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Electrochemical study of the capacity of *Moringa oleifera* to chelate paraquat and diquat

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ABSTRACT

The voltammetric behavior of paraquat and diquat was investigated at Natural phosphate (NP) modified carbon paste electrode NP-CPE in Na₂SO₄. A method was developed for the detection of the trace of these herbicides, based on their redox reaction. The reduction peaks of paraquat were observed around -1.2 V and 0.8 V (vs. SCE), and at about -0.8 V and 0.9 V for diquat in cyclic voltammetry. Experimental conditions were optimized by varying the accumulation time, apatite loading and measuring solution pH. The use of *Moringa oleifera* as natural chelating agent gave a significant improvement in the depollution of contaminated Water sample. © 2015 Trade Science Inc. - INDIA

KEYWORDS

Electroanalysis;
Modified electrodes;
Paraquat;
Diquat;
Moringa oleifera.

INTRODUCTION

Pesticides are rarely used in pure form for primarily safety reasons^[1], but they are diluted in the form of liquid or dry preparations. The various products used in these compositions are formulating adjuvants^[2]. In recent years, concern is growing because of the possible risks of the presence of pesticides in food and water^[3-5] for public health and ecosystems^[6-9] paraquat disappears only very slowly and is unlikely to reach the water table by leaching^[10]. When applied in aquatic systems, it disappears quickly, in the space of six to fourteen days, due to adsorption to sediments and plants and its uptake by

plants^[11]. The toxic effects of paraquat are mainly due to the cations and halogen anions^[12], The sharp poisoning can result in breathing system and affect the nervous system and kidneys. It causes many cases of human poisoning with lung tissue that is fundamental target^[13]. Death is usually caused by an evolutionary pulmonary fibrosis and proliferation of the pulmonary epithelium^[14] The Diquat is a cyclic hydrocarbon derivative pyridilium. Its synthesis conducted by Budavari in 1996^[15]. It is only more widely used. It is generally marketed as a dibromide salt or a dichloride monohydrate [Due to its double positive charge, the cation of the diquat is firmly adsorbed on the negative soil clay minerals^[16]. Therefore, it

remains in the upper layers of the soil for a long time^[17] and is unlikely to be leached into the water table. Diquat herbicide applied as in aquatic water disappears after four weeks by adsorption to plants and sediments^[18]. Photodecomposition also contributes to the disappearance of diquat in water^[18]. Diquat has a certain affinity for the liver and kidney but low affinity lung^[19]. Swallowing a massive amount of diquat is responsible for a widespread necrosis, and myocardial first digestive, liver and kidney^[20]. Digestive symptoms are in the foreground (mouth pain, throat). In 24 hours settle circulatory failure, acute renal failure, and toxic hepatitis, disorders of consciousness, convulsions and coma and sometimes addict dies of ventricular arrhythmias^[21]. The liver damage is moderate. Pulmonary fibrosis, characteristic of paraquat has not been described^[19], probably by low affinity for diquat lung tissue^[22]. Diquat therefore has the reputation of being less toxic than paraquat, partly unwarranted reputation by the six deaths of eleven published cases^[23]. Mortality is really high^[24] Retrosternal, with profuse vomiting and abdominal often bloody diarrhea.

The purpose of this work is to study the applicability of cyclic and square-wave voltammetry together with carbon paste electrode (CPE) modified with Natural Phosphate (NP) in the electroanalytical determination of paraquat and diquat in water. The advantages of using a NP-CPE include the availability of a wide potential range of CPE for analysis, easily renewable surface, and simplicity of fabrication. Among the different inorganic solids, NP has advantages because it is cheap, readily available, stable in water, nontoxic, and not a pollutant.

EXPERIMENTAL

Reagents

Potassium nitrate was dissolved into Bidistilled deionized water (BDW) to form $1\text{mg}\cdot\text{L}^{-1}$ stock solutions. Working standards for calibration were prepared by diluting the primary stock solution with BDW. Carbon paste was supplied from (Carbon, Lorraine, ref. 9900, French). All chemicals were of analytical grade and used without further purifica-

tion.

Electrodes preparation

Firstly, the carbon-paste electrode was prepared according the following procedure^[13]. The carbon-paste electrode was prepared by mixing the graphite powder with paraffin oil used as a binder.

