

Electrochemical determination of p-Aminophenol at clay modified carbon paste electrode: Application in water samples

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ABSTRACT

The behavior of a modified carbon paste electrode (CPE) for p-aminophenol detection by cyclic voltammetry (CV) was studied. The electrode was built by incorporating the clay to carbon paste. The overall analysis involved a two-step procedure: an accumulation step at open circuit, followed by medium exchange to a pure electrolyte solution for the voltammetric quantification. During the preconcentration step, para-aminophenol was adsorbed onto clay surface. The influence of various experimental parameters on the Clay-CPE response was investigated. © 2014 Trade Science Inc. - INDIA

KEYWORDS

p-aminophenol;
Clay modified carbon paste
electrode;
Cyclic voltammetry.

INTRODUCTION

Aminophenols are interesting electrochemical materials since, unlike aniline^[1] and other substituted anilines^[2], they have two groups ($-NH_2$ and OH), which could be oxidized. Therefore, they could show electrochemical behavior resembling anilines^[1-3] and/or phenols^[4,5]. An important factor would be the relative position of the amino and hydroxyl group in the aromatic ring. Accordingly, the reported electrochemical properties of the three positional isomers (ortho, meta and para) are strongly different. P-Aminophenol (p-AP) is a well-known compound which, in its simple form, or derivative^[6], has been used as redox agent in photography. In neutral media, it is oxidized to complex oligomeric dyes that could be used in enzymatic assays^[7]. Konopelnik et al.^[8] have studied the oxidation of m-aminophenol (m-AP) in aqueous solution on SnO_2 electrodes. According with these authors, only the amino group of m-aminophenol undergoes oxidation while the

hydroxyl group remains unchanged. Common laboratory-based analytical methods for determining para-aminophenol compounds such as primarily gas and liquid chromatography (HPLC)^[9-13], UV-vis spectrophotometry^[14,15] and spectrofluorimetry^[16] have been reported. The use of enzyme-linked immunosorbent assay (ELISA) has been studied^[17]. However, some sample pretreatment involving separation, extraction and/or adsorption is generally necessary, and this can also be time-consuming and complex. Electrochemical methods, such as differential pulse polarography (DPP), anodic stripping voltammetry (ASV) and differential pulse voltammetry (DPV), have been widely applied for the determination of pharmaceuticals, dyes, insecticides and pesticides^[18-20]. In recent years, chemically modified electrodes (CMEs) were used for the voltammetric quantification of various organic and inorganic species after their open circuit accumulation^[21,22]. Much of the work in this field was directed to exploit the chemical reactivity of the

modifier towards a target analyte for electroanalytical purpose. Multitudes of modifying agents were used either as coatings on solid electrode surfaces or dispersed within a conductive matrix. It is noteworthy that this last approach is well suited when using electronically insulating modifiers requiring a direct contact to an electronically conducting substrate as used in connection with electrochemistry. The application of silicates and related mineral materials in electrochemistry is rather recent and was directed to combine their intrinsic properties to selected electrochemical reactions in order to improve the response of the electrode. Modified electrodes are being used frequently in the voltammetric determination of organic compounds because of their efficiency, the selectivity that can be obtained by varying the modifier and the sensitivity which is equivalent to that reached in anodic and cathodic stripping. In doing so, zeolite and silica-modified electrodes were prepared, characterized and applied (sometimes tentatively) in various fields including for example electroanalysis and sensors, electrocatalysis, photochemistry, thin-film technology, fuel cells, molecular recognition. Kauffmann^[23] has reported that a carbon paste electrode (CPE) modified with lipids and proteins (enzymes) have potential application in environmental analysis. Recent works, reported in the literature, have shown several applications and electroanalytical methodologies employing glassy carbon electrode as working electrodes^[24,25]. Luz et al.^[25] constructed a glassy carbon electrode impregnated with a lithium tetracyanoethylene (LiTCNE) for the determination of para-aminophenol. The oxidation and reduction of this compound has been carried out on a modified glassy carbon electrode using cyclic and DPV^[26-28]. This study proposed a new modified carbon paste electrode which has been prepared by the clay (HAP) for para-aminophenol detection. It has shown a selective preconcentration and quantization of para-aminophenol by cyclic voltammetry (CV). This study has led to the development of a new modified electrode for the determination of para-aminophenol with improved qualities such as simplicity of electrode preparation, wider linear range, and low detection limit (DL), high selectivity and very good stability of modifier. The procedure is based on the oxidation and reduction of para-aminophenol after it was preconcentrated on a carbon paste electrode modified with the clay, under

open circuit conditions.

