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Electroanalysis of ascorbic acid (vitamin C) using a Clay modified carbon paste

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ABSTRACT

Ascorbic acid (Vitamin C) is a water soluble organic compound that participates in many biological processes. This paper reports the synthesis of Clay modified carbon paste electrode and its application for the electrochemical detection of ascorbic acid (AA). The influence of variables such the concentration of ascorbic acid adsorbed onto Clay, and the pH of solution were tested. The capacity of prepared electrode (Clay-CPE) for selective detection of AA was confirmed in a sufficient amount of ascorbic acid. The observed linear range for the determination of AA concentration was from 1.13 mM to 5.68 mM.

KEYWORDS

Ascorbic acid;
Carbon paste electrode;
Cyclic voltammetry;
Electrochemical detection.

INTRODUCTION

Ascorbic acid AA (vitamin C) is a water soluble organic compound involved in many biological processes. AA is used in large scale as an antioxidant in food, animal feed, beverages, pharmaceutical formulations and cosmetic applications. It is also important in helping to produce collagen, a protein needed in the development and maintenance of bones, cartilage, joint limings, skin, teeth, gums and blood vessels[1-3]. Due to the above importance of AA, its determination in their solution is more important. Many analytical techniques including sensors and biosensors[4 – 6] have been suggested for a detection of ascorbic acid in very varied types of samples. Other methods, based on the most commontly employed physico-chemical methods for identification of AA such high performance liquid chromatography[7-9] or capillary electrophoresis[10-13]. Investigations aimed at the development of modern analytical techniques for AA determination are directed towards increasing their sensitivity, specificity, simplicity and rapidity[14-17]. Electrochemical detection is an attractive alternative method for detection of electroactive species, because of its inherent advantages of simplicity, ease of miniaturization, high sensitivity and relatively low cost. In this paper, we describe the electrochemical analysis of ascorbic acid on a clay modified carbon paste electrode. The electrochemical characterization of adsorbed electroactive AA was evaluated using cyclic voltammetric (CV) and Electronic Impedance Spectroscopy (EIS) analysis.

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 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 0.1256cm^2. 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 AA. Standard solution of AA 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 -0.6 V to 1,5 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 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 trans-

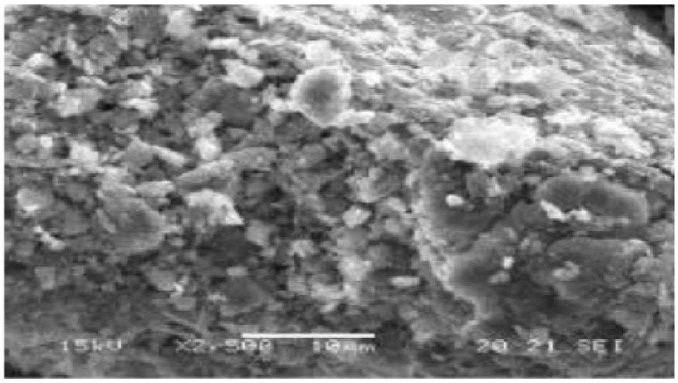


Figure 1 : Scanning electron micrograph of Clay paste electrode

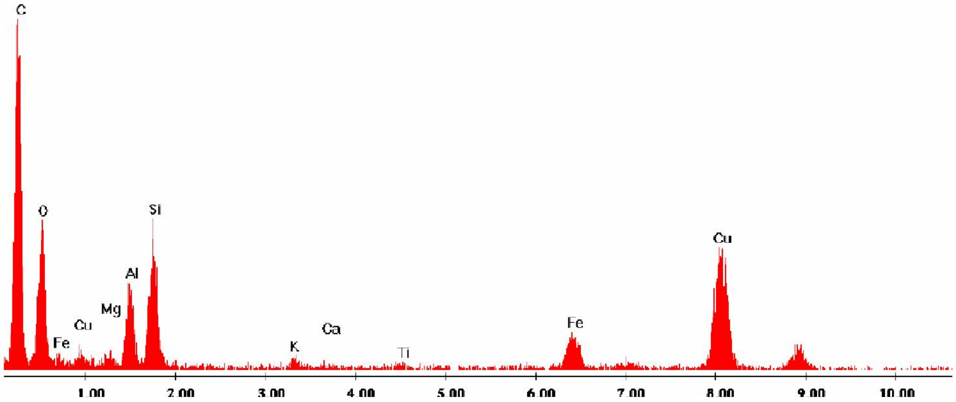


Figure 2 : Chemical composition treated clay

mission 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.

