

Full Paper

Electroanalysis of the Herbicide Diquat by Electrochemical Detector Containing Particles of Clay in Environmental Water

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Abstract- Clay modified carbon paste electrode (CPE-C) its applicability for electroanalysis of N, N'-ethylene-2,2'-bipyridinium (diquat) has been described in the present work. Electrochemical modification was performed by electronic impedance spectroscopy (EIS) and cyclic voltammetry (CV) in the range of -0.6 V to 1.2 V in 0.1 M K₂SO₄ (pH 3). The voltammetric method behavior of DQ is suggested where an anodic and cathodic peak appeared at E_{pa}=0.55 V and E_{pc}=0.1 V, successively. These peaks obtained from the reversible redox of DQ at the CPE-C surface. The optimal preconcentration time and percentage of clay insert were 10 min and 20% respectively. The proposed method exhibits certainly an electro-catalytic

success toward DQ redox. The peaks current recorded using cyclic voltammetry has been linearly dependent on the DQ concentration ranging from 1×10^{-5} to 5×10^{-5} molL⁻¹. The detection limit (DL) calculated for the anodic peak is 5.33×10^{-8} molL⁻¹. Then relative standard deviation for 2×10^{-5} molL⁻¹ diquat has been 4.3% for nine repetitions. The proposed detector has been successfully applied for DQ electroanalysis in a river water sample with a DL of 8.17×10^{-8} molL⁻¹.

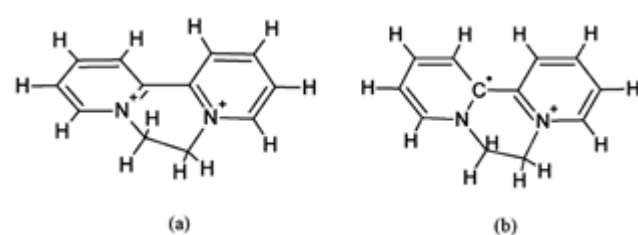
Keywords- Electroanalysis, N, N'-ethylene-2,2'-bipyridinium, Clay, Cyclic voltammetry, Electrochemical impedance spectroscopy

1. INTRODUCTION

N, N'-ethylene-2,2'-bipyridinium (DQ) (Scheme 1) was extensively utilized as pesticides in olives. Its harmful to fish, algae, insects and crayfish [1] acute oral LD50 for diquat (0.4 g/Kg) is relatively weak [2]. The harmful effect on human health of acute exposure is well documented [3]. DQ causes damage to the lungs at low concentrations. Nevertheless, DQ has had severe adverse effects on the functioning of the nervous system. The cationic nature of DQ makes their analysis very difficult. Several analytical methods have been reported for the analysis of DQ, such as liquid chromatography (LC)–electrospray ionization (ESI) mass spectrometry (MS) [4], Solid-phase extraction [5], Fluorescence and Raman spectroscopy [6], HPLC [7,8], capillary electrophoresis (CE) [9] and kinetic-spectrophotometric method [10]. The majority of these methods are inappropriate for on-site screening, nevertheless, because of the time required to do the analysis, their size and cost. There is, therefore, a great need for a clear, sensitive, less expensive and reliable technique for the analysis of harmful compounds in various fields of application such as biomedical, industrial and natural samples. Therefore, a rapid and precise analytical technique for determining the diquat was important. Over the past decade, the use of a sensor modified by different types of inorganic and organic substances has been one of the promising areas of the analytical sciences [11-13]. The biggest importance in the usage of a chemically modified sensor comes from it is the capability to operate as a redox intermediary, increasing the charge transfer among the redox species and the electrode surface, therefore encouraging an amelioration in the electroanalytical sensitivity [14]. More particularly, the electrochemical analysis of DQ was performed on several electrodes, including solid electrodes [15,16], dental amalgam electrode [17] and mercury electrode [18]. This electroanalytical method is, therefore, less sensitive to the influences of interference, which characterizes its success in the electrochemical analysis [19,20].

The electroanalysis methods available for use with modified electrodes are cyclic voltammetry and square wave voltammetry [21] has been shown to be very sensitive for the detection of pesticides [22-24]. The use of voltammetry makes it possible to record important information on the characteristics of the charge transfer mechanisms involved in the electrochemical reaction.