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 electrodes 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 clay. 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

Clay-CPE, at a fixed concentration of p-Aminophenol. Standard solution of p-Aminophenol 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.

RESULTS AND DISCUSSION

Surface characteristics

The morphology of the electrode surface of Clay

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was observed by scanning electron microscopy (Figure 1). We find that the matrix is formed by compact particles fractions between 1 and 15 μm . Clay treaty has the following chemical composition given by transmission electron microscopy (TEM): O (22%), Mg (5.4%), Al (22.4%), K (2.7%), Ca (1%), Ti (1.8%) Fe (17.1%), Si (27.8%) and more metals order ppm (Figure 2). An examination of clay modified carbon paste electrode indicates some kind of agglomeration.

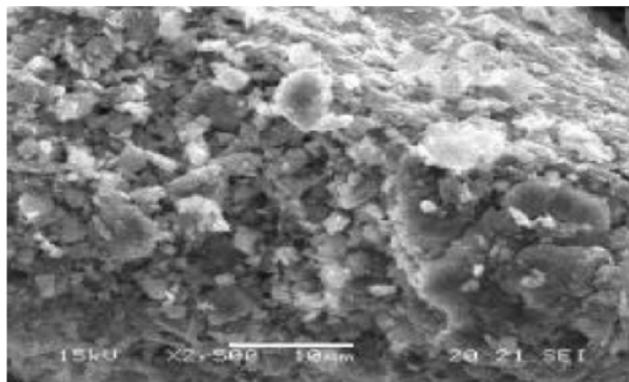


Figure 1: Scanning electron micrograph of Clay paste electrode

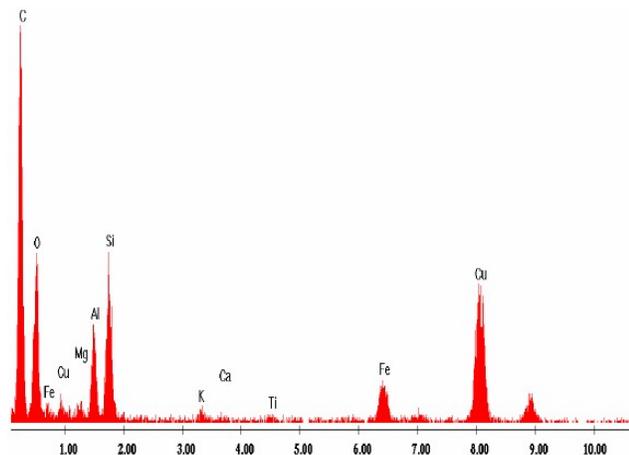


Figure 2: Chemical composition treated clay

p-Aminophenol oxidation-reduction

P-Aminophenol was studied at Clay/CPE by cyclic voltammetry study. Figure 3 shows the cyclic voltammogram of p-amino phenol which exhibited good anodic peak and a cathodic peak current at 16.79 mV and -283 mV respectively. Due to the electrostatic interaction between the positive charged p-aminophenol and the Clay/CPE increases the peak current which results in the good sensitivity. Scheme shows the p-aminophenol undergone oxidation with the loss of one electron and hydrogen transfer and it undergoes

reduction with addition of two electrons to the oxidised product of p-aminophenol. The current sensitivity may be due to the electrostatic repulsion between the quinone moiety of the p-aminophenol and the positively charged Clay modified carbon paste electrode. Electron-withdrawing groups accelerate reduction whereas electron donating groups lowers reduction.

