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## ORIGINAL ARTICLE

# Square wave voltammetric determination of diquat using natural phosphate modified platinum electrode



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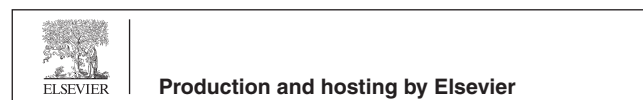
Platinum electrode;  
Natural phosphate;  
Diquat;  
Square wave voltammetry

**Abstract** A platinum electrode modified with natural phosphate (NP) was evaluated as an electrochemical sensor for diquat (DQ) in aqueous medium. The electrode was prepared by the deposition of natural phosphate on the platinum surface. Diquat was preconcentrated on the surface of the modified electrode by adsorbing with natural phosphate and reduced at a negative potential in 0.1 M K<sub>2</sub>SO<sub>4</sub> solution. The influence of accumulation time and pH of the electrolytic solution were investigated. The calibration graph obtained under the optimized conditions was linear with a correlation coefficient of 0.9813 at levels near the detection limits up to at least  $5.32 \times 10^{-9}$  mol L<sup>-1</sup> with the relative standard deviation (RSD) lower than 3.37%. Interferences by some metals were investigated. Fe, Zn, Cu, MnO<sub>4</sub> and Hg apparently affected the peak currents *P*<sub>1</sub> and *P*<sub>2</sub> of diquat. The natural phosphate modified platinum electrode was applied to the determination of diquat in natural water samples. The results indicate that this electrode is sensitive and effective for the determination of diquat. © 2012 Production and hosting by Elsevier B.V. on behalf of King Saud University. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/3.0/>).

## 1. Introduction

Diquat is still largely used for preharvest desiccation and weed control of various crops, and as really interesting materials for investigating novel chemically-modified electrochemical systems, owing to their reversible and electrocatalytic behavior

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(Murray, 1984; Bird and Kuhn, 1981). The incidence of diquat poisoning, often through suicidal intent rather than accidental ingestion, is still a major problem in many countries. Because of its acute toxicity to mammals and humans (Vale et al., 1987), the quantitative analysis of these compounds, and especially residue analysis, are of prime interest.

Several methods based on different analytical techniques have been reported for the determination of diquat; i.e. Liquid chromatography–electrospray ionization mass spectrometry (MRM) (Aramendía et al., 2006), Solid-phase extraction (SPE) (Grey et al., 2002), Fluorescence and Raman spectroscopy (Carrillo-Carrion et al., 2011), High performance liquid chromatography (HPLC) (Chiaki Fuke et al., 2002; Zougagh et al., 2008), Capillary electrophoresis (CE) (Núñez et al.,

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2001) and kinetic-spectrophotometric method (Díaz et al., 2002). Most of these methods are unsuitable for on-site screening, however, because of their size, cost, and the time required to perform the analysis. There is, therefore, an urgent need for a simple, relatively cheap, sensitive, and reliable method for on-site measurement of toxic compounds in many areas of application, for example biomedical, natural and industrial samples. Therefore a fast and accurate analytical method for the estimation of diquat exposure has been necessary.

In the last years, the use of an electrode modified chemically by different types of organic and inorganic compounds has been one of the most promising areas of analytical sciences (Chen et al., 2006; Yeh and Wang, 2006; Kotkar and Srivastava, 2006). The greatest interest in the use of a chemically modified electrode is due to its capacity to act as a redox mediator, increasing the charge transfer between the electrode and the redox species, thus promoting an improvement in the analytical sensitivity (Leznoff and Lever, 1989).

More specifically, the electrochemical detection of diquat has been performed on different electrode surfaces, including solid electrodes (El Mhammedi et al., 2008, 2009), dental amalgam electrode (DAE) (Melo et al., 2009) and mercury electrode (Walcarius and Lamberts, 1996). This electroanalytical technique is thus less sensitive to the effects of matrix interferences, a property which characterizes its success in electroanalysis (Melo et al., 2009; Kalcher et al., 2009).

This paper describes a square wave voltammetric (SWV) procedure for the determination of traces of diquat by using a natural phosphate film coated platinum electrode (NP-Pt). The interference of some common heavy metal ions, such as Fe, Zn, Cu and Hg was investigated. The performance of analytical method and the NP-Pt/DQ interaction was investigated using cyclic voltammetry, square wave voltammetry and electrochemical impedance spectroscopy. Some experimental conditions were optimized and a voltammetric method for the determination of diquat in natural water was proposed and the result was satisfactory.