In the present work, we have described the preparation of an electrochemical detector based on natural clay for the electroanalysis of DQ on the surface of the CPE-C in an electroanalytical medium. The success of the CPE-C surface towards the electrochemical analysis of DQ is evaluated by the CV and EIS methods. The prepared electrode was applied to detect traces of DQ in a real matrix such as water samples from the Oum Erbie river (Morocco) without any pretreatment in order to assess its reproducibility and repeatability.



Scheme 1. Structure of DQ (a) and cation DQ (b)

2. EXPERIMENTAL SECTION

2.1. Instrument and reagent

The electrocatalytic activity of the CPE-C surface at DQ redox was obtained by CV and EIS using a computer for control, data processing, and storage. The software utilized was the voltalab master 4. The redox reaction was carried out in an electrochemical cell with three electrodes: Ag/AgCl/KCl (3 M) was used as a reference electrode, a platinum wire as a counter electrode and working electrode CPE-C. The pH meter was utilized to adjust the pH values.

DQ and K_2SO_4 were purchased from Sigma Aldrich. The pH values were adjusted with sulfuric acid or potassium hydroxide. The natural red clay used was obtained in the region of Beni Mellal (Morocco). The aqueous solutions used in the present work have been prepared with distilled water. All the experiments were carried out at 25 °C.

2.2. Preparation of CPE-C and measurements procedure

CPE-C was prepared by mixing a carbon powder and the desired weight of clay. The body of the working electrode for all experiments was a cylinder that was tightly packed with mixed of carbon paste and clay. Electrical contact was made by means of a carbon rod. The working electrode used in this work has been a CPE-C (0.2 cm²).

Several solutions have been tested such as K_2SO_4 , H_2SO_4 , Na_2SO_4 , NaCl, and KCl. The better electroanalysis response has been recorded in pH=3 (K_2SO_4/H_2SO_4). The work process consists of measuring the electroanalysis responses on the surface of the CPE-C in the presence of DQ in the solution. A solution of known concentration of DQ was prepared in 0.1 molL⁻¹ K_2SO_4/H_2SO_4 (pH 3) and 20 ml of this solution were put in the electroanalysis cell. EIS and

CV were recorded from -0.6 to 1.2 V at 100 mVs^{-1} . Optimal conditions have been established by measuring the redox peak currents on all parameters.

3. RESULTS AND DISCUSSION

3.1. CV and EIS analysis

Figure 1 shows the cyclic voltammograms (CVs) recorded in the potential window from -0.6 V to 1.2 V on the CPE and CPE-C surface at the scan rate of 100 mVs^{-1} . It seems that the CVs have different forms, showing that the CPE surface has been effectively modified by the clay. The electroanalysis response of the CPE and CPE-C toward DQ redox has been studied by CV in 0.1 M K_2SO_4 (pH 3) in the presence of $1.0 \times 10^{-5} \text{ molL}^{-1}$ DQ. No peak is observed in the case of CPE (Figure 2a).

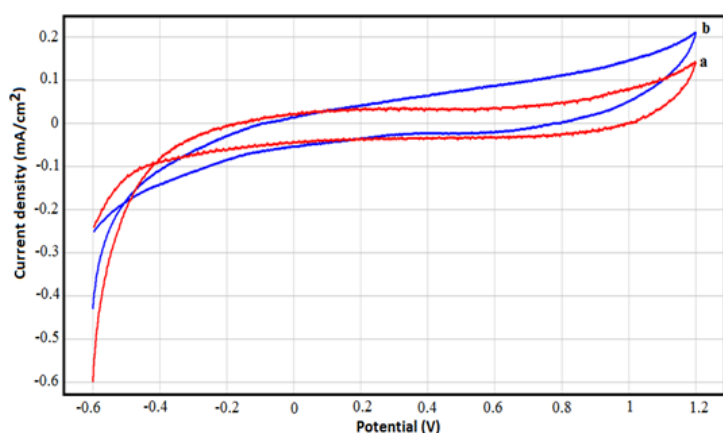


Fig. 1. CVs obtained for CPE (a) and CPE-C (b) in 0.1 M K_2SO_4 , pH 3, $t_p=10 \text{ min}$

