

## ELECTROCHEMICAL BEHAVIOR OF PARAQUAT ADSORBED ONTO CRYSTALLINE APATITE

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**Abstract:** The carbon paste electrode (CPE) has been used to analyze the electrochemical behavior of paraquat (PQ) adsorbed onto synthesized Ca-hydroxyapatite (HAP) in K<sub>2</sub>SO<sub>4</sub> (0.1M). The cyclic voltammetry results obtained were correlated with square wave voltammetry. The influence of variables such as the concentration of paraquat adsorbed onto apatite (PQ/HAP), and the potential scan rate was tested.

X-ray diffraction analysis (XRD), Fourier transformed infrared spectroscopy (FTIR) analysis, and inductively coupled plasma-atomic emission spectrometry (ICP, AES) were used for the characterization of the apatite.

**Keywords:** *paraquat, hydroxyapatite, carbon paste electrode, adsorption*

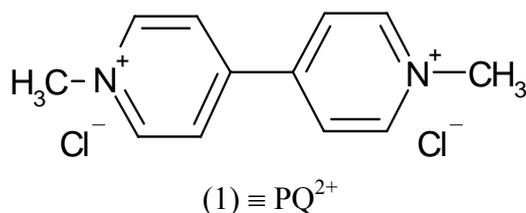
## INTRODUCTION

Paraquat (1, 1'-dimethyl-4, 4'-bipyridilium ion) also known as methyl viologen, is a defoliant and desiccant agent used to control herbal growth in terrestrial and aquatic environments. It is considered toxic for algae, fishes and other organisms, including humans. The adverse effect caused by chronically and acute exposures to this herbicide are well known and cases of death by casual ingestion or poisoning are documented in the literature.

Over the past 10 years, paraquat has been the source of nearly 700 poisoning cases in Malaysia. Out of these, about 73% were due to suicide while the reminders were a result of accidental and occupational exposures.

A wide number of analytical methods, based on the most commonly employed physico-chemical techniques for identification of organic compounds (UV, IR, HPLC, GC, MS) are available [1-5]. At present pollution of environment by pesticides is one of the main health risk factors [6, 7]. An effective control of maximum admissible concentrations of pesticides in water, soil, air, materials, and food is essential for improving the quality of life. Investigations aimed at the development of modern analytical techniques for pollutant detection are directed towards increasing their sensitivity, specificity, simplicity and rapidity [8, 9]; the electrodes have demonstrated to be increasingly suitable for diverse analytical application [10-13]. One of their most claimed advantages is the possibility of performing measurements in highly resistive media.

In this paper, we describe the electrochemical analysis of paraquat on a carbon paste electrode. Paraquat adsorbs on the surface of the apatite and provides a facile voltammetric quantitative method for some electroactive paraquat. The electrochemical characterization of adsorbed electroactive paraquat compounds was evaluated using cyclic voltammetric and square-wave voltammetric (SWV) analysis.



## EXPERIMENTAL

### Preparation of apatite

The apatite was synthesized by double decomposition [14]. A calcium nitrate Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O solution was added by slow rate (10 mL/min) into a boiling diammonium phosphate solution containing NH<sub>4</sub>OH. The pH of the mixture was about 10, and was maintained at this level throughout the reaction with a pH stat by addition of 3 vol % ammonia solution. After total addition of reactant the suspension was filtered in a large Buchner funnel. The precipitate obtained was rapidly washed with deionized water and calcined at 900°C about 3 h.

The powder prepared were characterized by X-ray diffraction analysis (XRD: Cu K $\alpha$  radiation, XPERT) to evaluate the purity of the synthesized hydroxyapatite powder. The IR spectra of the specimens have been obtained on a PERKIN-ELMER FTIR spectrophotometer from KBr pellets in order to determine hydroxyapatite stoichiometry deviations; in particular PO $_4^{3-}$  and/or OH $^-$  groups. In order to evaluate Ca/P ratio of powder, inductively coupled plasma-atomic emission spectrometry (ICP-AES) analysis was performed.