Electrochemical detection of ascorbic acid

Figure 3 shows a cyclic voltammograms (CV) in the potential range -0.6 V to 1.5 V recorded, respectively, for carbon paste and clay modified carbon paste electrode at 100 mV.s^{-1}. The voltammograms take different forms. No peak is observed in the case of Clay-CPE, it is recognized that carbon surface was effectively modified by clay.

The voltammograms of the Na2SO4 buffer as well as 2.27mM ascorbic acid in the buffer are shown as I and II in Figure 4. No anodic peak current was observed in the voltammogram of the buffer but was observed at 0.42V in the 2.27 mM ascorbic acid solution in the buffer as shown in II of Figure 4. No cathodic peak current was found indicating an irreversible heterogenous charge transfer in this system[18].

The scheme shows the oxidation of L-ascorbate to dehydro-L-ascorbic acid involves the transfer of two electrons and one proton[19,20].

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

Figure 5 shows the effect of the accumulation time; this significantly affects the oxidation peak current of AA. The peak current of 2.27 mmol L$^{”1}$ AA increases greatly within the first 6min. Further increase in accumulation time does not increase the amount of AA at the electrode surface owing to surface

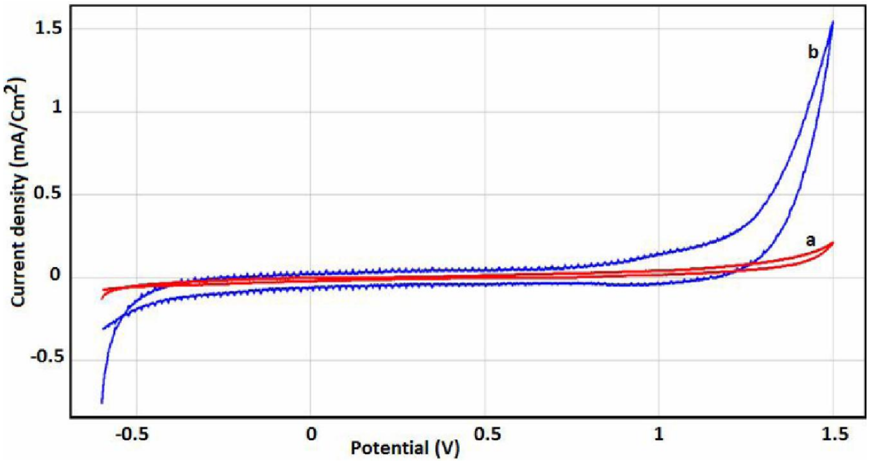


Figure 3 : Cyclic voltammograms recorded for CPE (a) and bare Clay-CPE (b), in 0.1 M Na_2SO_4 at 100 mV/s

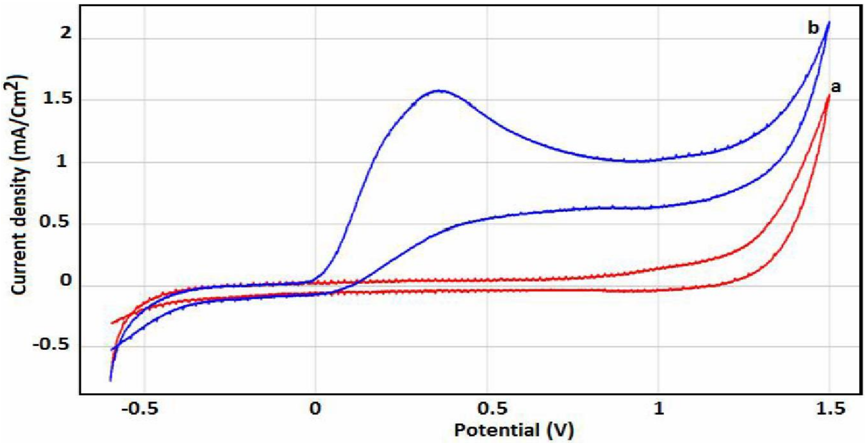
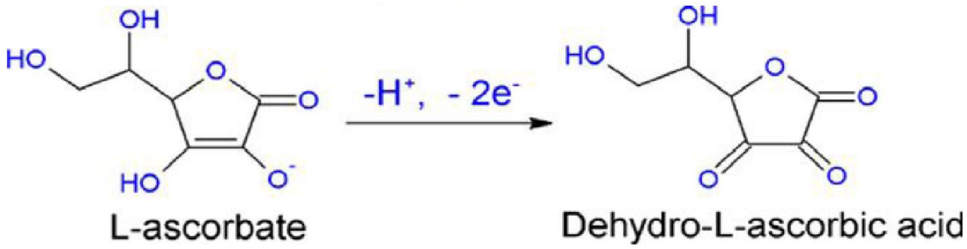