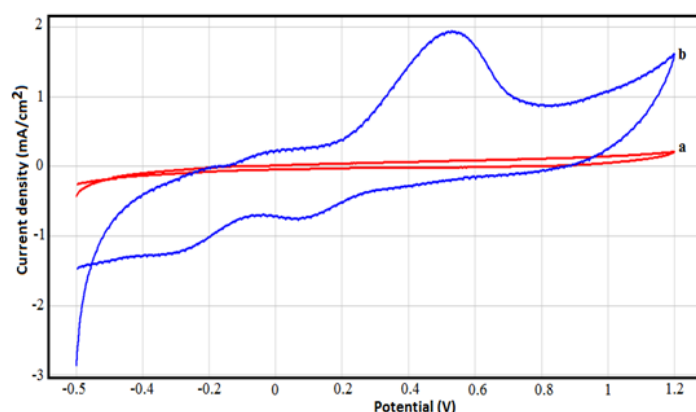


Fig. 2. CVs obtained for CPE (a) and CPE-C (b), $10^{-5} \text{ molL}^{-1}$ DQ, 100 mVs^{-1} , pH 3, $t_p=10 \text{ min}$

Figure 2b shows the anodic and cathodic peak at about $E_{pa}=0.55 \text{ V}$ and $E_{pc}=0.1 \text{ V}$, respectively. The CPE-C exhibited an excellent electrocatalytic redox of DQ compared to CPE.

The high sensitivity of this electrode has been confirmed by the EIS method (Figure 3). This EIS indicates an explanation for the adsorption of DQ on the CPE-C according to a process electrolytic redox of DQ on the CPE-C. The remarkable decrease in resistance to charge transfer explains why the CPE-C is more conductive, which means the presence of DQ on the surface of this electrode. According to this study, scheme 2 shows the possible mechanism of the redox reaction of DQ [25].

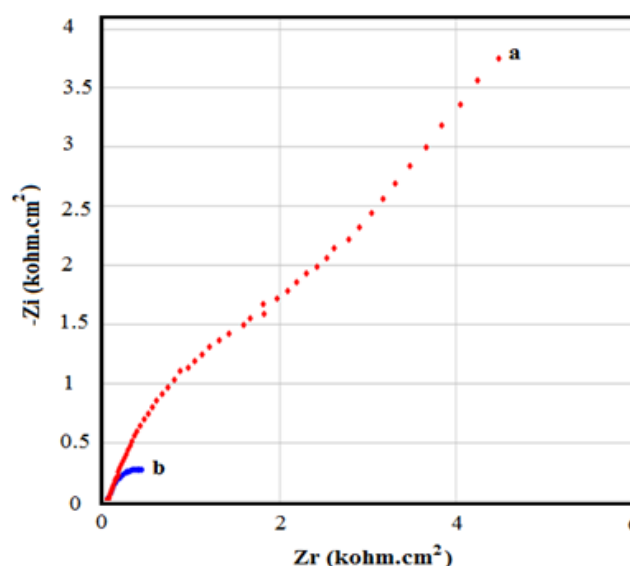
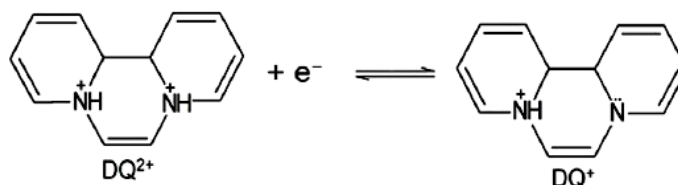


Fig. 3. EIS recorded for CPE (a) and CPE-C (b), $10^{-5} \text{ molL}^{-1}$ DQ, pH 3, $t_p=10 \text{ min}$



Scheme 2. Possible mechanism of DQ electrochemical redox

3.2. Effect of preconcentration time and percentage of clay insert

In addition to its electroanalytic properties, the CPE-C shows an excellent capacity for electroanalysis of DQ. This electrochemical analysis investigate has been performed by CV in 0.1 M K_2SO_4 (pH 3) containing $10^{-5} \text{ molL}^{-1}$ of DQ. The influence of the preconcentration time (t_p) on the voltammetric measurements has been made. Figure 4 shows an increase of the anodic peak current intensity during the first 10 min after this time has a stable plateau due to the saturation of the CPE-C surface. Then, 10 min has been utilized in all the experiments.

The increase of the clay loading from 5 to 70% by weight of carbon affects the DQ detection at the CPE-C (Figure 5). The anodic peak current of DQ increases with the increasing the clay

until 20%, beyond this value the peak current intensity decreases. So, a 20% of ratio by weight was utilized in the present work.