### **Adsorption measurements**

The solution of paraquat 10 $^{-3}$  M was prepared by dissolving the appropriate amount of paraquat in 20 mL of ethanol, in glass bottles, at room temperature. The apatite (100 mg) was contacted for 5, 10, 15, 30, 50, 80, 120, and 1200 minutes with the paraquat. The suspension was centrifuged at 6000 rpm during 20 min, and the supernatant was analyzed to determine the concentration of paraquat by measuring the absorbance value of paraquat at 259 nm using Shimadzu UV-161 UV-Vis spectrophotometer.

### **Electrochemical measurements**

The precipitate apatite contacted with paraquat for 1200 minutes, was added to the graphite powder to give a mixture that was (50, 75, 96 and 99%) apatite by weigh. The K $_2$ SO $_4$  (1mL, 0.1 M) was then added and ground with the mixture (HAP, CP); the obtained paste was packed into a home built electrode assembly consisting of two concentric lengths of tubing in a pistonlike configuration. The geometric surface area of electrode was 0.1256 cm $^2$ . A vitreous carbon rod inserted into carbon paste provided the electrical contact.

Cyclic voltammetric and SWV measurements were performed using an electrochemical analyzer Voltalab 10, piloted by Master 4 software connected to a personal computer. The electrochemical measurements were performed using a three electrode system, including a mixture (HAP, CP) as the working electrode, a platinum wire as a counter electrode and a saturated calomel reference electrode (SCE). The electrolytic solution (K $_2$ SO $_4$ , 0.1 M) was deoxygenated out at ambient temperature of the laboratory.

## **RESULTS AND DISCUSSIONS**

### **Characterization of apatite**

The XRD patterns of the prepared powders shown in Fig. 1 reveal a crystalline apatite. No other phase has been detected. The IR spectra (Fig. 2) showed bands characteristic of calcium phosphate. No spectral bands corresponding to carbonate ion were detected. All spectra show bands that can be assigned to phosphate groups, and hydroxyl in apatite environment [15]. The ICP analysis of synthetic apatite gives a Ca/P molar ratio of 1.667.

