

## **Electrochemical Studies of Adsorption of Paraquat onto $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ from Aqueous Solution**

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### **Abstract**

Paraquat is one of the most widely used herbicides in the world. It has had a tarnished reputation because of its acute oral toxicity and ill-health associated with operators - particularly in the plantation sectors of many developing countries. Paraquat binds rapidly and tightly to clay materials in soils, and when adsorbed it is biologically inactive. It also binds to humus and other organic material: this results in no, or very low soil residues or leaching into water sources. This article presents a studies of kinetic of adsorption onto hydroxyapatite phosphocalcique  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$  (HAP) from aqueous solution. Measurements are performed by electrochemical methods using the cyclic voltammetric, chronoamperometry and square wave voltammetry at carbon paste electrode (CPE).

### **Keywords**

Paraquat; Apatite; Adsorption; Carbon paste electrode.

### **Introduction**

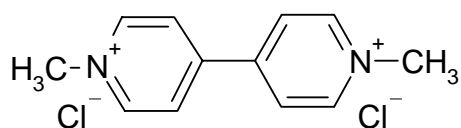
Pesticides have been detected in different kinds of samples such as soil [1], liver samples of birds [2], agrochemicals [3,4] and waters samples [5,6]. Nevertheless, a certain amount of pesticides used is transferred from agriculture land and can cause a spectrum of

toxic effects on aquatic organisms and human beings. An effective control of maximum admissible concentration and/or elimination of pesticides are essential for improving the quality of life.

Paraquat (1, 1'-dimethyl-4, 4'-bipyridilium dichloride) (1) was first synthesized in 1882. Its herbicidal properties were discovered only in 1955 in the ICI (now Zeneca) laboratories, which produced it commercially in 1961. This chemical type of herbicide - a bipyridyl - is shared with few other pesticides. It is one of the most widely used herbicides, and held the largest share of the global herbicide market until recently overtaken by glyphosate. Paraquat is sold in about 130 countries for use on large and small farms, plantations and estates and in non-agricultural weed control. It is a quick acting, non-selective herbicide, which destroys green plant tissue on contact and by translocation within the plant. It is used for weed control on non-crop land and can be used as a defoliant for cotton and hops before harvesting. It is used as a desiccant for pineapples, sugar cane, soya beans and sunflower [7].

Paraquat is one of the most hazardous compounds for human health [8]; the repeated exposures may cause skin irritation, sensitization, or ulcerations on contact [9, 10]. It is a potential contaminant of waters due to its high solubility (about 620g/l at 25°C) [11] and to the cation, and to the halogen anions have little toxic effects [10]. Therefore, it is necessary to remove these hazardous materials from water as much as possible [8, 12-14]. literature reports show that paraquat has been removed onto natural and synthesized compounds [15-19].

The aim of the present paper is studies the kinetic adsorption of paraquat onto apatite using the electrochemical methods as well as chronoamperometry, cyclic voltammetry and square wave voltammetry.



(1) ≡ PQ

## Experimental

### *Apatite preparation*

The apatite was synthesized by doubly decomposition [20]. A calcium nitrate

$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  solution was added by slow rate (10ml/min) into a boiling diammonium phosphate solution containing  $\text{NH}_4\text{OH}$ . 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 the reactant the suspension was filtered in a large Buchner. The precipitate obtained was rapidly washed with deionized water and calcined at  $900^\circ\text{C}$  at 3h. The powder prepared were characterized by X-ray diffraction analysis (XRD: Cu  $\text{K}\alpha$  radiation, XPERT) to evaluate the purity of the synthesized hydroxyapatite powder. Fourier transform infrared (FTIR) spectra of the specimen have been obtained on a PERKIN-ELMER FTIR) spectrophotometer from KBr pellets in order to determine hydroxyapatite stoichiometry deviations; in particular  $\text{PO}_4^{3-}$  and/or  $\text{OH}^-$  groups. FTIR spectra were recorded in the  $400\text{-}4000\text{ cm}^{-1}$  range. Chemical composition of apatite powder was obtained with inductively coupled plasma-atomic emission spectrometry (ICP-AES) analysis.