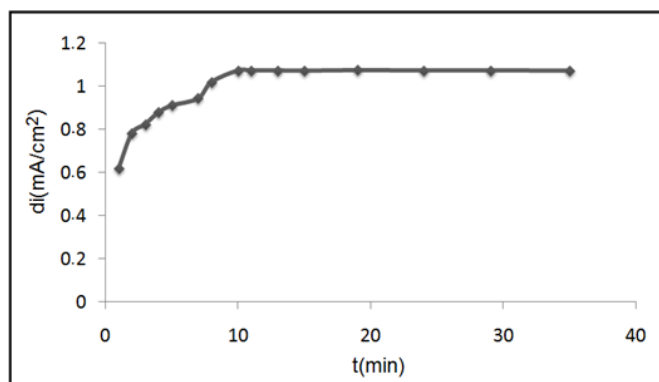


Fig. 4. Effect of t_p on the oxidation peak currents of DQ ($1 \times 10^{-5} \text{ molL}^{-1}$) at the CPE-C, 0.1 M K_2SO_4 (pH 3)

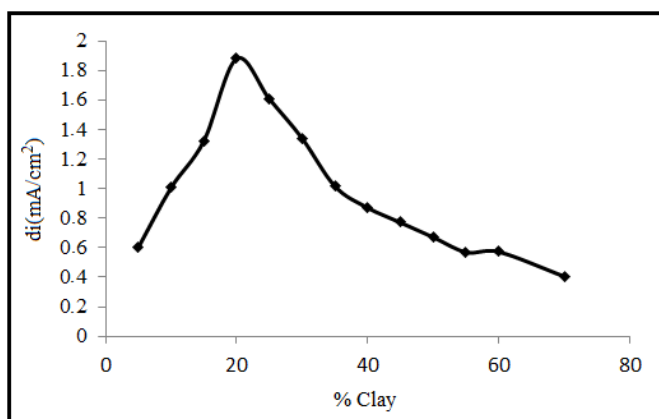


Fig. 5. Influence of the % clay on the oxidation peak currents of DQ ($10^{-5} \text{ molL}^{-1}$) at the CPE-C, K_2SO_4 (0.1 M, pH 3)

3.3. Scan rate and pH effect

The scanning rate effect on redox peaks current of DQ was studied at the CPE-C surface under the concentration of $2 \times 10^{-5} \text{ molL}^{-1}$ DQ in 0.1 M K_2SO_4 (pH 3). The redox peaks current of DQ increased by increasing the scan rate (Figure 6). The relationship of redox peaks current and scan rate has been a linear when the scanning rate increased between 60 and 160 mVs^{-1} (Figure 7). The cathodic and anodic peak shifted towards negative and positive potential respectively with increasing the scan rate. The adsorption phenomenon proposed a diffusion-controlled mechanism at the surface of CPE-C.

Figures 8 and 9 shows that the DQ adsorption on the CPE-C surface is dependent on pH. The excellent responses have been obtained at pH 3 on the working electrode surface toward

DQ redox. Therefore, at feeble pH, the complex obtained by the interaction of DQ with C is provided to be destabilized because of the values of stability constants decrease according to pH. Consequently, the DQ ions have been desorbed in the electrolytic medium. Another clarification is that into acidic solution, there are more H^+ competing with DQ at the adsorption onto CPE-C.

However, the peak potentials are not affected by the H^+ concentration due to the absence of protonation in the redox reaction, which is in agreement with previous work [18,20]. The potential of the oxidation peak shifted to positive values and the potential of the reduction peak shifted to negative values with increasing pH.

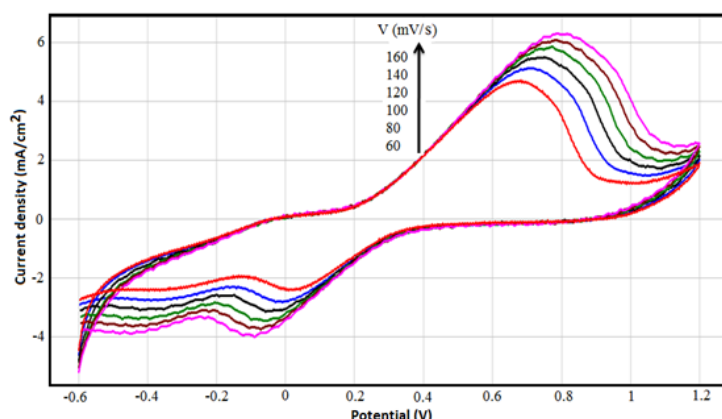


Fig. 6. CVs obtained on the CPE-C surface for $2 \times 10^{-5} \text{ mol/L}$ DQ at different scan rates, pH 3, $t_p = 10 \text{ min}$