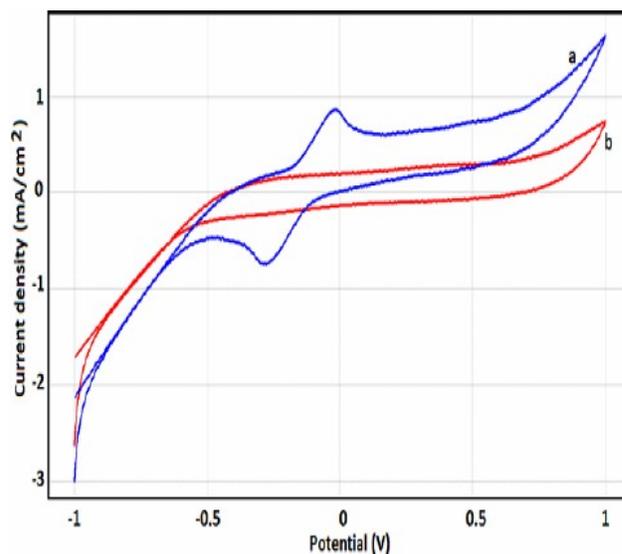
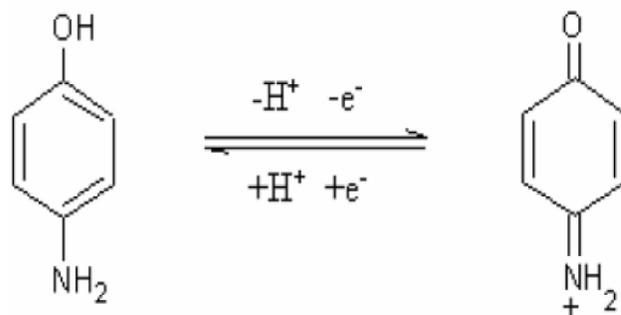


Figure 3: CVs recorded for 0.45 mM p-aminophenol at pH 7 at bare Clay-CPE/p-aminophenol, (a) and Clay-CPE (b), scan rate 100 mV/s, preconcentration time (tp) =13min



Scheme 1: mechanism of electrochemical redox reaction of p-aminophenol at Clay-CPE

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 4); this significantly affects the oxidation peak current of p-aminophenol. The peak current of 0.9 mmol L⁻¹ p-aminophenol increases greatly within the first

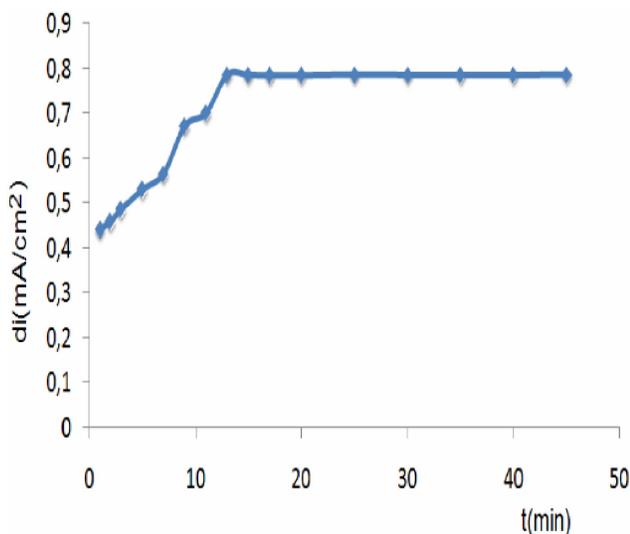


Figure 4: Effects of accumulation time on oxidation peak currents of 0.9 mmol L^{-1} P-aminophenol (pH= 7) at Clay-CPE, supporting electrolyte is Na_2SO_4 0.1M