#### *Adsorption measurements*

The adsorption studies was performed on 20ml of paraquat ( $10^{-3}$ ) solution in a glass bottles in the presence of 0.1g of apatite, at room temperature, the suspension was shaken for 5, 15, 30, 50, 80 and 120minutes, then the solid was collected by centrifugation at 6000 rpm during 20 minutes, the precipitate obtained was washed with deionized water and dried at room temperature. finally the powder was analyzed at carbon paste electrode (CPE) to determine the paraquat adsorbed onto hydroxyapatite.

#### *Electrochemical measurements*

The electrochemical cell was configured to work with three electrodes, using platinum plate for counter electrode, saturated calomel electrode (SCE) as reference electrode, and modified carbon paste as the working electrode. The modified carbon paste was obtained by a mixture of hydroxyapatite phosphocalcique (HAP) with paste carbon (CP), to give a weigh ratio HAP/CP=0.96. The mixture paste was packed into working electrode (figure 1). The geometric surface area of the working electrode was  $0.1256\text{ cm}^2$ . The electrolytic solution  $\text{K}_2\text{SO}_4$  (0.1M) was deoxygenated with nitrogen during experiment at ambient temperature.

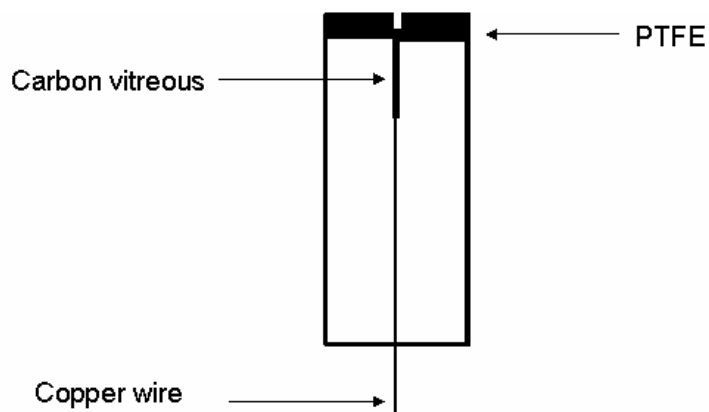


Figure 1. Diagram of the Carbon Paste Electrode.

## Results

### *Powders synthesis*

FTIR spectra of powder calcined at  $900^\circ\text{C}$  for 3h (figure 2) are characteristic of apatite compounds. All spectra show bands that can be assigned to phosphate groups, and hydroxyl in an apatite environment [21].