The mixture was grinding in a mortar agate and then a portion of the resulting composite material was housed in PTFE cylinder. The geometric surface area of the working electrode was 0.1256cm^2 . A bare of carbon vitreous inserted into carbon paste provided the electrical contact, and then the natural phosphate film is electrodeposited onto carbon paste electrode. The deposit of natural phosphate on carbon paste electrode surfaces was processed at 20 V. The current was maintained by a galvanostat with a function generator.

Prepared electrode characterization

All the electrochemical experiments were performed in a standard one-compartment three-electrode cell. The reference electrode was SCE and the counter electrode was platinum. All electrode potentials were referred to this reference electrode. The working electrode was natural phosphate modified carbon paste electrode (NP-CPE).

Apparatus

Electrochemical 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).

RESULTS AND DISCUSSION

Characterization of prepared electrodes surfaces

The surface structure of natural phosphate modified carbon paste surface was observed using scanning electron microscopy (Figure 1). The film layer of natural phosphate was formed on the surface of carbon paste electrode; it was not disintegrated or detached from the surface when immersed in the electrolytic

Solution ($0.1\text{M Na}_2\text{SO}_4$)

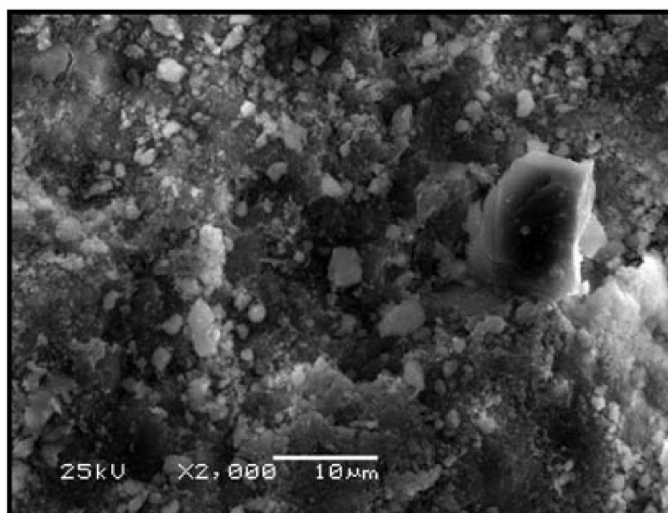


Figure 1 : Scanning electron micrograph of NP-CPE

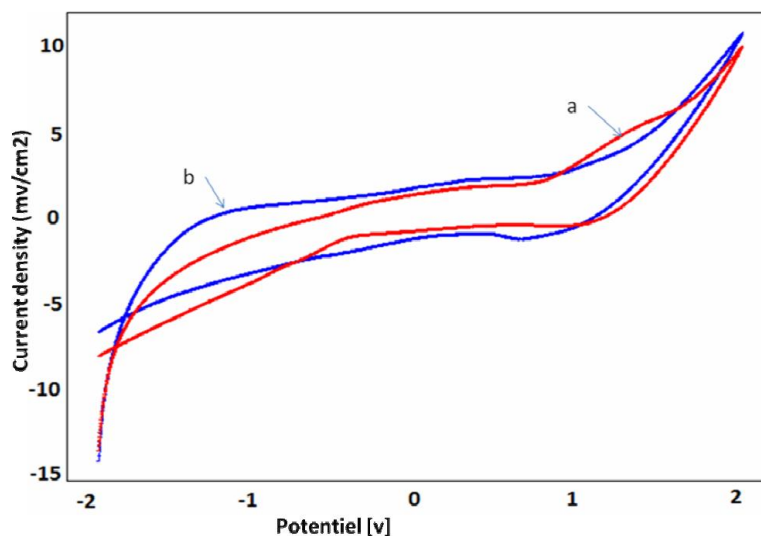


Figure 2 : Cyclic voltammograms recorded in electrolytic solution, at 100 mV/s, at a- carbon paste electrode, b- NP modified carbon paste electrode

The cyclic voltammograms (CVs) of the natural phosphate modified carbon paste electrode (NP-CPE) and carbon paste electrode (CPE) were recorded in the supporting electrolyte (0.1 M Na_2SO_4) (Figure 2).

We can see that the shape of the cyclic voltammogram was modified in the presence of natural phosphate onto CPE surface, suggesting that the carbon paste electrode was effectively modified by natural phosphate.