Figure 4 : CVs recorded for 2.67 mM AA at pH=7 at bare Clay-CPE (a) and Clay-CPE/AA (b), scan rate 100 mV/s, preconcentration time (tp)= 6min



Scheme : mechanism of electrochemical oxydation reaction of AA at Clay/CPE

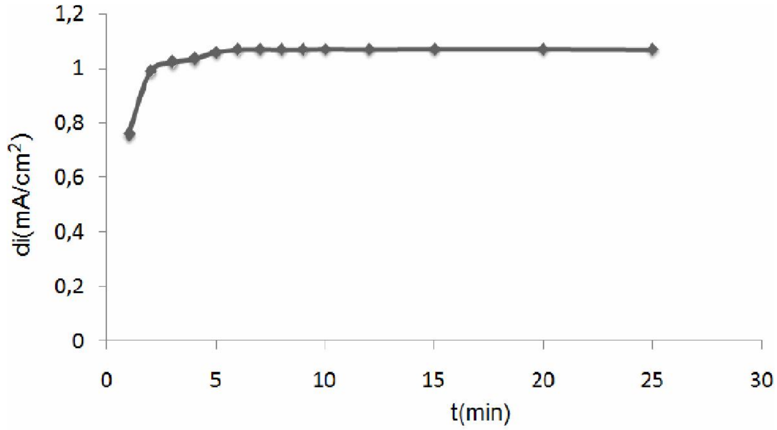


Figure 5 : Effects of accumulation time on oxidation peak currents of 2.27 mmol L^{-1} AA (pH=7) at Clay-CPE, supporting electrolyte is Na_2SO_4 0.1M

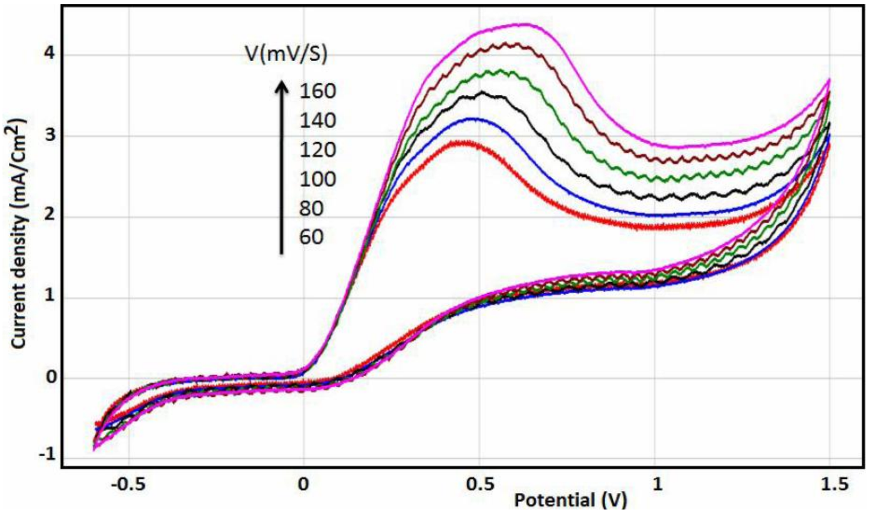


Figure 6 : CVs acquired on Clay-CPE with 4.5 mM AA in the buffer solution at different scan rates from 60 to 160 mV.s^{-1}. Inset is the plot of the peak current of AA versus scan rate