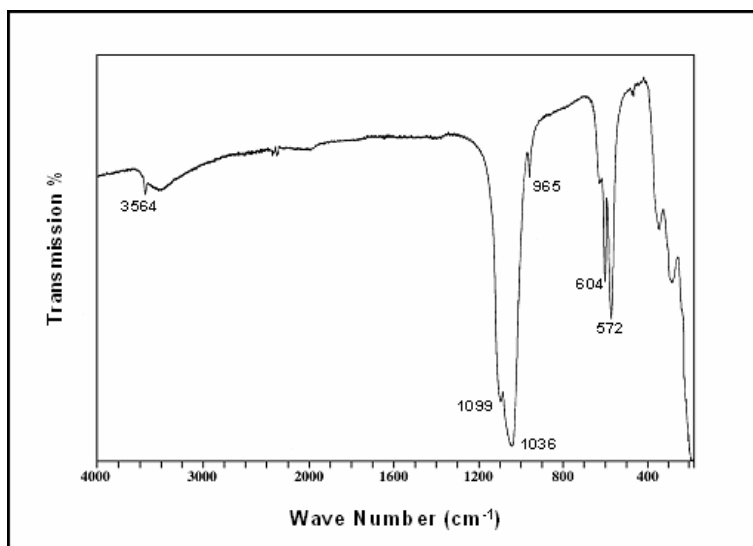


Figure 2. IR spectra of the apatite powder

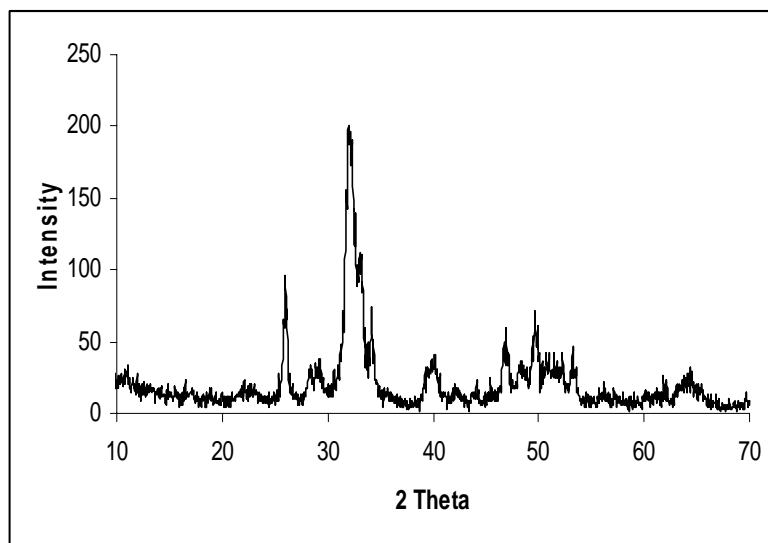


Figure 3. XRD pattern of the synthetic apatite.

The X-ray diffraction (XRD) pattern of the powder shown in figure 3 is typical of poorly crystalline apatite. No other phase has been observed. The ICP analysis of synthesized apatite gives a Ca/P molar ratio of 1.667 (tab. 1).

**Table 1. Chemical composition (ICP-AES) of apatite calcined for 3 h at 900°C.**

	%Ca	%P	Ca/P
Apatite	35.115	16.171	1.678

### *Electrochemical behavior at CPE*

#### *Cyclic voltammetry*

The synthesized apatite contacted with paraquat for a range between 5 and 120min, was analyzed at carbon paste electrode at room temperature in  $K_2SO_4$  (0.1M). In figure 4 we observe two pairs peaks ( $P_1$ ,  $P_4$ ) and ( $P_2$ ,  $P_3$ ) corresponded a presence of paraquat adsorbed onto apatite from solution aqueous [18]. We observe (figure 5) that the peaks currents increase with increasing of the contact time (CT) between paraquat and apatite; this demonstrated that the paraquat was adsorbed continuously vs. time onto apatite surfaces.

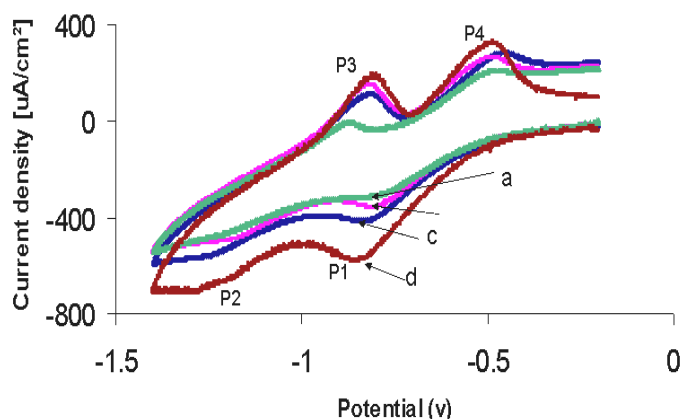


Figure 4. Cyclic voltammetric response of paraquat adsorbed onto apatite versus contact time (CT), 5 (a), 30 (b), 80 (c) and 120min (d) at carbon paste electrode, at  $v=50\text{mv/s}$  in  $\text{K}_2\text{SO}_4$ .

