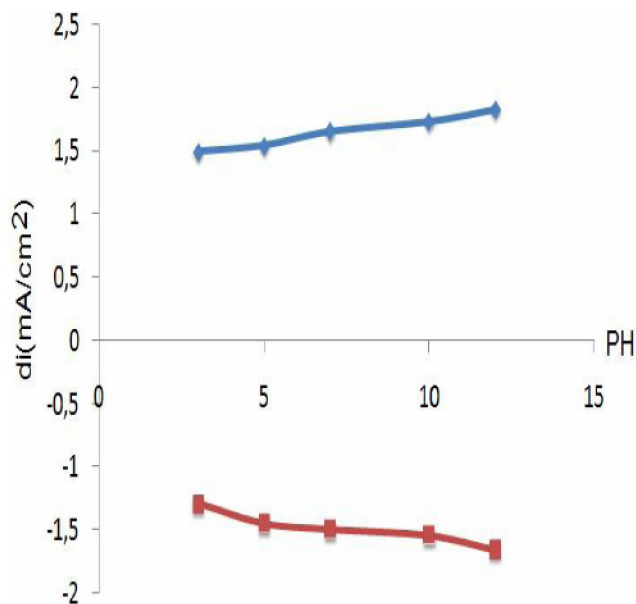


Figure 10 : Plot of the relationship between solution pH and the oxidation and reduction peak current

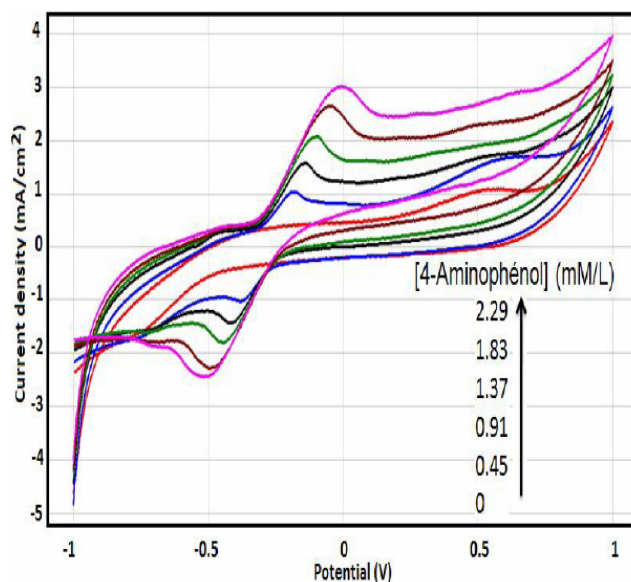


Figure 11 : Cyclic Voltammograms of different concentration of 4-aminophénol (0.45mM to 2.29mM) at NP-CPE in 100ml tap water, Scan rate 100 mV/s

the cathodic peak potential shift towards negative values and anodic peak potential shift towards positive side. This kind of shift in E_p in the cathodic and anodic direction with increasing concentration of the 4-aminophenol indicates that the product of 4-aminophenol molecules are adsorbed over the electrode surface.

Effect of pH variation of buffer solution

In most cases, the solution pH is important to the electrochemical reaction. The pH was varied in the range

from 3 to 12. The Figure 9 shows the cyclic voltammograms of the 4-aminophenol at different pH. The anodic peak potential shifted towards positive side and cathodic peak potential Epc shifted towards more negative potential. The anodic and cathodic peak current of 4-aminophenol increased at pH= 7. The figure 10 shows the graph of different pH versus peak current, it could be confirmed that at pH 12 the electrode acts as a good sensor.

ANALYTICAL APPLICATION

In order to evaluate the performance of the analytical methodology described above, the determination of 4-Aminophenol at NP-CPE was carried out in tap water. The analytical curves were obtained by CV experiments in supporting electrode (Figure 11). It was founded that the peaks currents increase linearly versus 4-Aminophenol added into the tap water (Figure 12).

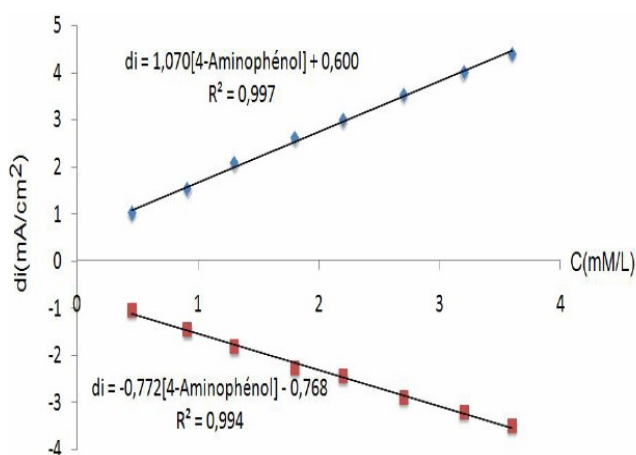


Figure 12 : Plot of peaks area versus added concentration of 4-Aminophénol

CONCLUSION

We have demonstrated the use of phosphate-modified carbon paste electrode for a greatly cyclic voltammetry sensing of 4-Aminophenol compounds. The modified electrode increased the amplitude of the current signal of 4-aminophenol and produced good response.

The oxidation of this compound on the modified electrode occurs in an reversible manner. The modified electrode was successfully applied in tap water samples.

The method could be improved in a simple way without introducing additional procedures and without increasing the time required for 4-aminophenol quantification. The electrode construction was extremely simple and with low cost. No unstable or toxic reagents were used.

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