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Biomaterials Electrodes for Degradation of Phenol

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Abstract- A novel bio electrode containing bacteria immobilized on clay mixed carbon paste electrode (Bactria-clay-CPE) is developed for detection and degradation of the phenolic solutions based on electrochemical techniques such cyclic voltammetry, square wave voltammetry, electroctrochemical impedence spectroscopy. The results obtained showed that bacteria-clay-CPE exhibited excellent electro-catalytic activity towards phenol. The recorded cyclic voltammogram shows that the oxidation of phenol is manifested by the appearance of four oxidation peaks.

Keywords- Modified electrodes, Cyclic voltammetry, Clay, Impedance spectroscopy, Bacteria, Phenol

1. INTRODUCTION

Phenol and related compounds are widely used in industry for the manufacture of a wide variety of aromatic compounds, including rubber, fertilizers, paints, drug preparations, petroleum and agricultural industries [1,2]. Phenol is considered carcinogenic and exposure to phenol causes several symptoms such as convulsions, dizziness and irregular breathing [1,3]. Phenol is one of 129 compound chemicals considered important pollutants listed by the Environmental Protection Agency (EPA) [4,5]. Due to severe legislation, prohibit the release of toxic products into the environment.

Current research has focused on the development of a simple, cost-effective, fast and reliable technology that can be used for the immediate detection of heavy metals and toxic products in the environment.

In this context, a technology seems to fully correspond to the requirements necessary for sustainable development and the preservation of the ecosystem: "bioelectrochemistry". This discipline can be defined as a science involving the principles of electrochemistry associated with the field of living. Here we will focus on the electrochemistry / bacteria coupling. Indeed, the conversion of the catalytic activity of a bacterium into an electric current has paved the way for the development of various and varied bioelectrodes. Their fields of application are currently numerous and particularly in fields such as energy (biopiles) and analytical applications (bacterial biosensors) [6,7].

With regard to electro-analytical techniques, procedures involving the oxidation of phenol on solid electrodes [8-9] have been reported. In addition, chemically modified carbon paste electrodes have proved very useful for analytical applications [10]. In previous work [11,12], the electrochemical oxidation of phenol has been studied. We present a simple and sensitive method of determining these compounds based on their reaction. The purpose of the work presented here was to study the electrochemical properties of phenol on the bacterial- clay modified carbon paste electrode as well as the electrochemical characterization of electrodes by the cyclic voltammetric technique, Square Wave Voltammetry and Impedance Spectroscopy.

2. EXPERIMENTAL

2.1. Equipment

The electrochemical experiments were carried out using a voltalab potentiostat (model PGSTAT 100, Eco Chemie BV, Utrecht, The Netherlands) controlled by the software voltalab master 4. The electrode made of carbon paste modified with clay and bacteria was used as the working electrode; the saturated calomel electrode serving as a reference electrode and a platinum plate were used as a counter-electrode. The pH meter (Copenhagen, PHM210, Tacussel, French) was used to adjust the pH values.

2.2. Bacterial cultivation

The bacterial strain of Staphylococcus aureus ATCC 25923 was used in this study as a bio- material. The strain was grown in Luria Burtani broth and incubated at 37 °C for 24 h. The suspension of resuspended bacteria was diluted with distilled water to stabilize to obtain the necessary suspension of different concentrations before use.

2.3. Electrodes preparation

The modified carbon paste electrode was prepared by thoroughly mixing the clay with the graphite powder, in proportions of 1:1, in a small mortar until a homogeneous paste was obtained. Subsequently, the paste is inserted manually into the cylindrical cavity of the body of the electrode (geometrical surface of approximately 0.1256 cm^2). The modified electrodes were immersed in a cell containing bacteria for 15 min, thus the bacterial electrode is ready for use. The electrical contact is established with a carbon bar. The clay used in this work comes from BOULA-IBIB (Garoua) North-Cameroon.

2.4. Procedure

The resulting electrode surface was smoothed with clean, smooth paper, washed with bidistilled water, and dried at laboratory temperature. Finally the electrode is transferred into an electrochemical cell of 20 ml capacity, containing the electrolytic solution, 0.1 mol/L of Na_2SO_4. The whole is bubbled with pure nitrogen for 10 min. The working electrode has been preconcentrated in the solution containing the analyte to an open circuit, the time which makes it possible to obtain the best peak is retained, and hereinafter referred to as pre-concentration time.