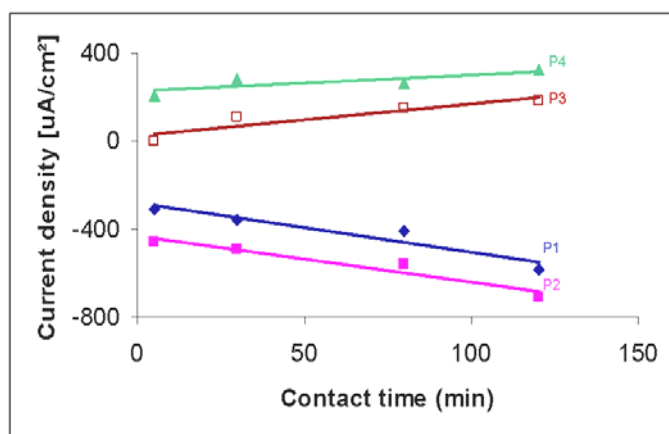


Figure 5. Dependence of the peaks current of paraquat on the contact time (CT) at carbon paste electrode in  $\text{K}_2\text{SO}_4$ ,  $v=50\text{mv/s}$ .

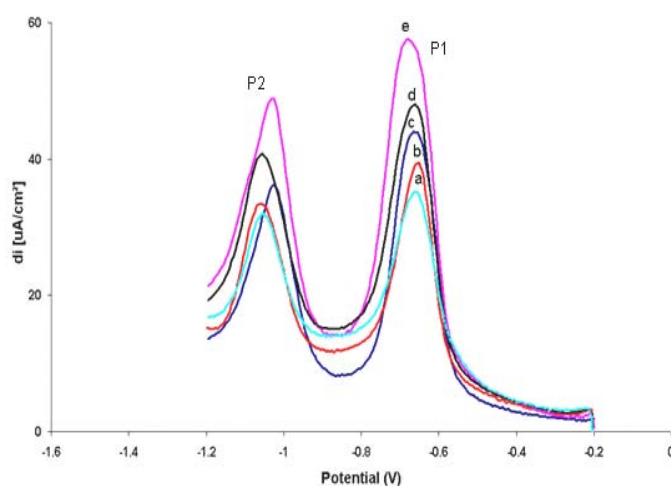


Figure 6. Square wave voltammograms of paraquat adsorbed onto apatite at carbon paste electrode, in  $\text{K}_2\text{SO}_4$  ( $\text{pH}=5$ ) versus contact time between paraquat and apatite, 5 (a), 15 (b), 30 (c), 50 (d) and 120 min (e).

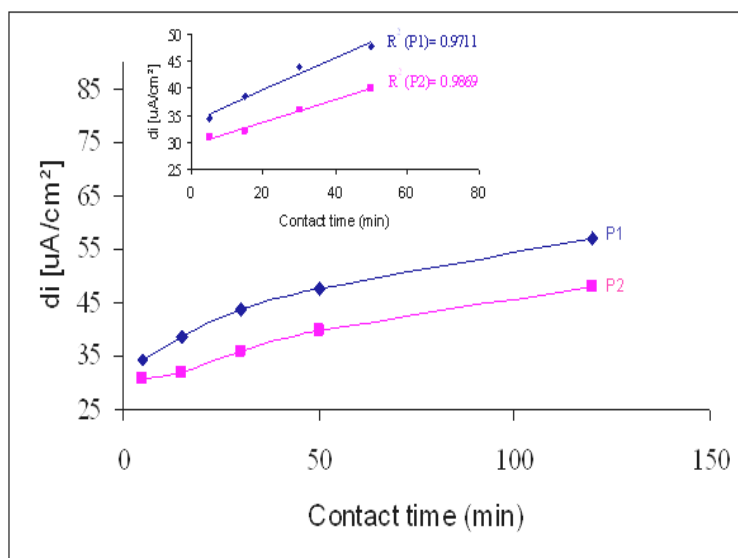


Figure 7. Calibration curves for paraquat adsorbed onto apatite versus the contact time at CPE in  $K_2SO_4$  ( $pH=5$ ), considering the current responses of peaks  $P_1$  and  $P_2$

#### Chronoamperometry studies

Figure 6 shows the chronoamperograms that were obtained for a series of apatite powders contacted with paraquat in dionized water, between 5 and 120 min. the results show that an increase in contact times was accompanied by an increase in current for a potential step of  $-700$  mv vs. SCE.