## 2. Experimental

### 2.1. Reagent

Diquat, potassium sulfate, and nitric acid were of analytical grade and from Aldrich. Standard metal solutions of mercury, zinc, iron and copper nitrates were purchased from Fisher Scientific. A natural phosphate (NP) used in this work was obtained in the Khouribga region (Morocco) (El Mhammedi et al., 2007). Stock solutions of diquat were prepared by dissolving diquat in deionized water (DW). All preparations and dilution of solutions were made with deionized water.

Provisions were made for oxygen removal by bubbling the solution with azotes gas for about 5 min then the solution was blanketed with azotes gas while the experiment was in progress. For reproducible results, a fresh solution was made for each experiment.

### 2.2. Instrumental

Electrochemical measurements were performed using a voltmeter potentiostat (model PGSTAT 402, Eco Chemie B.V., Utrecht, The Netherlands) driven by the general purpose

electrochemical systems data processing software (voltalab master 4 software) connected to a Pentium IV computer run under windows 98 and a conventional three electrode cell. All voltages were reported with respect to Ag/AgCl (3 M KCl) reference electrode, Platinum was used as the auxiliary electrode and NP-Pt as a working electrode.

The pH-meter (Radiometer Copenhagen, PHM210, Tacussel, French) was used for adjusting pH values. The coated specimen was examined using a scanning electron microscope (SEM, Jeol JSM-5500).

### 2.3. Electrode preparation

Prior to all measurements, the platinum plate, with a dimension of  $0.5 \times 0.5 \text{ cm}^2$ , was polished with a different emery paper up to 1200 grade, washed thoroughly with bidistilled water degreased and dried with acetone. The natural phosphate was treated by techniques involving attrition, sifting, calcinations ( $900 \text{ }^\circ\text{C}$ ), washing, and recalcination. Glycidoxypolytrimethoxysilane, and aminopropyltrimethoxysilane were mixed and diluted by water containing glycerol and ethanol to make a sol-gel paste to bind natural phosphate particles. A special NP-paste suspension was prepared by mixing the fine NP powder with the paste solution with a solid/liquid ratio of 2.0. The paste was spread on the platinum electrode for electrochemical studies. Deposits were heated at  $25 \text{ }^\circ\text{C}$  for 24 h.

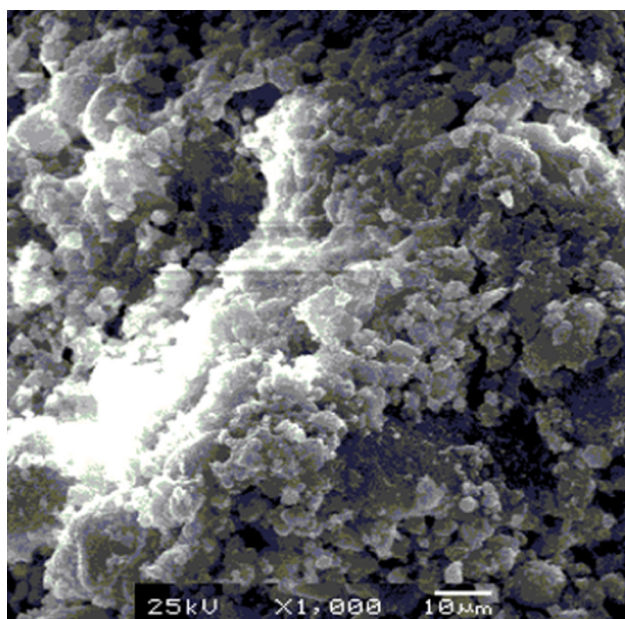
### 2.4. Procedure

Under ambient conditions the platinum electrode modified with natural phosphate was immersed in a cell containing a standard solution of diquat and 20 mL of supporting electrolyte ( $0.1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ ). Meanwhile the solution was stirred by a 1.2 cm magnetic stirrer bar (rotating about 600 rpm) at open circuit to get the chemical deposition. Cyclic voltammetry was used to evaluate the electrochemical properties of the electrodes. To monitor the uptake and release of the analyte from the electrodes, square wave voltammetry was employed because of its better detection limit. The square wave voltammetry was recorded in the range from  $-0.3 \text{ V}$  to  $-1.3 \text{ V}$ , for which the scan rate is  $1 \text{ mV s}^{-1}$ , step potential 25 mV; amplitude 5 mV and duration 5 s. Optimum conditions were established by measuring the peak currents in dependence on all parameters. Electrochemical impedance spectroscopy (EIS) was carried out by the same three electrode-cell setup described above before and after the accumulation step. Impedance spectra were obtained in the frequency range between 100 kHz and 10 mHz with 10 points per decade at the potential of 0 V after 30 min of immersion in non-de-aerated solutions.