Electrochemical detection of studied metals

The experimental conditions have been optimized and the response characteristics determined in a previous work^[13]. The results obtained are:

- pH \approx 7.2
- Preconcentration time = 15 min.

Two reduction peaks P1 and P2 (Figure 3) were observed in the potential range scanned from 0.8 to 0.8 V probably due respectively to $\text{PQ}^{2+}/\text{PQ}^+$ and PQ^+/PQ^0 redox couple. These illustrations are consistent with those described elsewhere for paraquat^[25, 26]. Although, as a precautionary measure, all solutions were de-aerated by bubbling pure nitrogen gas prior to each electrochemical measurement, we did not observe any detectable effect on the analytical response of the electrodes when solutions were not de-aerated, indicating that residual oxygen in the sample solutions has no observable effect on the adsorption of paraquat onto NP. A control experi-

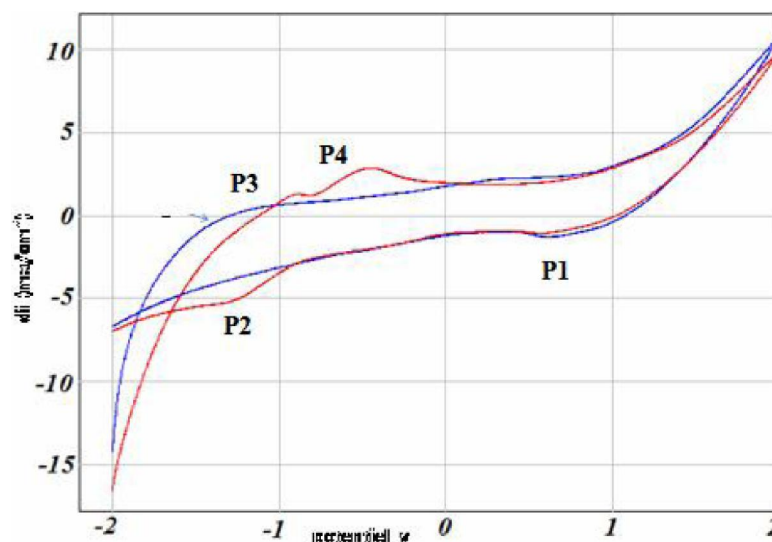


Figure 3 : Cyclic voltammograms recorded in electrolytic solution, at 100 mV/s, phosphate naturelle modified carbon paste electrode, in 0.1 M Na₂SO₄ solution (a), and after exposing to paraquat solution (b)

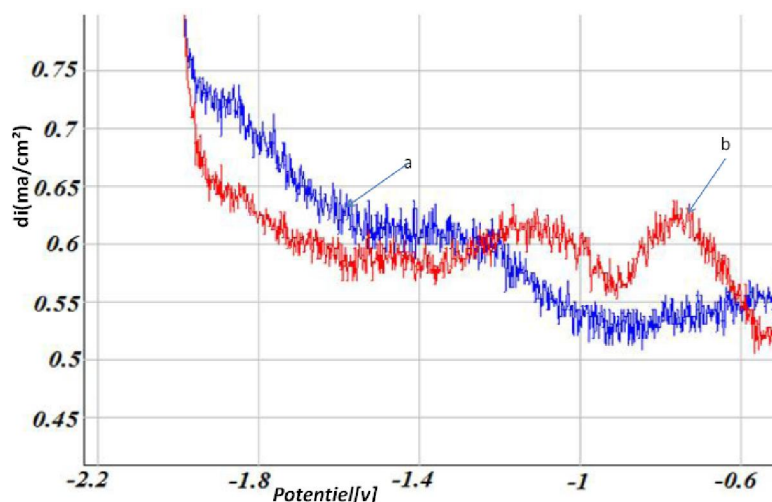


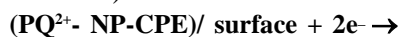
Figure 4 : Square wave voltammograms obtained for PN-pectively, in supporting solution (a), and after exposing electrode to paraquat solution (b)

ment was investigated under the same conditions in the absence of NP; no redox peaks were observed at low concentration. A possible mechanism for the NP-CPE reactions is attributed to the following steps:

Preconcentration step via paraquat adsorption (open circuit cell)



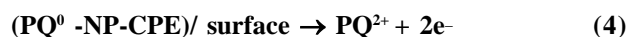
Accumulation and reduction steps (closed circuit cell)



Mass transport of PQ²⁺ to the electrode surface and subsequent reduction of the received paraquat ions as:



Stripping step (closed circuit cell)



The influence of the scan rate was studied with NP-CPE immersed for 15 min in 7,8.10⁻³ mol L⁻¹ of paraquat.

