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## Electrochemical detection of paraquat at clay modified copper electrode

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### ABSTRACT

The copper electrode modified by clay has been utilized for the determination of pesticides with high sensitivity based on their redox behavior. The experiment is performed on the use of cyclic and square wave voltammetry. Square wave voltammetric response showed a linear calibration curve in the range  $10^{-3}$  to  $10^{-7}$  mol.L<sup>-1</sup>.

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### KEYWORDS

Paraquat;  
Square wave voltammetry;  
Modified electrodes.

### 1. INTRODUCTION

All fatalities of paraquat poisoning have been due to accidental intake. The ingestion of toxic paraquat is followed by an initial phase of gastrointestinal disturbances due to the irritant action of the chemical, followed by a second intermediate phase of transitory hepto-renal changes, subsequently to this, a third phase of delayed and lethal lung effect. The intensive use of paraquat, as herbicides, in recent years has increased agricultural productivity, but at the same time it has generated herbicide and pesticide residues, which exceed legal limits. The increasing use of pesticides in agriculture, forestry, and domestic activities for controlling pests is polluting our water resources. The leaching run-off from agricultural and forest lands, deposition from aerial applications and discharge of industrial wastewater are responsible for this water contamination<sup>[1]</sup>. The pesticides form a strong class of water pollutants, as they are

sometimes nonbiodegradable. Moreover, pesticides are carcinogenic in nature. Therefore, toxicity of pesticides and their degradation products is making these chemical substances a potential hazard by contaminating our environment<sup>[2]</sup>.

Paraquat (1, 1' dimethyl-4,4'-bipyridylium chloride), which was extensively used as a non-selective herbicide, is one of the bipyridium compounds<sup>[3]</sup>. However, it is well known that this compound is also one of the most acutely toxic compounds because it has caused many cases of human poisoning, with the lung being the primary target tissue<sup>[4]</sup>.

Several approaches have been proposed to determine the paraquat in soils, tissues, ground and drinking water, capillary electrophoresis (CE)<sup>[5,6]</sup> and ion-pair high-performance liquid chromatography (HPLC) using UV detection<sup>[7,10]</sup>, immunoassay<sup>[11,12]</sup>. Various electrochemical techniques have been employed for the detection of paraquat<sup>[13,20]</sup>.

Once paraquat enters the soil environment, it is rapidly strongly bound to clay minerals, holloysite, dickite, and nacrite<sup>[23]</sup>. It's used to refer to white clays whose principal menial is kaolonite and minor amount of impurities as micas. It's particles are usually hexagonal whnch is composed so thet (001) crystal plane is parallel to the surface of kaolin particle<sup>[24]</sup>.

In this paper, we describe the electrochemical analysis of paraquat on a copper electrode modified with clay (CCME). The electrochemical characterization and voltammetric performance of adsorbed electroactive paraquat were evaluated using cyclic square wave voltammetric analyses.

## 2. EXPERIMENTAL

### 2.1. Apparatus

The electrochemical studies were performed with a potentiostat PGSTAT 100 driven by the general purpose electrochemical systems data processing software (Voltalab Master 4 software). The cell includes a three-electrodes system, an Ag-AgCl reference electrode, a platinum auxiliary electrode and a clay modified copper electrode working electrode.

### 2.2. Preparation of CCME

The Clay from Ccameroon was electrochemically deposited on copper substrate. The morphology of modified electrode was examined using scanning electron microscopy. Figure 1 shows the SEM image of a clay sample, which it can be observed to clay as a dense

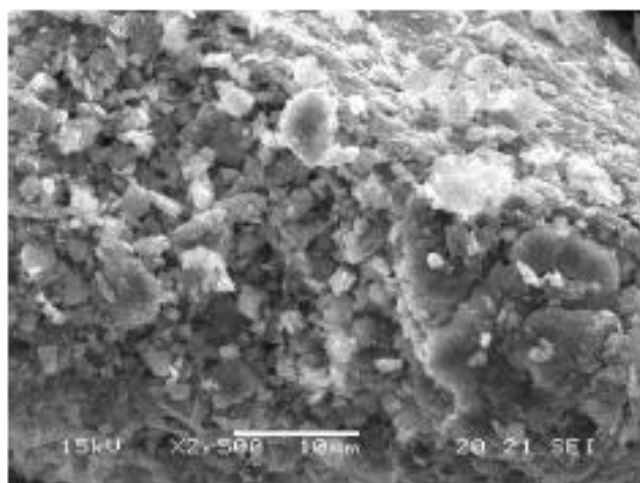


Figure 1 : SEM of Cameroon clay

material. The Clay presents a characteristic structure a 0.5-6  $\mu\text{m}$  with rengo and a 0.05-0.5  $\mu\text{m}$  thickness range.

### 2.3. Procedure

A copper electrode modified with clay was washed with distilled water carefully, heated at room temperature and transferred to electrochemical cell containing  $\text{HClO}_4$  electrolyte and the desired concentration of paraquat.