## 3. Results

### 3.1. Voltammetric and adsorptive characteristics of the diquat modifier complex

Scanning electron microscopy (SEM) was used to study the surface of a typical modified electrode. The result is shown in Fig. 1. Natural phosphate particle sizes can be seen to be between  $\sim 1 \text{ }\mu\text{m}$  and  $\sim 20 \text{ }\mu\text{m}$ . This film was not disintegrated or detached from the surface when immersed in the electrolytic solution. The porosity of coating, especially the porosity



**Figure 1** Scanning electron micrograph of natural phosphate/platinum.

connected with the substrate is a very important factor for fixing diquat onto NP/Pt surfaces.

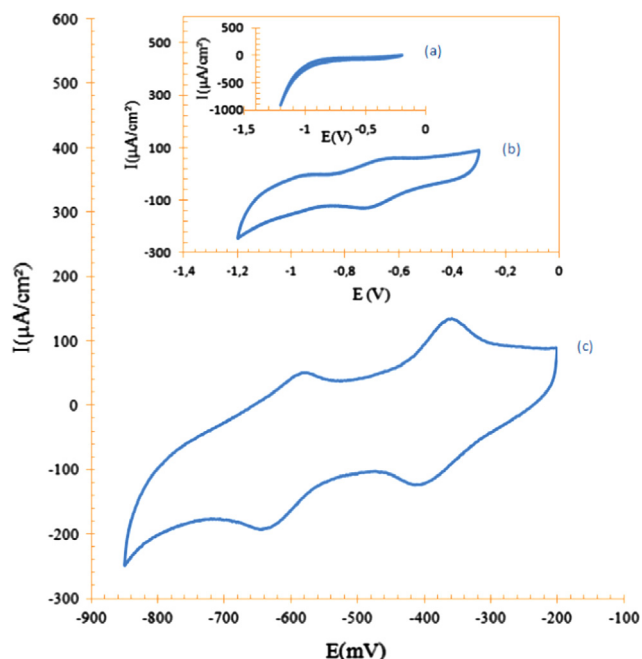
Cyclic voltammetry revealed a reversible reduction and oxidation of diquat at electrode surfaces. It was observed that the signal of diquat obtained from natural phosphate modified platinum electrode is higher compared to that from the unmodified platinum electrode (Fig. 2). Although the cyclic voltammetry technique is limited for the determination of diquat at unmodified platinum electrode, in the presence of natural phosphate modifier the peak current was rapidly increased and therefore the detection limit decreased.

### 3.2. Electrochemical impedance spectroscopy (EIS)

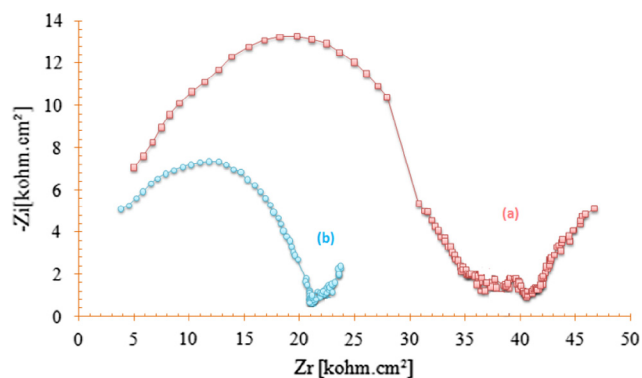
EIS was carried out on a natural phosphate modified platinum electrode (NP/Pt) surface in  $0.1 \text{ mol L}^{-1} \text{ K}_2\text{SO}_4$  in the absence and the presence of diquat at 298 K after 10 min of immersion (Fig. 3) in a frequency ranging from 100 kHz to 10 mHz with an AC amplitude of 5 mV. The charge-transfer resistance ( $R_t$ ) values are calculated from the difference in impedance at lower and higher frequencies, as suggested by Tsuru et al. (1978). The double layer capacitance ( $C_{dl}$ ) and the frequency at which the imaginary component of the impedance is maximal ( $-Z_{max}$ ) are found as represented in the equation:

$$C_{dl} = (1/\omega)R_t; \quad \text{where} \quad \omega = 2f_{max}$$

The impedance parameters derived from these investigations are mentioned in Table 1. It appears clearly from these data that the capacitance at the interface increases when the natural phosphate film is exposed to diquat. This observation gives another evidence for diquat adsorption on the natural phosphate surface as part of an integrated process leading to the electrolytic reduction of diquat at the natural phosphate surface. The observed decrease of the charge-transfer resistance means also that the modified electrode becomes more conductive, which can be explained by the presence of diquat on the electrode surface.