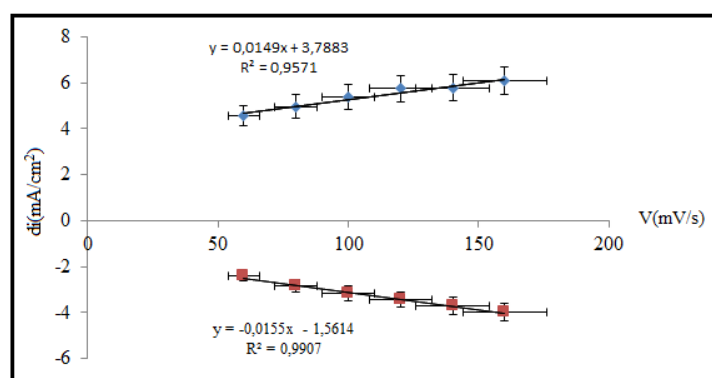


Fig. 7. The linearity between the redox peaks intensity and the scanning rates, pH 3, $t_p = 10 \text{ min}$

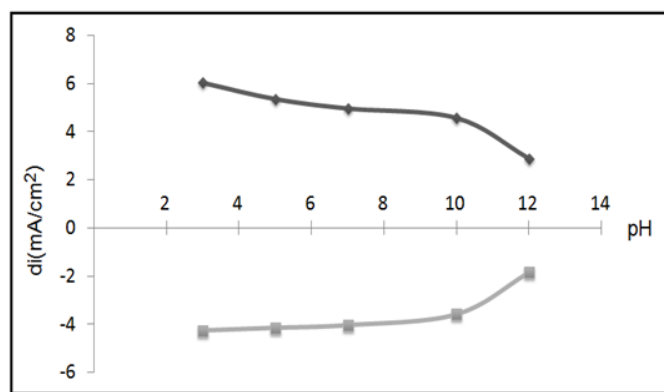


Fig. 8. Curves of the evolution of redox peaks current according to pH, $2 \times 10^{-5} \text{ molL}^{-1}$ DQ, 100 mVs^{-1} , $t_p=10 \text{ min}$

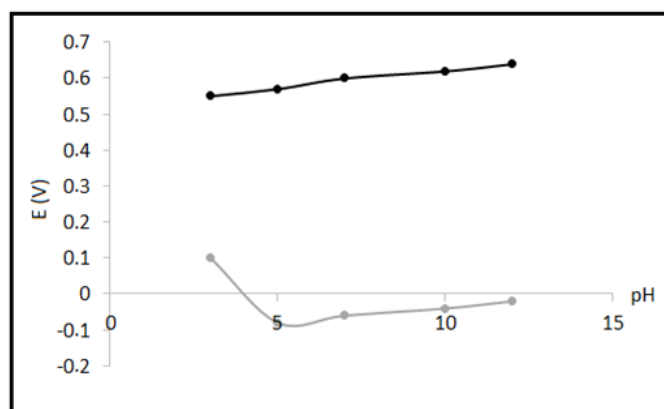


Fig. 9. Curves of the evolution of redox peaks potential according to pH, $2 \times 10^{-5} \text{ molL}^{-1}$ DQ, 100 mVs^{-1} , $t_p=10 \text{ min}$

3.4. Concentration effect

Before determining the effect of concentration, we were interested in optimizing the several electrochemical parameters (step, pulse, width, and period) that affect the determination of DQ at CPE-C using the CV. According to the obtained results, it was found that the excellent responses to DQ have been recorded with 30 mVs^{-1} , 140 ms, 100 mV, and 180 ms for step, pulse, width, and period, respectively.