The electrochemical behavior of the adsorbed substance was studied by cyclic voltammetry and square wave voltammetry at the modified carbon paste electrode surface.

The optimal conditions were established by measuring the variation of the maximum current intensity according to the physicochemical parameters, such as: the preconcentration time, the modifier charge and the pH of the solution at room temperature.

3. RESULTS AND DISCUSSION

3.1. Clay characteristics

The morphology of the surface of the clay-modified electrode was observed by scanning electron microscopy (Fig. 1). We note the presence of pores that play an important role against corrosion of the surface of the electrode [1].

The treated clay has the following chemical composition given by transmission microscopy (TEM): O (22%), Mg (5.4%), Al (22.4%), K (2.7%), Ca (1%), Ti (1.8%), Fe (17.1%), Si (27.8%) and several ppm order metals (Fig. 2).

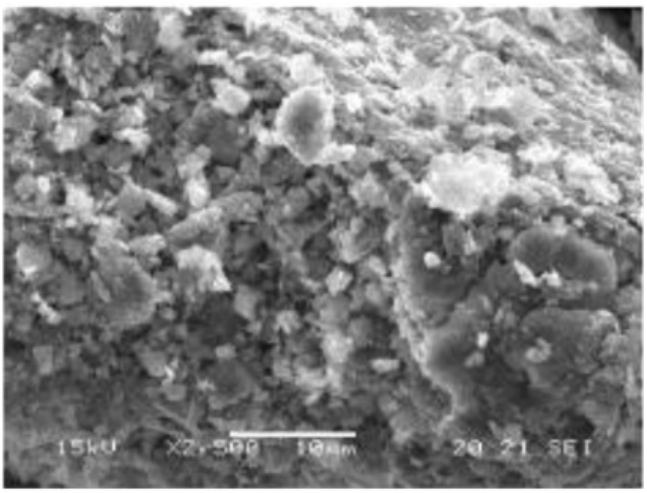


Fig. 1. Scanning electron micrograph of Clay paste electrode

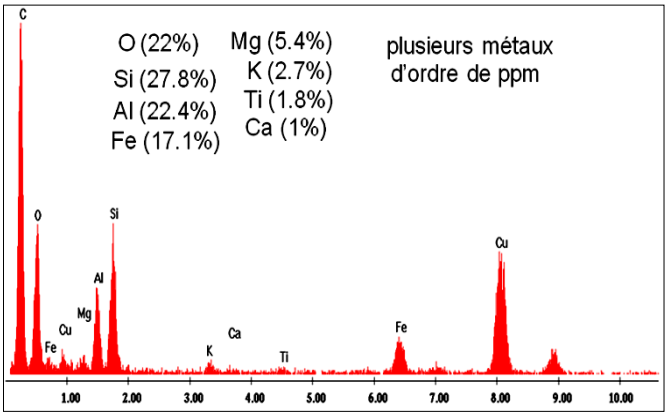


Fig. 2. Chemical composition treated clay

3.2. Electrochemical characterization of prepared electrode

The oxidation of phenol on the CPE-clay-bacteria electrode was studied by cyclic voltammetry (Fig. 3) by electrochemical impedance spectroscopy (EIS). The cyclic voltammograms (CV) recorded respectively at the clay-modified carbon clay (CPE-clay) electrode (curve 1) and at the clay modified with bacteria-modified carbon paste electrode (Clay)-bacteria-CPE) (curve 2), in the supporting electrolyte (0.1 M Na_2SO_4), are shown in Fig. 3. We can notice that in both cases, the CVs keep the same speed, with a slight increase the density of electric currents for the Clay-bacteria-CPE electrode [4].