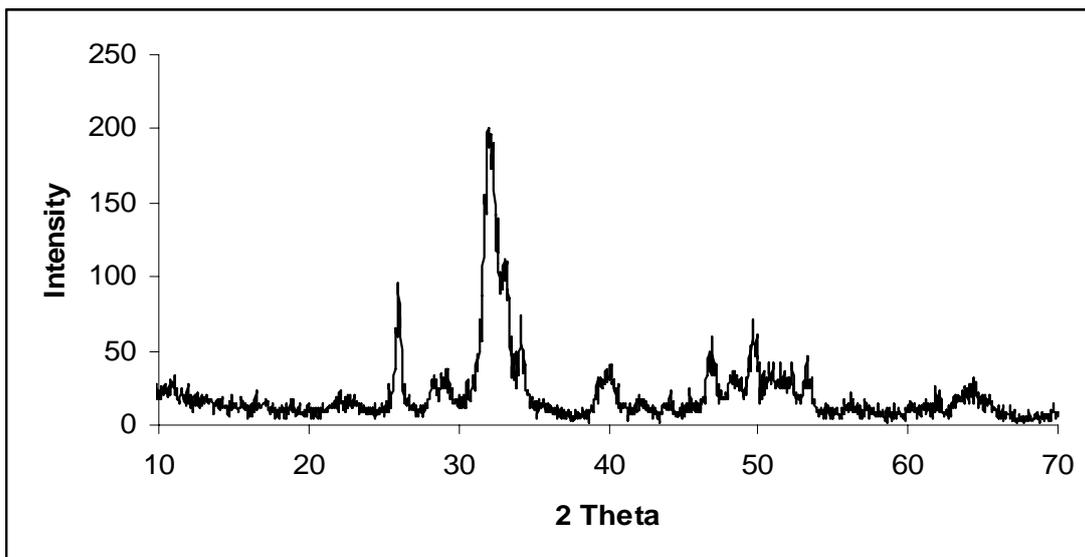


Figure 1. XRD pattern of the synthetic apatite calcined at 900°C for 3 h

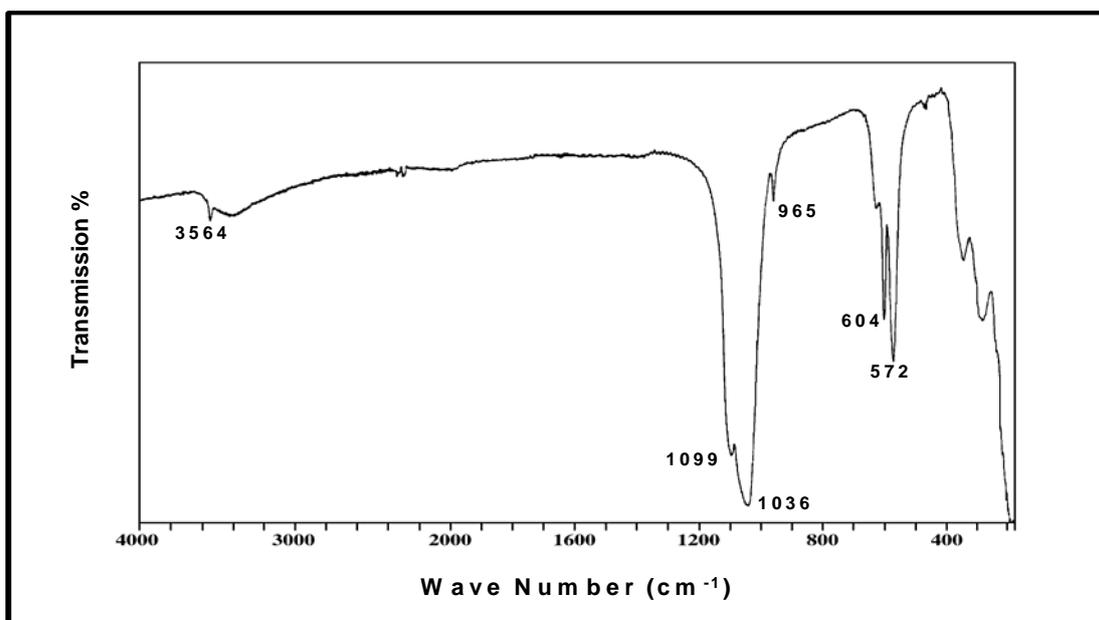


Figure 2. IR spectra of the synthetic apatite calcined for 3 h at 900 °C

### Adsorption of paraquat onto apatite

The amount of paraquat adsorbed was obtained by subtracting the equilibrium concentration of paraquat from the initial concentration before the adsorption process. The adsorption isotherms obtained for the paraquat are plotted in Fig. 3 as may be seen, that sharply rising adsorption versus time is indicate of high affinity between paraquat and adsorbent surface in ethanol.

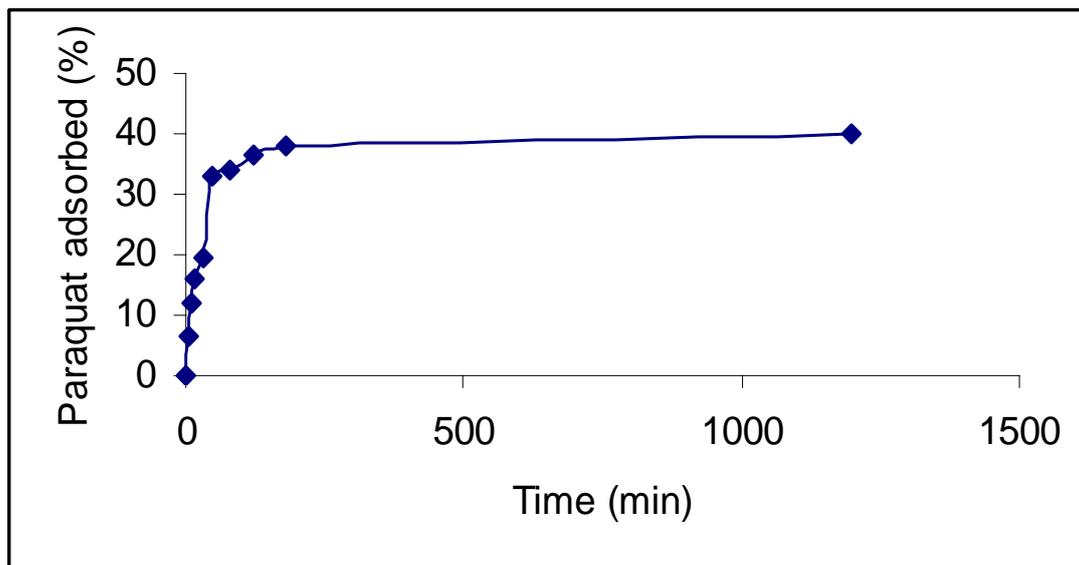


Figure 3. Percentage of adsorbed paraquat onto apatite in ethanol solution

#### Behavior of cyclic voltammetry

Figure 4 shows the voltammogram unregistered for adsorbed paraquat onto apatite in  $K_2SO_4$  (0.1M) electrolyte. We observe two redox system ( $P_1$ ,  $P_4$ ) and ( $P_2$ ,  $P_3$ ) respectively, at -700 mV and at -100 mV.