**Figure 2** Cyclic voltammogram of: (a) NP/Pt electrode before any contact with diquat, (b) platinum electrode and (c) PN/Pt electrode after preconcentration in diquat solution during 10 min; supporting electrolyte is  $0.1 \text{ mol L}^{-1} \text{ K}_2\text{SO}_4$ , pH 7.5; the scan rate was  $100 \text{ mV s}^{-1}$ .  $[\text{DQ(II)}] = 3 \times 10^{-3} \text{ mol L}^{-1}$ .



**Figure 3** Impedance spectra at 0 V (a) natural phosphate modified platinum electrode and (b) DQ(II)-NP/Pt. Conditions are as described in Fig. 2.

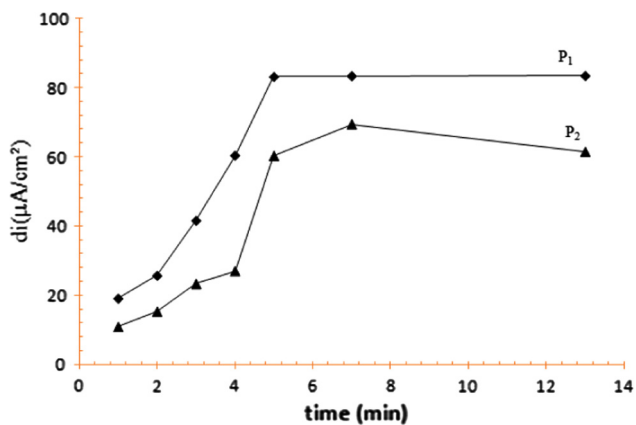
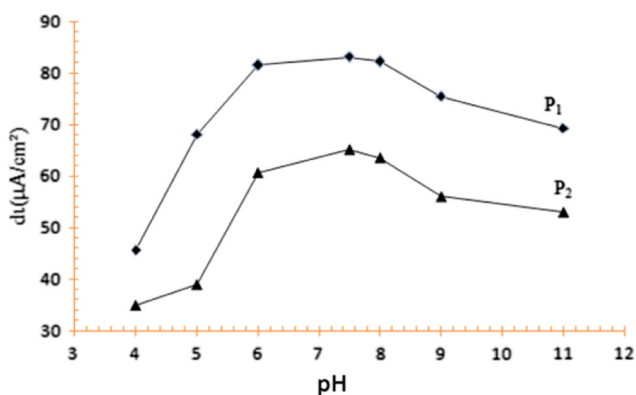
### 3.3. Optimization of the analytical conditions

The dependence of square wave voltammetric peak current on the accumulation time for  $1.0 \times 10^{-4} \text{ mol L}^{-1} \text{ DQ(II)}$  is shown in Fig. 4. The peak current increases with increasing accumulation time, indicating an enhancement of DQ(II) ion concentration at the surface of the electrode, when  $t = 5 \text{ min}$ , the peak current becomes constant. Hence for all subsequent measurements an accumulation time of 5 min was employed.

Fig. 5 demonstrates that the diquat adsorption by natural phosphate is pH dependent. The optimum pH ranges for diquat adsorption were 6–8.5. So pH 7.5 was selected for the recommended procedure. Also at low pH, the complex formed via the interaction between diquat ions and natural phosphate

**Table 1** Electrical parameters calculated from the impedance spectra in  $0.1 \text{ mol L}^{-1} \text{ K}_2\text{SO}_4$  for the NP/Pt and DQ(II)-NP/Pt solution interfaces.