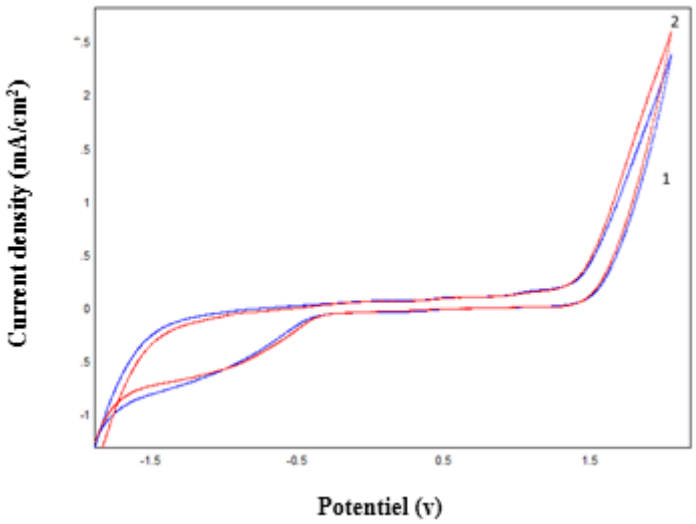


Fig. 3. CV's recorded at, 1-Clay-CPE and, 2-Clay-bacteria-CPE, in 0.1 M Na_2SO_4 solution

Fig. 4 shows the EIS curves recorded at different residence times of the Clay-CPE electrode in the solution containing the bacteria (pH~7). The registered EIS's have the form of a half-loop whose diameter corresponds to the electron transfer resistance (R_t). It is noted that the electron transfer resistance decreases with increasing residence time. The bacterial film developed on the surface has an electrical conductivity that changes with the residence time.

Fig. 5 illustrate the evolution of the capacity of the double layer, formed at the metal/solution interface (C_{dl} in $\mu F/cm^2$) with the residence time. The C_{dl} values increase linearly with the residence time, which shows that the density of the microbial film depends on the contact time.

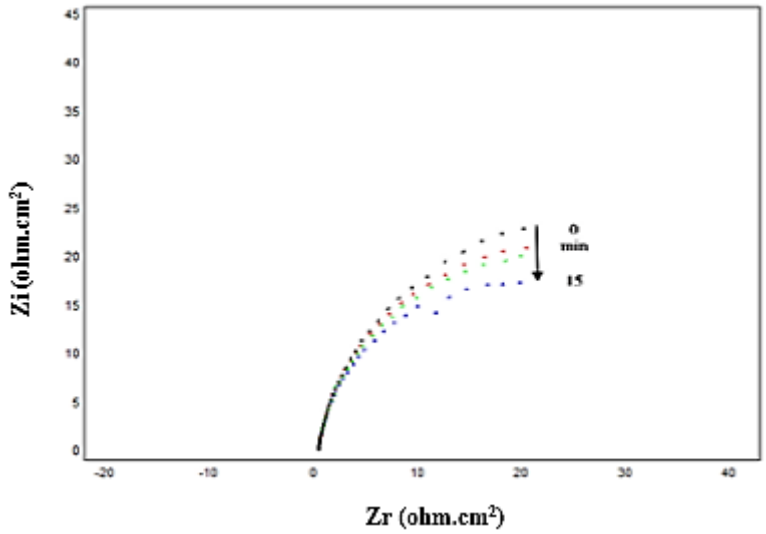


Fig. 4. Impedance diagram at different contact times of CPE-Ar with the bacteria

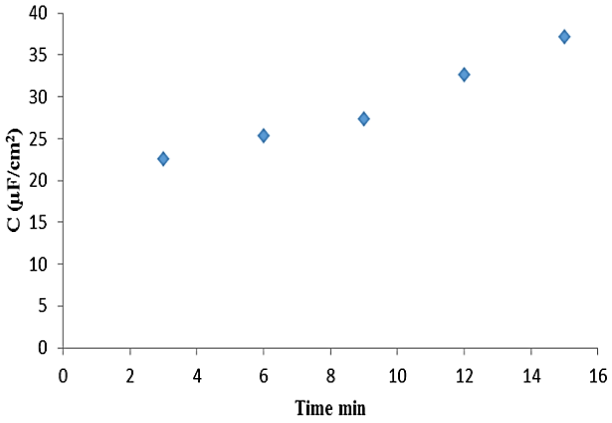


Fig. 5. The double layer capacity as a function of the contact time of CPE-Ar with the bacteria

The electrochemical behavior of phenol has been studied on bacteria-clay-CPE, by cyclic voltammetry (CV) and by square wave voltammetry (SWV). Fig. 7 shows CVs recorded at bacteria-clay-CPE when phenol was added to the electrolytic medium. The CVs had four defined anodic peaks P1, P2, P3 and P4 at -0.2 V, 0.05 V, 0.3 V and 0.8 V, respectively. The presence of only anodic peaks suggests that the electrochemical oxidation of phenol is completely irreversible, and we propose the following scheme, in agreement with previous work [8] (Fig. 7 and 8 and Fig. 1).