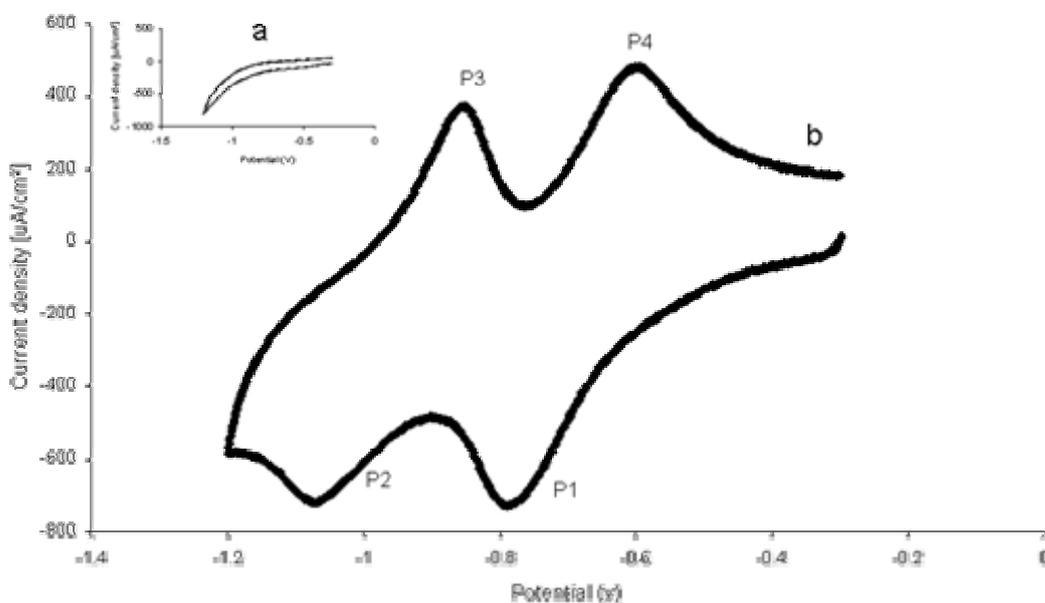
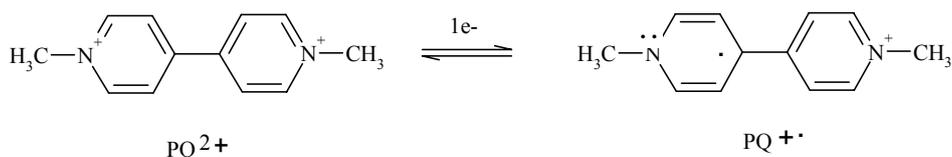
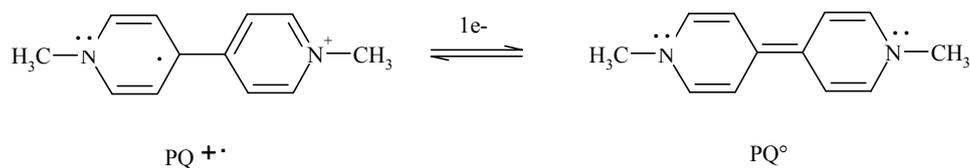


Figure 4. Cyclic voltammograms of (a) HAP, (b) paraquat adsorbed onto HAP, at CPE in  $K_2SO_4$  0.1M, PQ (HAP)/CP = 0.5 at  $v = 50mV/s$ .