	$R_1$ ( $\text{k}\Omega \text{ cm}^2$ )	$R_2$ ( $\text{k}\Omega \text{ cm}^2$ )	$C$ ( $\text{pF/cm}^2$ )	Diameter of circle
NP/Pt	1.934	33.18	149.8	34.17
DQ(II)-NP/Pt	1.0	20.13	191.8	21.13

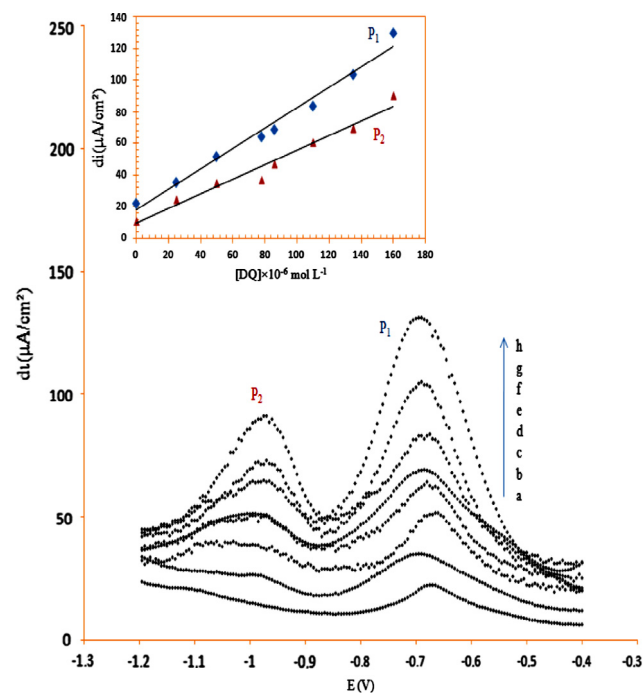
**Figure 4** Effect of preconcentration time on the SWV peak height obtained at NP/Pt of  $1.0 \times 10^{-4} \text{ mol L}^{-1}$  diquat in  $0.1 \text{ mol L}^{-1} \text{ K}_2\text{SO}_4$ ,  $\text{pH} = 7.5$ .**Figure 5** Effect of pH on SWV peak height of  $1.0 \times 10^{-4} \text{ mol L}^{-1}$  diquat at NP/Pt preconcentrated in  $1.0 \times 10^{-4} \text{ mol L}^{-1} \text{ K}_2\text{SO}_4$  during 5 min.

groups is expected to be destabilized since the values of conditional stability constants decrease with pH. As a result, the diquat ions were desorbed into the solution. Another explanation is that in acidic solution, there are more proton ions competing with diquat on the adsorption onto natural phosphate. However, the peak potentials do not seem to be affected by the concentration of  $\text{H}^+$ , suggesting the absence of any protonation step in the reduction mechanism, which is in close agreement with published works (Walcarius and Lamberts, 1996; Lu and Sun, 2000).

#### 3.4. Calibration curve

The square wave voltammetric determination of a series of standard solutions of diquat was performed under the

optimized working conditions described above (Fig. 6). The cathodic peak current at the platinum electrode modified with natural phosphate was proportional to the concentration of the DQ(II) in a range from  $9.5 \times 10^{-8} \text{ mol L}^{-1}$  to  $1.6 \times 10^{-4} \text{ mol L}^{-1}$ . However at concentrations starting from  $2.0 \times 10^{-4} \text{ mol L}^{-1}$  the signal tends to level-off corresponding to the saturation region of the natural phosphate. This represents the point where the accessible active site becomes full or saturated. It can be inferred that it is best to perform succeeding experiments within this linear region where the signal obtained is directly proportional to the amount of the analyte; not in the saturated part where there might not be enough exchange sites available or a very low concentration like  $9.5 \times 10^{-8} \text{ mol L}^{-1}$  where the effect of background errors will be bigger. The detection limit (DL,  $3\sigma$ ) was found to be  $5.32 \times 10^{-9} \text{ mol L}^{-1}$  and the quantification limit (QL,  $10\sigma$ ) was  $7.2 \times 10^{-8} \text{ mol L}^{-1}$ . The precision, expressed as a relative standard deviation (RDS), was 3.37% and 4.01% for peaks 1 and 2, respectively at a concentration level of  $1.0 \times 10^{-4} \text{ mol L}^{-1}$ . This precision is attributed to the properties of natural phosphate such as homogeneity, thermal stability and the high mechanical properties.

**Figure 6** Square wave voltammograms of diquat (II) accumulated at natural phosphate modified platinum electrode under optimization conditions: (a)  $9.5 \times 10^{-8} \text{ mol L}^{-1}$ ; (b)  $25 \times 10^{-6} \text{ mol L}^{-1}$ ; (c)  $50 \times 10^{-6} \text{ mol L}^{-1}$ ; (d)  $78 \times 10^{-6} \text{ mol L}^{-1}$ ; (e)  $86 \times 10^{-6} \text{ mol L}^{-1}$ ; (f)  $110 \times 10^{-6} \text{ mol L}^{-1}$ ; (g)  $140 \times 10^{-6} \text{ mol L}^{-1}$  and (h)  $160 \times 10^{-6} \text{ mol L}^{-1}$ .