The square wave voltammograms (SWV's) corresponding to the determination of paraquat, were recorded in the supporting electrolyte are illustrated in Figure 4. a and after, 15 min of accumulation in a

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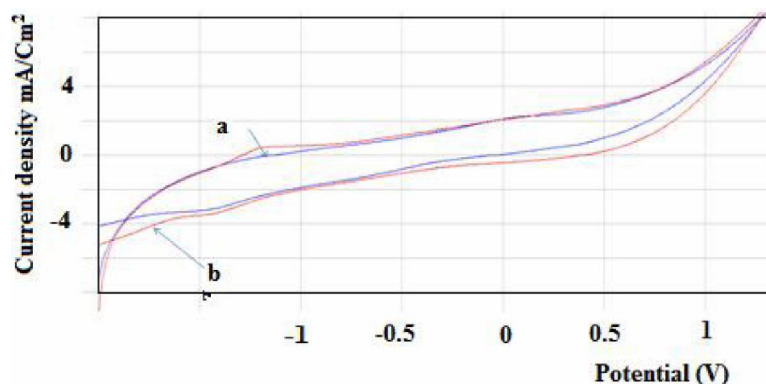


Figure 5 : Cyclic voltammograms recorded in electrolytic solution, at 100 mV/s, at PN modified carbon paste electrode, in 0.1 M Na_2SO_4 solution (a), and after exposing to diquat (b)

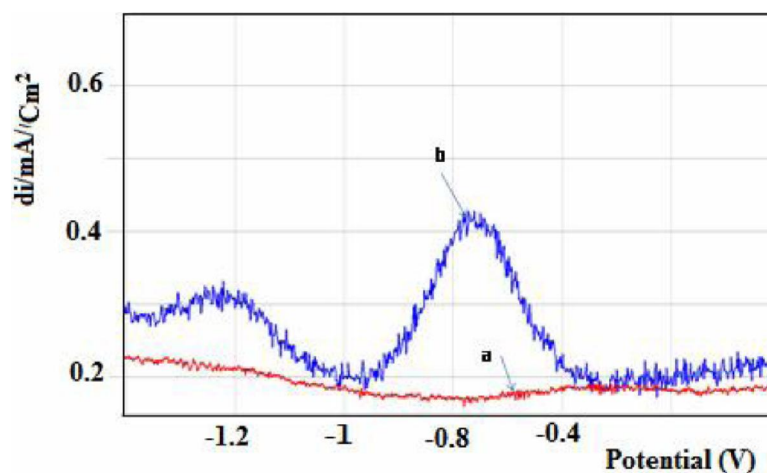


Figure 6 : Square wave voltammograms obtained for PN-respectively, in supporting solution (a), and after exposing electrode diquat solution (b)

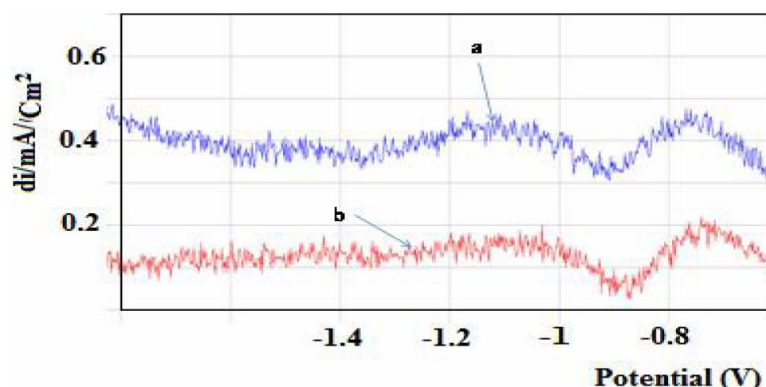


Figure 7 : Square wave voltammograms obtained for PN-respectively, in supporting solution, after exposing electrode to 7.8mM/l paraquat contaminated solution. (a) – before moringa treatment, b – after moringa treatment

solution containing paraquat (Figure 4.b).