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 AA. Maybe this is attributed to the saturated adsorption of AA on the Clay–CPE surface. Taking account of sensitivity and efficiency, accumulation time was 6 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 AA, (0.1M Na_2SO_4, pH=7) were studied by cyclic voltammetry. The Figure 6 shows both the anodic currents linearly increase with the scan rate over the range of 60 to 160 mVs-1, the oxidation potential of AA moves to positive values, suggesting that the electron transfers for AA at the clay modified CPE is adsorption controlled reaction. The Figure 7 shows the linear relation-

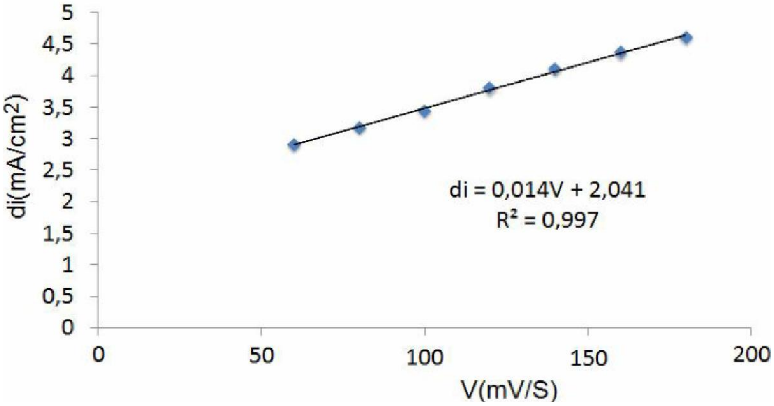


Figure 7 : Plot of peaks area versus scan rate

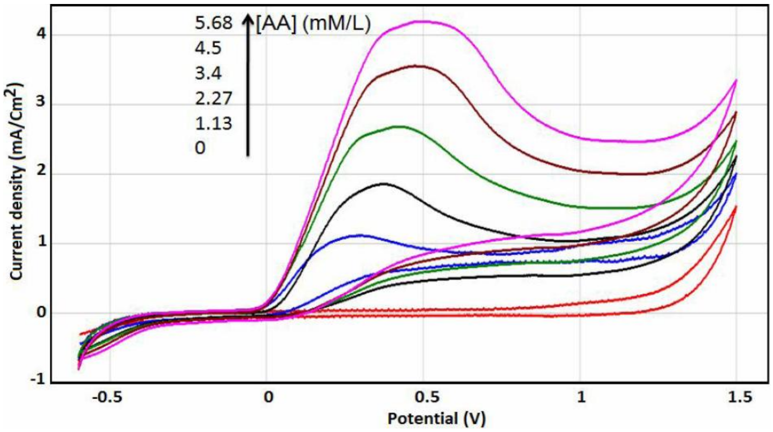


Figure 8 : Cyclic Voltammograms of different concentration of AA (1.13mM to 5.68mM) at Clay/CPE in 0.1 M Na_2SO_4 PH=7, Scan rate 100 mV/s

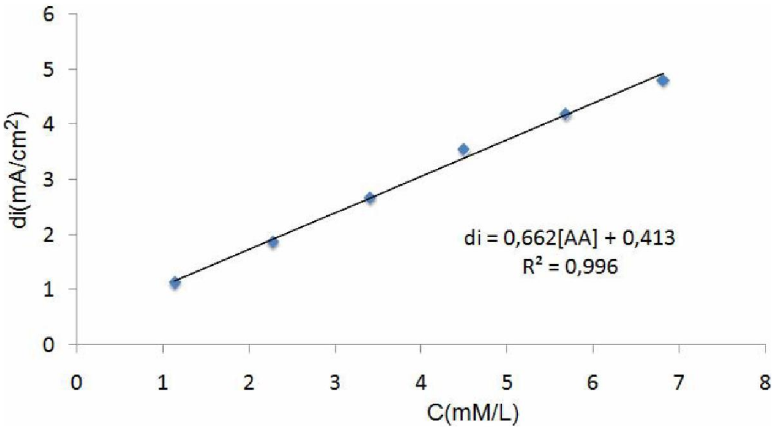


Figure 9 : Plot of peaks area versus added concentration of AA

ship between the scan rate anodic peak currents of AA at Clay/CPE.