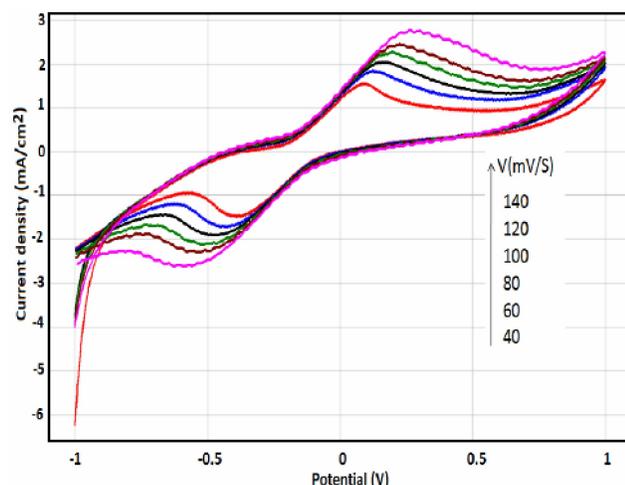


Figure 5: CVs acquired on Clay-CPE with 1.83 mM p-aminophenol in the buffer solution at different scan rates, from 40 to 140 mV.s^{-1} . Inset is the plot of the peak current of p-aminophenol versus scan rate

13 min . Further increase in accumulation time does not increase the amount of p-aminophenol at the electrode surface owing to surface saturation, and the peak current remains constant. This phenomenon is due to the cavity structure of clay-CPE that improves the ability of the electrode to adsorb electroactive p-aminophenol. Maybe this is attributed to the saturated adsorption of p-aminophenol on the Clay-CPE surface. Taking account of sensitivity and efficiency, accumulation time was 13 min in the following experiments.

Effect of scan rate

The influences of scan rate on the oxidation peak

potential (E_p) and, peak current (I_p) and the reduction peak potential (E_c) and, peak current (I_c) of p-aminophenol, ($0.1\text{M Na}_2\text{SO}_4$, pH=7) were studied by cyclic voltammetry. 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 mVs^{-1} , suggesting that the electron transfers for p-aminophenol at the clay 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 relationship between the scan rate anodic peak and cathodic peak currents of p-aminophenol at Clay-CPE.

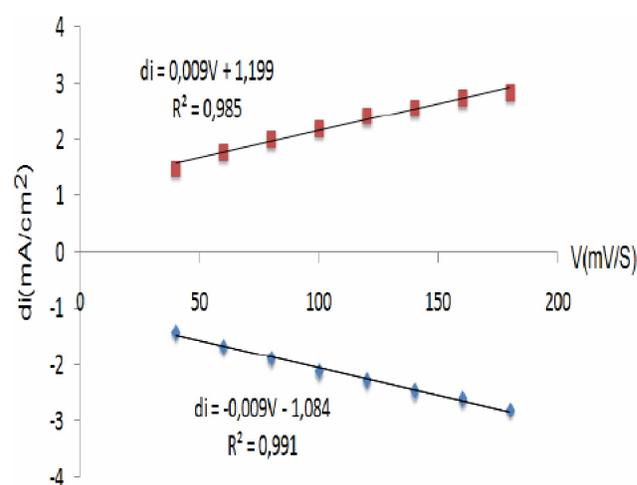


Figure 6 : Plot of peaks area versus scan rate

Calibration graph

In order to obtain an analytical curve for the developed sensor, we carried out cyclic voltammograms for p-aminophenol oxidation and reduction at different concentrations, in $0.1\text{M Na}_2\text{SO}_4$ (pH 7), the sweep rate was fixed at 100 mVs^{-1} .

Figure 7 shows the CV curves recorded, for different concentrations of p-aminophenol, at Clay-CPE was increased from 0.45 mM to 2.29 mM . Both the anodic and cathodic peak current increases linearly with the concentration of p-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 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