The paraquat was accumulated at the clay modified copper electrode. Square wave voltammetry scanning was performed from -1.4 to 0.2 V with a step potential 25 mV, amplitude 5 mV and duration 5 secondes at scan rate 1 mV/s. Cyclic voltammetric measurements were performed between -1 to 0.2 V at scan rate of 50 mV/s. All measurements were performed at room temperature.

## 3. RESULTS AND DISCUSSION

### 3.1. Corosion resistance of CCME

The cathodic and anodic Tafel curves of CCME and copper in 0.1M  $\text{HClO}_4$  solution are shown in Figure 2. The electrochemical parameters deduced from the Tafel curves (Figure 3) are given in TABLE 1. we note a slight increase of the corrosion rate of CCME versus copper electrode accompnagned with an increase of anodic slope which corresponds to a slight dissociation of the electrode (CCME).

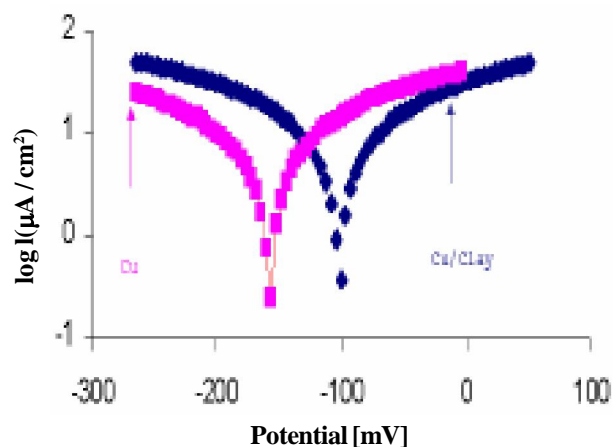


Figure 2 : Tafel curves of CCME and copper electrode.

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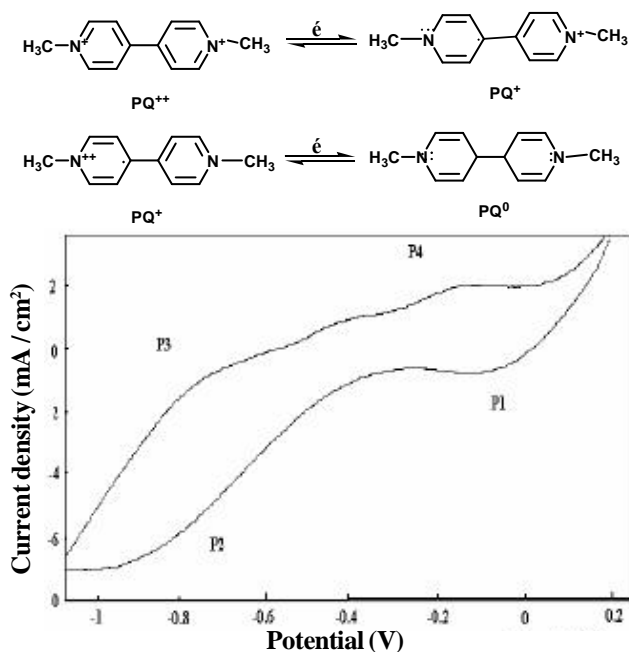


Figure 3 : Cyclic voltammogram of 0.02 mg/l paraquat in 0.1M HClO<sub>4</sub>, scan rate 50 mV/s, on a CCME.

TABLE 1 : Electrochemical parameters for the corrosion of CCME and copper electrode in 0.1M HClO<sub>4</sub> solution.

	E(i=0)mV	Rp Kohm.cm <sup>2</sup>	Jcorr mA/cm <sup>2</sup>	Ba mV	Bc mV
Cu	-157	4.02	10.52	255.2	-291.3
Cu/clay	-101.2	3.16	14.54	274	-292.4

### 3.2. Electrochemical behavior

Figure 3 shows the voltammogram of adsorbed paraquat on a clay modified copper electrode at 0.1M HClO<sub>4</sub>. Two reduction waves were observed for paraquat, one between 0 to -0.2 V (peak P1) and the other between -0.6 to -0.8V (peak P2). The reduction of paraquat can be attributed to the following processes<sup>[25]</sup>:

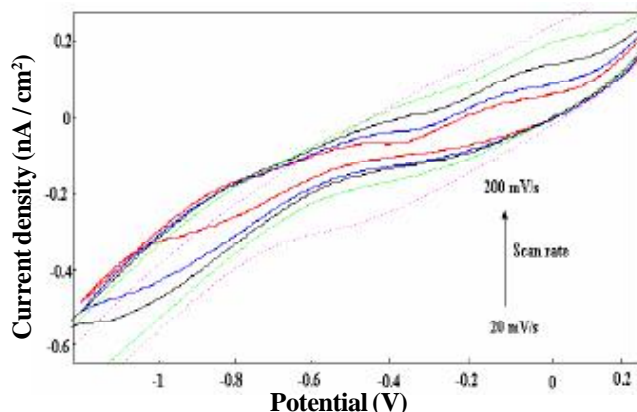


Figure 4 : Voltammograms curves at CCME for different scan rates (from 20 to 200 mV/s) in 0.1M HClO<sub>4</sub> + 0.02 mg/l paraquat.