The calibration curve was obtained for DQ underneath optimum experimental conditions. Figure 10 shows the CVs obtained on the CPE-C surface in the window between 1.0×10^{-5} and $5.0 \times 10^{-5} \text{ molL}^{-1}$ of DQ. The anodic and cathodic peaks current increases with the increasing of the concentration of DQ. It has also been noted that the potentials of the cathode and anode peaks move in the negative and positive directions respectively, indicating that the DQ molecule is adsorbed on the surface of the electrode. Figure 11 shows the linearity between the peak currents and the DQ concentration at the surface of CPE-C.

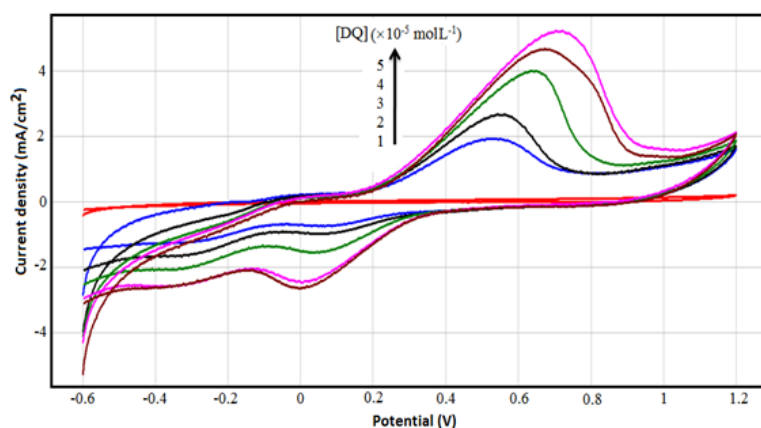


Fig. 10. CVs obtained for several concentrations of DQ on the CPE-C surface in 0.1 M K₂SO₄, pH 3, 100 mVs⁻¹, t_p=10 min

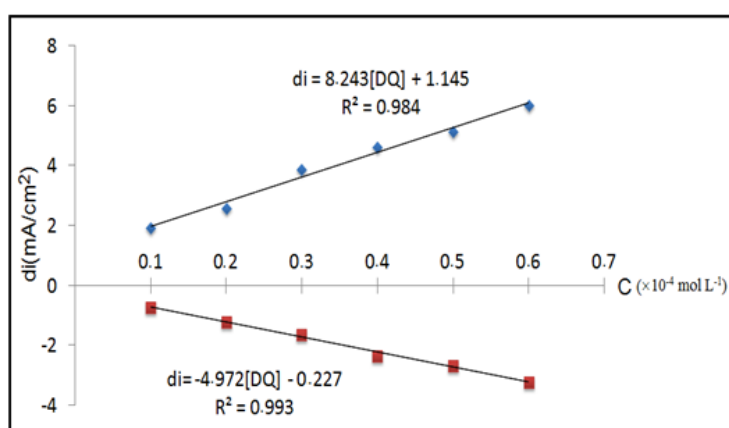


Fig. 11. Linearity between redox peaks versus the added DQ concentration, pH 3, 100 mVs⁻¹, t_p=10 min

Table 1. Comparison of the various electrodes using for DQ electroanalysis

Modified electrode	Analytical technique	DL	Ref.
Dental amalgam electrode	Cyclic voltammetry	$1 \times 10^{-7} \text{ mol L}^{-1}$	[17]
ND-MS/GCE	Square wave voltammetry	$1.1 \times 10^{-7} \text{ mol L}^{-1}$	[25]
Glassy carbon electrode	Square wave voltammetry	$1.3 \times 10^{-6} \text{ mol L}^{-1}$	[26]
Bismuth film minisensor	Square wave voltammetry	$8.7 \times 10^{-8} \text{ mol L}^{-1}$	[27]
Custom-made gold microelectrode	Square wave voltammetry	$6 \times 10^{-8} \text{ mol L}^{-1}$	[28]
Custom-made gold microelectrode	Square wave voltammetry	$1.31 \times 10^{-7} \text{ mol L}^{-1}$	[29]
CPE-C	Cyclic voltammetry	$5.33 \times 10^{-8} \text{ mol L}^{-1}$	Present work

The reactivity of the CPE-C surface towards the DQ electrochemical analysis is well-improved thanks to the clay. DL and QL were found on the oxidation peak current by the equations: $DL=3\ S/M$, $QL=10\ S/M$ (S: Standard deviation of the peak currents nine runs; M: Slope of the calibration curve). DL and QL have been found as $5.33\times 10^{-8}\ \text{molL}^{-1}$ and $1.77\times 10^{-7}\ \text{molL}^{-1}$, respectively. The DL obtained by CPE-C is comparable than those provided by the previous electrodes recapitulated in Table 1 [17,25-29]. The relative standard deviation (RSD) for nine measurements was calculated as 4.3% for $2.0\times 10^{-5}\ \text{molL}^{-1}$ of DQ. Figure 12 shows the behavior of impedance diagrams recorded for CPE-C in the presence of different concentrations of DQ.