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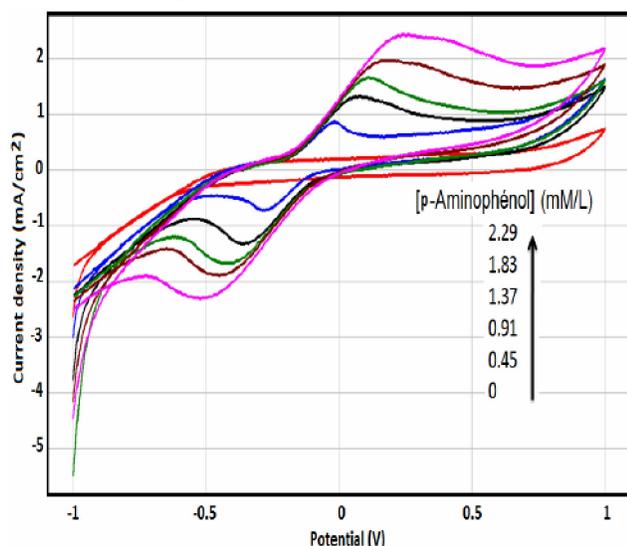


Figure 7 : Cyclic Voltammogram of different concentration of p-aminophenol (0.45mM to 2.29mM) at Clay-CPE in 0.1 M Na_2SO_4 , Scan rate 100 mV/s

direction with increasing concentration of the p-aminophenol indicates that the product of p-aminophenol molecules is adsorbed over the electrode surface.

Influences of pH

In a first step, the effect of pH on electrode response was investigated. In most cases, the solution pH is important to the electrochemical reaction. Figure 9 shows the cyclic voltammogram of the p-aminophenol at different pH. The current of the peak depend on the solution pH. The anodic peak potential shifted towards positive side and cathodic peak potential E_{pc} shifted towards more negative potential. The anodic and

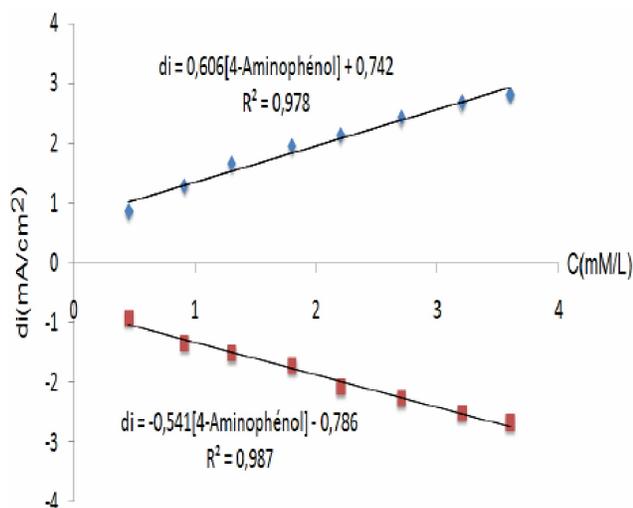


Figure 8: Plot of peaks area versus added concentration of p-Aminophenol

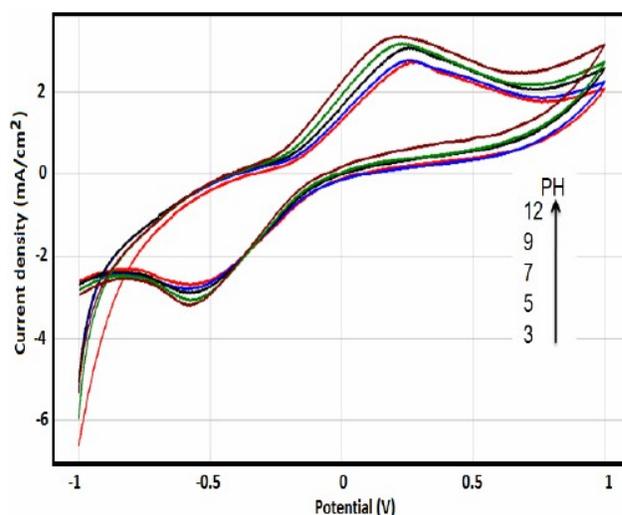


Figure 9: Effect of pH on the oxidation and the reduction of p-aminophenol at the Clay modified CPE