The first redox system peaks ( $P_1$ ,  $P_4$ ) may be attributed to the following processes [16]:

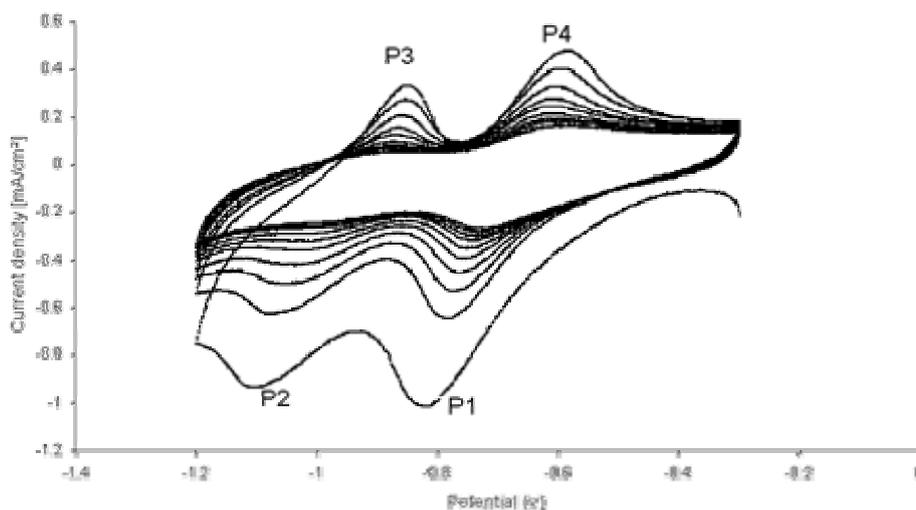


The second one to the process:



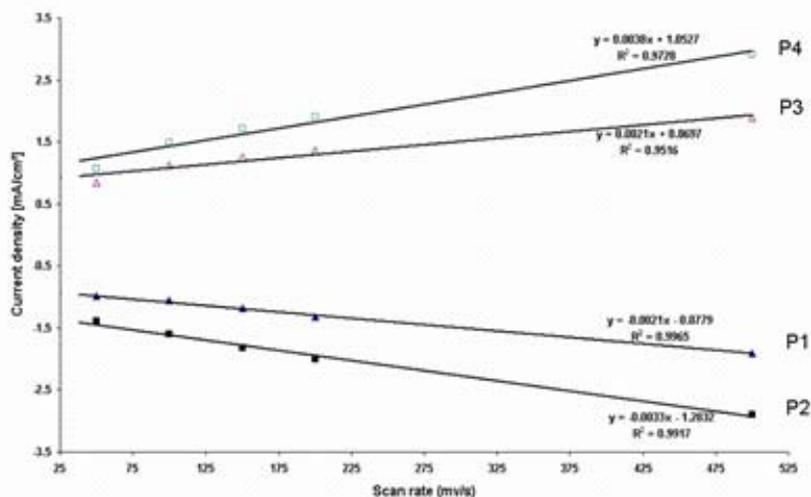
The paraquat cation  $\text{PQ}^{2+}$ , suffers a fast and reversible reduction to the radical  $\text{PQ}^{+\cdot}$  at approximately -700 mV. This radical cation adsorbs to the electrode surface and upon scanning the potential to more negative values, its reversibility is reduced to the neutral species  $\text{PQ}^{\circ}$  at -1000 mV [17].

Figure 5 shows, with increase of the scan number, the currents for both anodic and cathodic peaks decrease steadily, which indicates that the paraquat are eliminated continuously on the apatite surface.

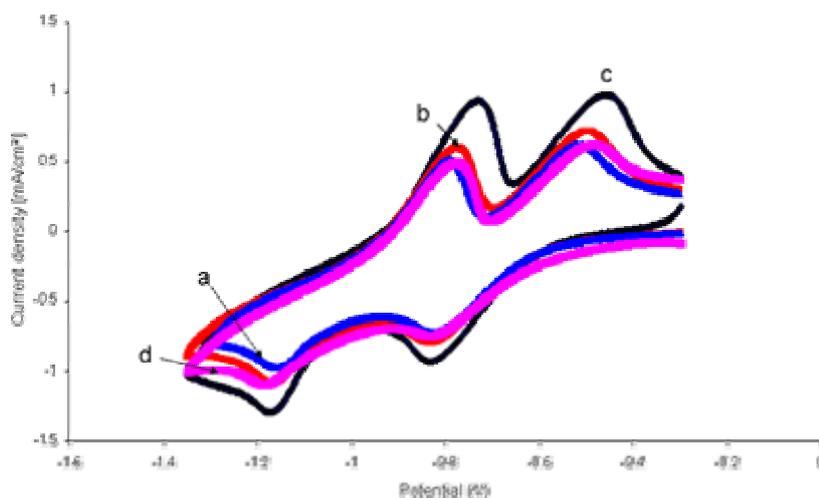


**Figure 5.** The cyclic voltammogram at CPE of paraquat adsorbed onto HAP, PQ (HAP)/CP=0.5 in  $\text{K}_2\text{SO}_4$  0.1 M; at  $v = 50\text{mV/s}$ , 10 cycles