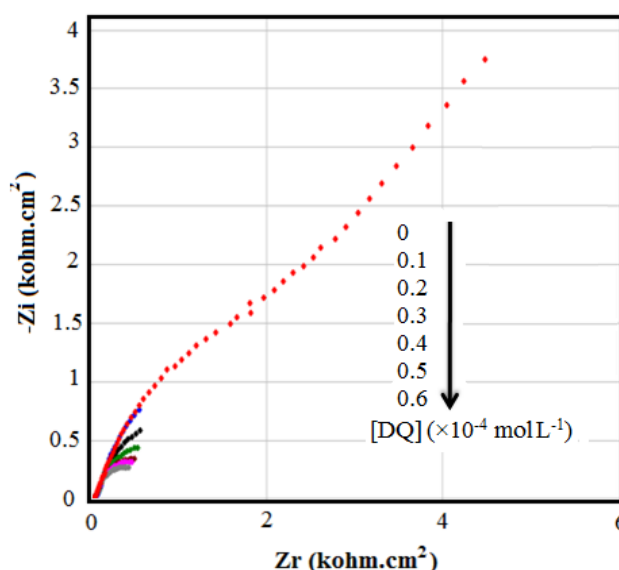


Fig. 12. EIS recorded in the presence of different concentrations of DQ, pH 3, $t_p=10\ \text{min}$

3.5. Detection of DQ in river water

To confirm the repeatability of the sensitivity of the CPE-C, the detection of DQ was done in samples of river water without any pretreatment.

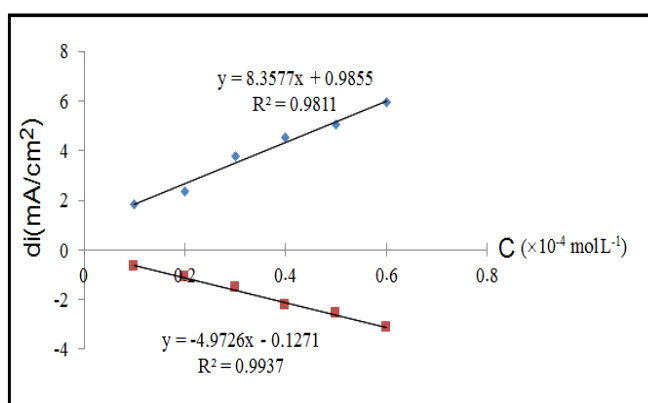


Fig. 13. Plot of peaks current versus DQ concentration in the optimum conditions

The proposed method was used to analyze river water samples contaminated with DQ at different concentrations. The redox peaks of DQ was well displayed. The linear calibration curve of DQ was obtained by varying the concentration from $1.0 \times 10^{-5} \text{ molL}^{-1}$ to $6.0 \times 10^{-5} \text{ molL}^{-1}$ for river water samples (Figure 13). The DL was found to be $8.17 \times 10^{-8} \text{ molL}^{-1}$ with RSD of 4.77%.

4. CONCLUSION

The CPE-C was utilized to determine DQ in 0.1 M K_2SO_4 (pH 3). DQ can produce a reversible redox process about $E_{pa}=0.55 \text{ V}$ and $E_{pc}=0.1 \text{ V}$. The electrochemical redox of DQ was followed by CV. This study has shown that CPE-C exhibits good electrocatalytic activity toward DQ redox. CV measurements exhibit a linear relationship in a concentration ranging from 1×10^{-5} to $5 \times 10^{-5} \text{ molL}^{-1}$. The DL calculated is $5.33 \times 10^{-8} \text{ molL}^{-1}$. At last, the presented working electrode has been successfully applied for the detection of DQ in river water. The simplicity of preparation, excellent reproducibility, and cheaper of the CPE-clay, also as vast linear concentration range, feeble DL, and good repeatability for DQ electroanalysis are the interesting advantages of CPE-C.

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