**Table 2** Interferences of some metal ions on the determination of  $3 \times 10^{-3}$  mol L<sup>-1</sup> diquat.

Interfering ions	Concentration (mol L <sup>-1</sup> )	Peak current change (%)
Zn <sup>2+</sup>	$4 \times 10^{-3}$	-1.41
Cu <sup>2+</sup>	$4 \times 10^{-3}$	-1.39
Fe <sup>2+</sup>	$4 \times 10^{-3}$	-0.52
Hg <sup>2+</sup>	$3 \times 10^{-6}$	7.13
MnO <sub>4</sub> <sup>-</sup>	$3 \times 10^{-6}$	-2.92

**Table 3** Results obtained from the linear regression curves for the determination of DQ(II) at NP/Pt in natural waters.

Parameters	Peak 1	Peak 2
Equation	$y = 0.63X + 14.1$	$y = 0.45X + 9.03$
R <sup>2</sup>	0.989	0.985
Slope (A mol <sup>-1</sup> L)	0.63	0.45
Standard deviation ( $\sigma$ ) ( $\times 10^{-10}$ A)	66.36	79.05
Detection limit (mol L <sup>-1</sup> )	3.16	5.27
Quantification limit (mol L <sup>-1</sup> )	10.54	17.57
Relative standard deviation (%)	3.6	4.4
Recovery (%)	97.15	96.83

### 3.5. Interferences

The selectivity of this approach for the determination of diquat was evaluated by introducing concentrations of other ions into the diquat sample solution during the preconcentration step. Results are shown in Table 2. Metal ions can interfere with the determination of diquat (II) if they compete for complexation with the modifier. The presence of other ions such as Fe<sup>2+</sup>, Zn<sup>2+</sup>, Cu<sup>2+</sup> and Hg<sup>2+</sup> interfere seriously with the determination of  $3.0 \times 10^{-3}$  mol L DQ(II). Fe<sup>2+</sup>, Zn<sup>2+</sup> and Cu<sup>2+</sup> ions interfere because of their precipitation with the SO<sub>4</sub><sup>2-</sup> and their competition with diquat for adsorbing onto natural phosphate at modified electrode and decreased peak currents of diquat. The KCN were added into the sample cell to remove the interference. The Hg<sup>2+</sup> tends to reduce at electrode and form a film on the surface of electrode, which can promote the reduction of diquat at the modified electrode. The stripping peak currents of diquat increase in the presence of Hg<sup>2+</sup>, due to the preconcentration of these ions by forming a complex with a reduced mercury film onto the surface of the modified electrode. Permanganate can be directly electrochemically reduced, and results in a significant Faradaic current, which interferes with the determination of diquat.

### 3.6. Application

The natural phosphate modified platinum electrode was applied to the determination of diquat in river water (Oum Er Rabia; Tadla-azilal region, Morocco) by square wave voltammetry under the optimized conditions using the standard addition method. All of the samples were used without any further treatment to prepare the support electrolyte (0.1 mol L<sup>-1</sup> K<sub>2</sub>SO<sub>4</sub>). No diquat traces were found when the proposed procedure was used. However, it was observed that the peak

current versus diquat added into the real sample solution increased linearly; hence the proposed method is suitable for the determination of diquat in these waters. Recovery experiments were also carried out in order to evaluate the interference of matrix effects of the natural water samples on the reduction of diquat on natural phosphate modified platinum electrode (Table 3). Recovery found for the samples spiked with  $1.0 \times 10^{-4}$  mol L<sup>-1</sup> diquat were 97.15% and 96.83% for the peaks 1 and 2, respectively. The percentages obtained presented satisfactory values for the proposed electroanalytical methods (El Mhammedi et al., 2008, 2009), thus indicating the suitability of the proposed method for use in natural water samples.

## 4. Conclusion

A highly sensitive platinum electrode modified with natural phosphate was fabricated and successfully applied to diquat analysis. This method is very simple, offering a relatively short analysis time of 5 min, is inexpensive, with easy operability, and is applicable for field use. It has a low detection limit of 5.32 nmol L<sup>-1</sup> and is applicable with sufficient reliability to the determination of diquat in natural water.

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