The cyclic voltammograms corresponding to the response of paraquat adsorbed onto apatite at carbon paste electrode in 0.1 M  $\text{K}_2\text{SO}_4$  solution at pH = 5.6 at different scan rates is represented in Fig. 6. As this figure shows, the anodic and cathodic peak currents are linearly proportional to the scan rate. On the other hand, fig. 7 shows that the current for peaks increase continuously with increasing of an amount of PQ/HAP included with carbon paste (CP) into working electrode; the obtained maximum is at PQ (HAP)/CP of about 96%.



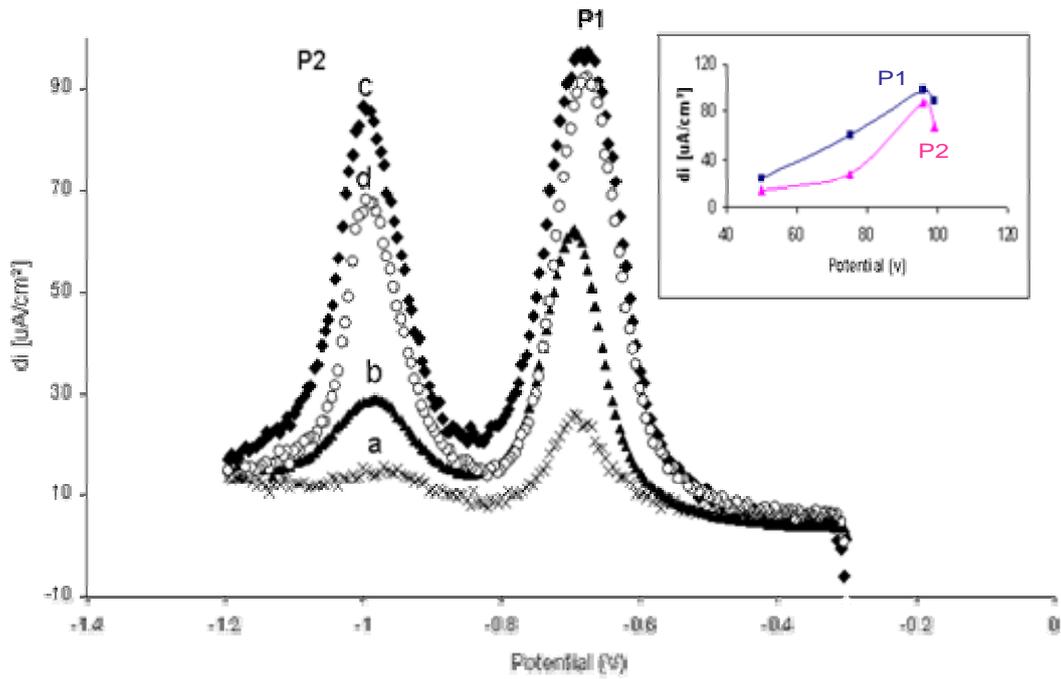
**Figure 6.** Dependence of the peak currents of paraquat adsorbed onto HAP on the scan rate, at CPE in  $K_2SO_4$  0.1 M, PQ (HAP)/CP = 0.9