Calibration graph

In order to obtain an analytical curve for the developed sensor, we carried out cyclic voltammograms for oxidation an AA at different concentrations in 0.1mol L^{-1} Na_2SO_4 (pH=7) at a sweep rate of 100 mVs^{-1}. Figure 8 shows the CV curves of different concentration of AA at Clay/CPE was increased from 1.13 mM to 5.68 mM. The anodic peak current increases linearly with the concentraton of AA (Figure 9). These results show that ascorbic acid concentration can be measured quantitatively by cyclic voltammetry.

Figure 10 shows the behavior of impedance diagrams recorded for clay modified carbon paste elec-

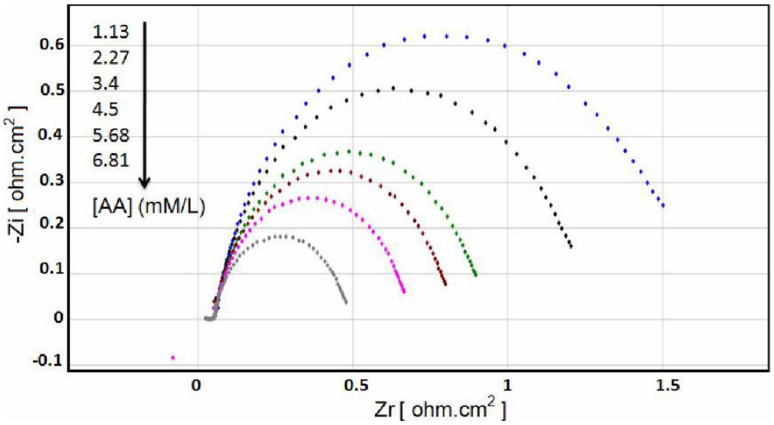


Figure 10 : Nyquist diagrams of clay modified carbon electrode, in presence of different concentration of AA, at open circuit potential

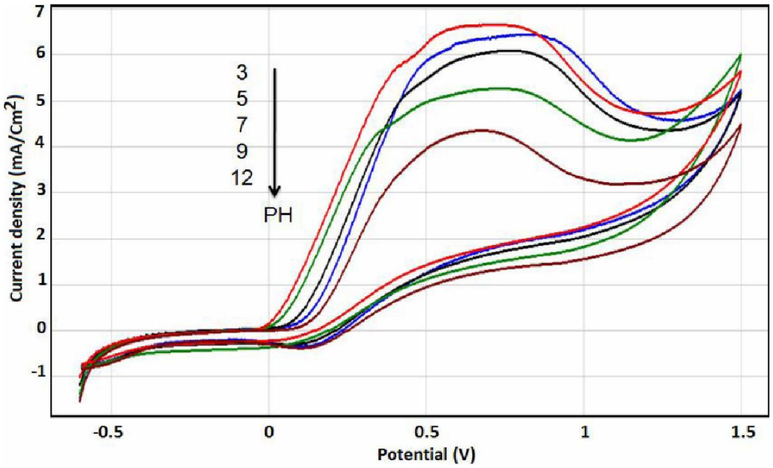


Figure 11 : Effect of pH on the oxidation of AA at the Clay modified CPE

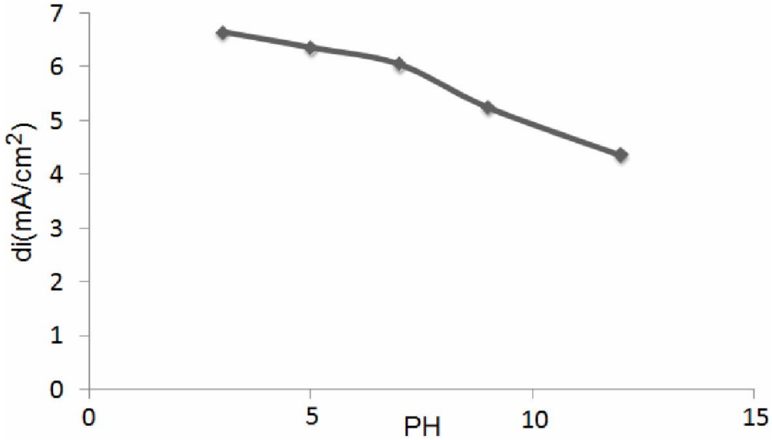


Figure 12 : Plot of the relationship between solution pH and the oxidation peak current

trode in buffer solution, in the presence of different concentrations of AA compound. We conclude that modified electrode reacts with the studied compound.