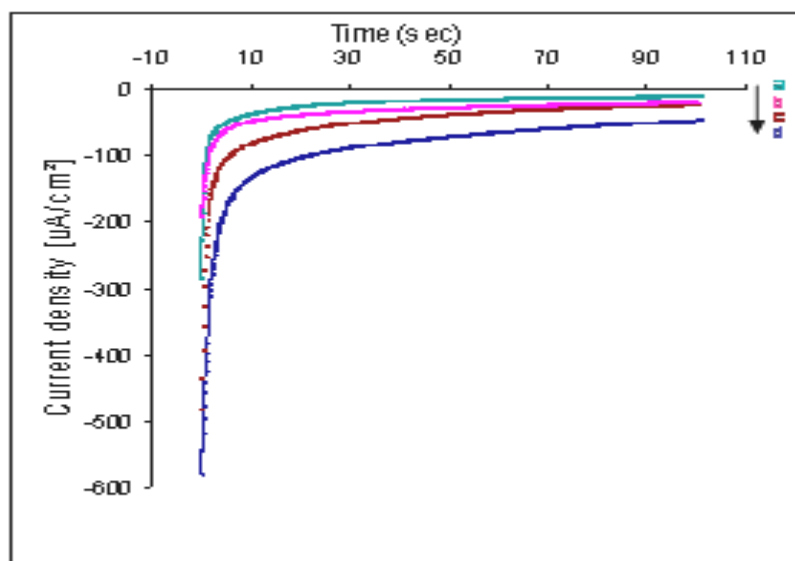


Figure 8. Chronoamperometric response of paraquat adsorbed onto apatite versus contact times, 5 (a), 30 (b), 80 (c) and 120 min (d), at CPE in  $K_2SO_4$  ( $pH=5$ )

The variation of chronoamperometric current at  $t = 50$  sec vs. contact times of apatite with paraquat are shown in figure 7 as these calibration curve show, that in the range 5-120min the response is linearly proportional to the contact time of apatite with paraquat.

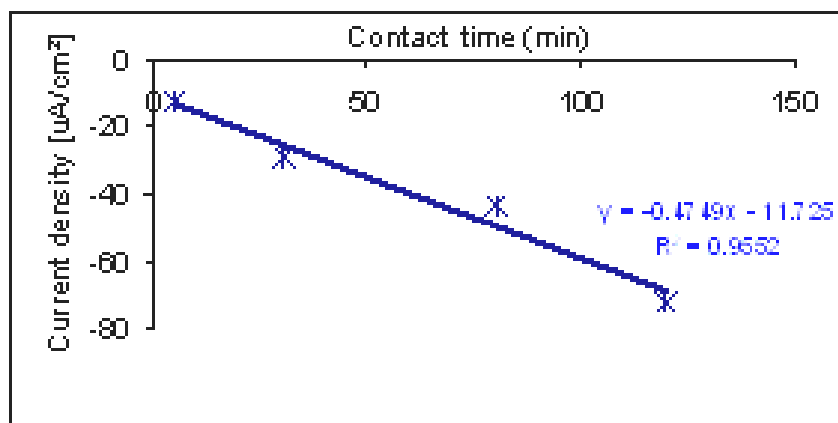


Figure 9. Plot of current vs. contact times obtained from chronoamperometric experiments for a paraquat adsorbed onto apatite at CPE in  $\text{K}_2\text{SO}_4$

## Conclusion

The present studies investigated the adsorption of paraquat onto hydroxyapatite phosphocalcique; the results obtained give information on the kinetic adsorption of paraquat, and demonstrate that the carbon paste electrode is particularly capable to detect a trace of paraquat on the apatite surface.

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