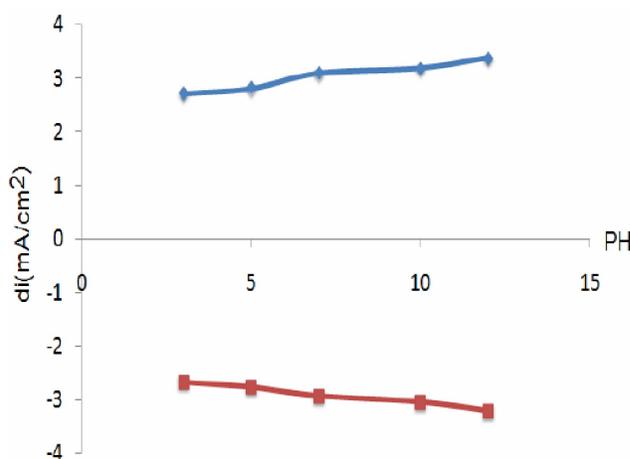


Figure 10: Plot of the relationship between solution pH and the oxidation and reduction peak Current

cathodic peak current of p-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.

PRACTICAL APPLICATION

In order to evaluate the performance of Clay-modified carbon paste electrode by practical analytical applications, the determination of p-aminophenol was carried out in tap water without any pretreatment. No p-aminophenol traces were found when the proposed procedure was used. The analytical curves were obtained by CV experiments in supporting electrode (Figure 11). It was founded that the peaks currents increase linearly versus

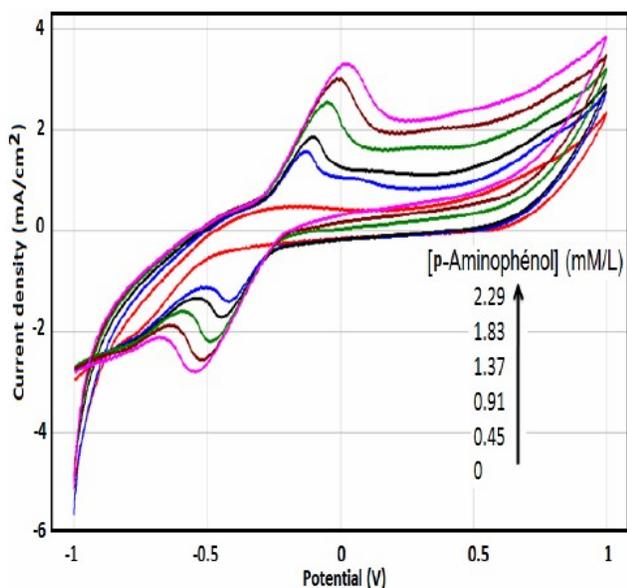


Figure 11: Cyclic Voltammograms of different concentration of p-aminophenol (0.45mM to 2.29mM) at Clay-CPE in 100ml tap water, Scan rate 100 mV/s

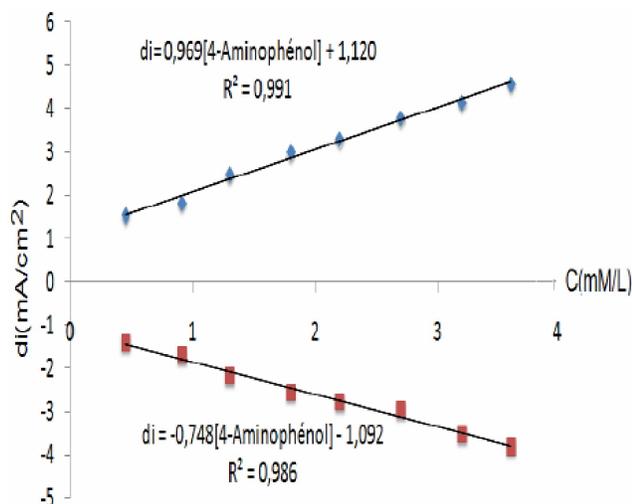


Figure 12: Plot of peaks area versus added concentration of p-Aminophenol

p-Aminophenol added into the tap water (Figure 12).

CONCLUSION

Electroanalytical techniques require only very small sample volumes. In this work, electrochemical behavior of p-aminophenol was evaluated using the voltammetric measurements. A novel method is described for the determination of p-aminophenol which is simple, quick and sensitive with a low cost of analysis.

The modifier is not soluble in water, non-toxic, and

not a pollutant.

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