No peak is observed in the electrolytic medium, however after accumulation of the electrode in the solution containing paraquat it there's appearance of two peaks.

The performance of the PN-CPE is tested to, on the preconcentration of diquat from aqueous solu-

tion. As can be seen from Figs. 5 and 6, two peaks appears, respectively, in SQW and cyclic voltammograms, the first one attributed to diquat reduction, at -0.9 V, the second at -0.6 V corresponding to the oxidation of diduat.

Chelating effect of moringa oleifera

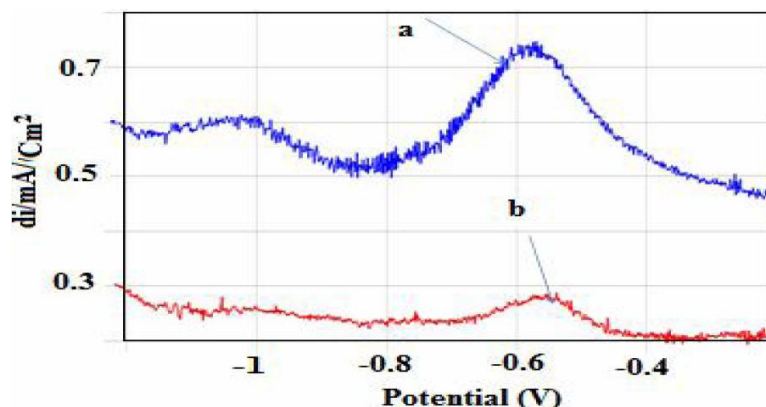
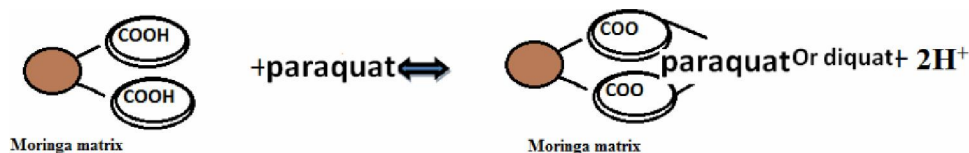


Figure 8 : Square wave voltammograms obtained for PN-respectively, in supporting solution, after exposing electrode to diquat contaminated solution. (a) – before moringa treatment, b – after moringa treatment



Moringa oleifera is the best known species of the *Moringaceae* family. *Moringaceae* is a family of plants belonging to the order *Brassicales*. It is represented by fourteen species and a single genus (*Moringa*), being considered an angiosperm plant. It is a shrub or small tree which is fast growing, reaching 12 meters in height. It has an open crown and usually a single trunk. It grows mainly in the semi-arid tropics and subtropics. Since its preferred habitat is dry sandy soil, it tolerates poor soils, such as those in coastal areas^[15].

Firstly, the *Moringa oleifera* was prepared according the following procedure^[14]. *Moringa oleifera* seeds collected for the analysis were shelled off and sun-dried to maintain constant weight. The sun-dried seeds were grinded into powdered form using machine. The powdered was added to the solutions containing pesticides. After 15 min of contact with moringa oleifera, the solutions were purified and analysis in electrochemical sensor.

The SQWV's recorded at carbon paste electrode modified with NP film, in supporting solution containing paraquat (curve a) and after addition of the moringa oleifera (curve b), are shown in Figure 7. The peak current decreased considerably after moringa treatment. This current density reduction is due to a sharp decline in paraquat and diquat concentrations, which suggests that moringa has a strong complexing power of pesticides (Figures 7 and 8).

We note that the solution pH was varied after moringa treatment. It was decreased from 7.2 to 6.5.

The decrease in pH of the treated solution, suggests to us that the moringa exchanged two protons against the metal ion. The proposed mechanism is as follows:

CONCLUSION

In conclusion, it was possible demonstrating the potentiality of the proposed electrodes for determining pesticides. Such a sensor is characterized by a higher sensitivity and reproducibility.

The *Moringa oleifera* seeds have the ability to retain pesticides. The herbicides is sequestered by chemical sites naturally present in the moringa matrix. The chelating process is rapid and takes place under normal temperature and pressure. *Moringa oleifera* is an environmentally-friendly natural complexing most suitable for the treatment of water containing undesirable pesticides concentrations. The removal efficiencies were 70% for diquat and 60 for paraquat. It is an eco-friendly technology that is economically more advantageous than other treatment alternatives.

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