Figure 4 shows the voltammograms of CCME in 0.1M HClO<sub>4</sub> in presence of 0.02 mg/l paraquat as a function of scan rate. The cathodic peaks are shifted to more negative potentials as the scan rate increases.

### 3.3. Analytical curves

The analytical curves were constructed for a range of concentration from 0.02 to 0.3 mg/l and Figure 5 shows the multiple voltammograms obtained. In all analytical curves constructed, the analytical responses presented a similar profile, where a linear increase can be observed in the responses with the variation in the analytical concentration.

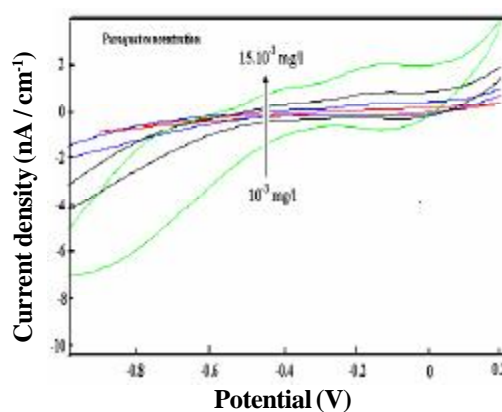


Figure 5 : Multiple voltammograms for paraquat in 0.1M HClO<sub>4</sub> on CCME at 50 mV/s scan rate, for concentrations between 0.02 and 0.3 mg/l.

The square wave voltametry (SWV) was performed to determine the electroanalytical responses of paraquat with the clay modified copper electrode (CCME) and to evaluate the presence of forward and backward current components that can be applied to determine the reversibility of the electrochemical redox process that occurs.

For this purpose, SWV experiments were performed for 0.02 mg/l paraquat in 0.1M HClO<sub>4</sub>, with a step potential 25 mV, amplitude 5 mV and duration 5 seconds at scan rate 1 mV/s. The responses obtained showed that the paraquat gave two voltammetric peaks towards the negative sweep direction, the first one around 0.1 V and the second at approximately -1.2 V.

Figure 6 shows the different square wave voltammograms obtained. We note the linear increase in the responses with the variation in the analytical concentration.

Figure 7 shows, with increase of scan rate number,

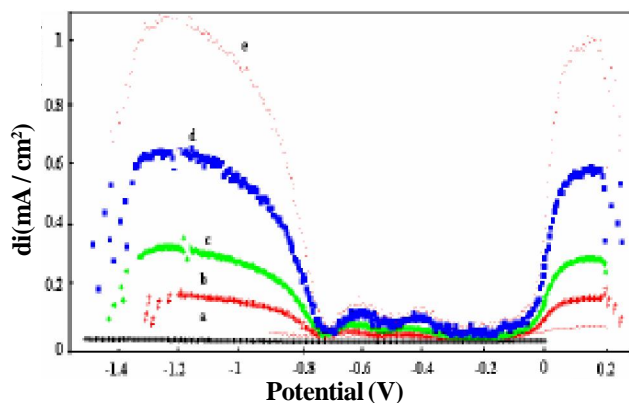


Figure 6 : Multiple square voltammograms enregistered for CCME in 0.1M HClO<sub>4</sub> + different concentrations of paraquat.

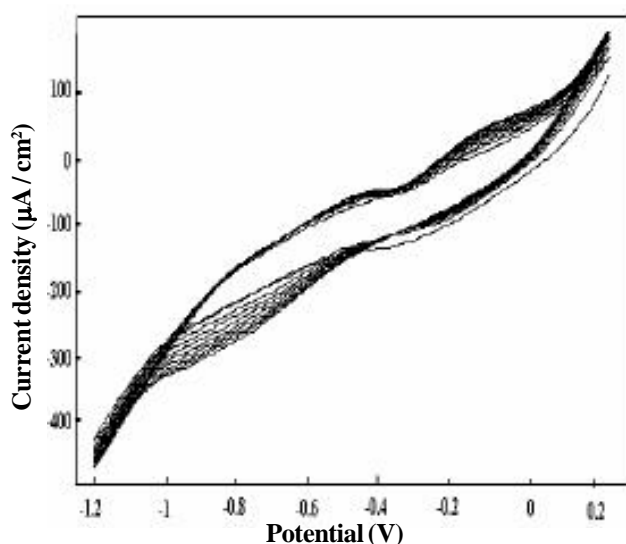


Figure 7 : The cyclic voltammograms at CCME of paraquat in 0.1M HClO<sub>4</sub>, at 50 mV/s scan rate.

the currents for both anodic and cathodic peaks decrease steadily, which indicates that the paraquat are eliminated continuously on the clay matrix.

## CONCLUSION

The results presented in this work demonstrated that the use of the use of the clay modified copper electrode allied to a very sensitive voltammetric technique, such as the cyclic voltametry and square wave voltametry, is a suitable analytical procedure that allows for easy application in a variety of different natural matrices. The use of CCME makes direct analysis of the samples with acquisition of the analytical response sensitive.

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