Effect of pH

The effect of varying pH on the current response of Clay modified carbon paste electrode at constant ascorbic acid concentration (6.81 mM) is shown in Figures 11 and 12. As can be seen, the peak current gradually reduce with the increase of pH.

DETERMINATION OF AA IN PHARMACEU-

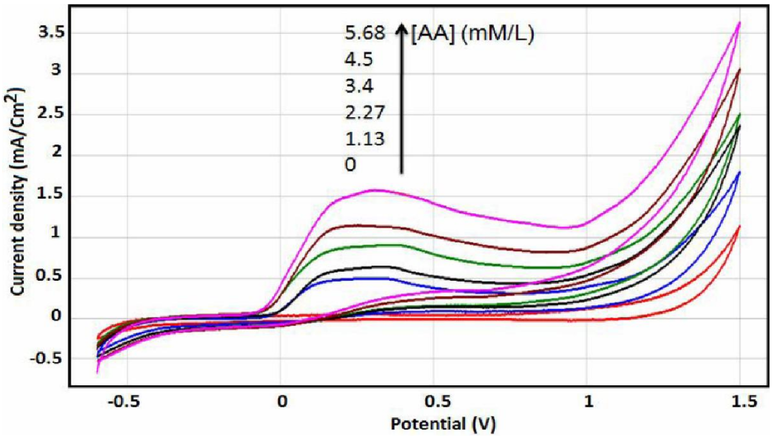


Figure 13 : Cyclics Voltammograms of different concentration of AA (1.13mM to 5.68mM) at Clay/CPE in 0.1M Na_2SO_4, Scan rate 100 mV/s

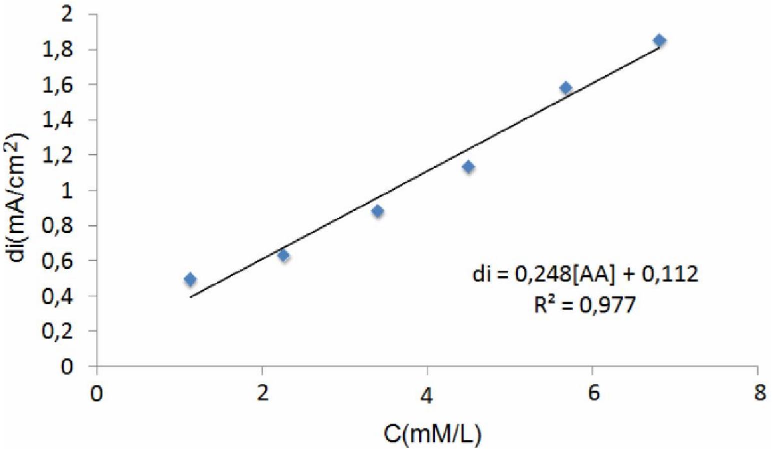


Figure 14 : Plot of peaks area versus added concentration of AA.

TICAL SAMPLE

In order to evaluate the performance of Clay-modified carbon paste electrode by practical analytical applications, the determination of AA was carried out in A vitamin C tablet is finely powdered. The analytical curves were obtained by CV experiments in supporting electrode (Figure13). It was founded that the peaks currents increase linearly versus AA added into the buffer solution (Figure 14).

CONCLUSION

It was demonstrated here that Clay modified electrode exhibits higher electrocatalytic activity towards ascorbic acid oxidation. The obtained results revealed that determination of AA can be easily performed using the clay. The proposed methodology was successfully applied in quantifying ascorbic acid in electrolyte solution with very satisfactory recovery percentages values for the application of the analytic methods proposed. The sensitivity signal is proportional to the concentration value of AA.

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