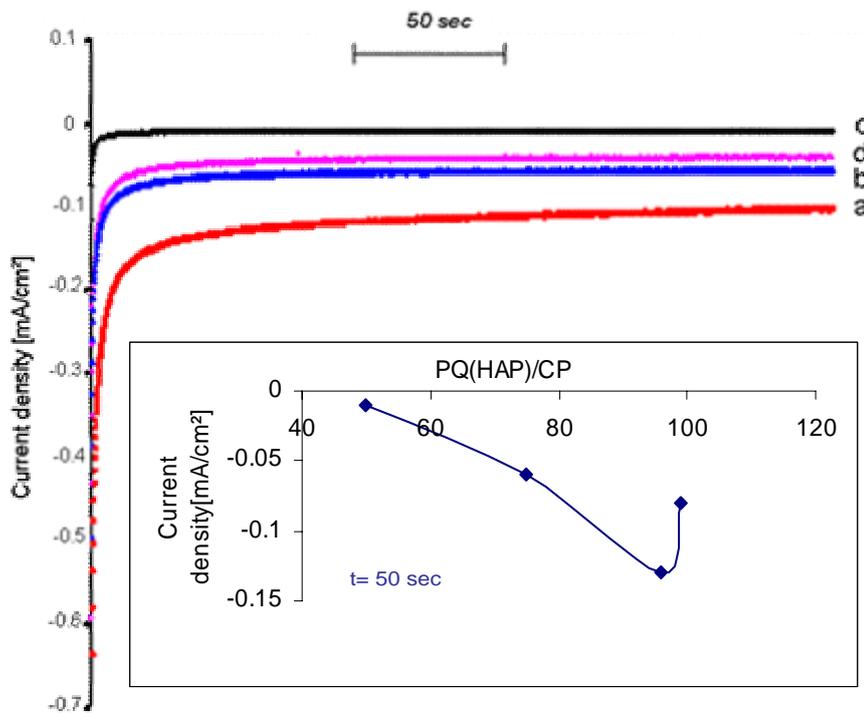
**Figure 7.** Cyclic voltammetric response of paraquat adsorbed onto HAP at different ratio [PQ (HAP)/CP] included into working electrode; (a) 0.50, (b) 0.75, (c) 0.96, (d) 0.99

### Square wave voltammetry

Fig. 8 shows the square wave voltammetry (SWV) of paraquat adsorbed onto apatite (PQ/HAP) at carbon paste electrode (CPE). Here peak (P<sub>1</sub>) was observed at -700 mV and peak (P<sub>2</sub>) at -1000 mV versus SCE. Which is in close agreement with values obtained in cyclic voltammetry. And we found that the peak potential on the carbon paste electrode almost not change with increase or decrease of PQ(HAP)/CPE ratio comparing with a potential obtained in cyclic voltammetry. The reductive peak increased along with the increase of the amount of PQ (HAP) inserted in the carbon paste; to give a maximum at 96% of PQ (HAP) inserted. The following calibration equation at -700 mV, was obtained  $i$  ( $\mu A$ ) = 47.166 + 1.436 PQ (HAP)/CP.



**Figure 8.** Square wave voltammograms at CPE in  $\text{K}_2\text{SO}_4$  (0.1M), for paraquat adsorbed onto HAP at different ratio PQ (HAP)/CP; (a) 0.50, (b) 0.75, (c) 0.96, (d) 0.99



**Figure 9.** Chronoamperometric response of paraquat adsorbed onto HAP, at different ratio PQ (HAP) /CP, at CPE in  $\text{K}_2\text{SO}_4$  0.1 M

### Chronoamperometric studies

The influence of accumulation time on the peak currents of paraquat adsorbed onto apatite was investigated. Fig. 9 shows the chronoamperograms that were obtained for a series of PQ (HAP)/CP ratio. The results show that an increase of PQ (HAP)/CP was accompanied by an increase in cathodic current obtained for a potential step of -700 mV vs SCE.

Calibration curves were recorded at 50 sec, in 0.1 M K<sub>2</sub>SO<sub>4</sub> with a PQ (HAP)/CP ratio between 0.50 to 0.99 (fig. 9). It was found that a maximum is obtained when PQ (HAP)/CP is about 0.96. The following calibration equation was obtained:

$$i \text{ (mA/cm}^2\text{)} = 0.1241 - 0.0026 \text{ PQ (HAP)/CP}$$

### CONCLUSION

In conclusion, the calcium phosphate hydroxyapatite used in this study is a good support to determine the electrochemical behavior of the organic compounds (PQ) at carbon paste electrode.

A sensitive method for electrochemical analysis of paraquat has been demonstrated. This electrode in a square wave voltammetry and a voltammetric measurement was sufficiently sensitive to quantify paraquat adsorbed onto apatite.

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