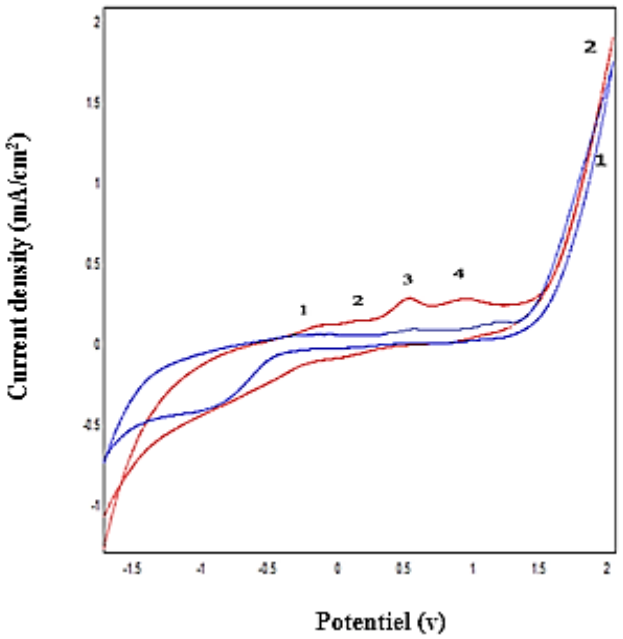


Fig. 6. CVs recorded for 4 mM phenol at pH=7 at bare Clay-bacteria-CPE(1) and Clay-bacteria-CPE/phenol (2), scan rate 100 mV/s

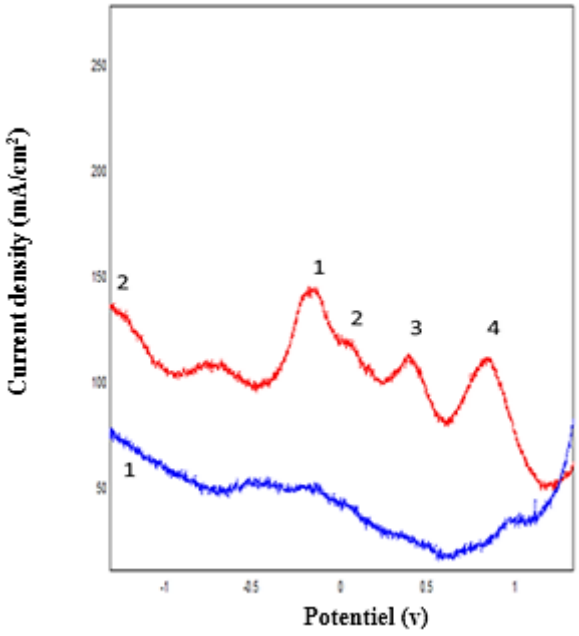
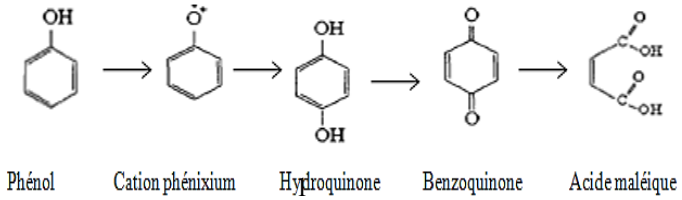


Fig. 7. SQW recorded for 4 mM phenol at pH=7 at bare Clay-bacteria-CPE (1) and Clay-bacteria-CPE/phenol (2), scan rate 100 mV/s



Scheme 1. Mechanism of electrochemical oxidation of phenol at Clay-bacteria-CPE

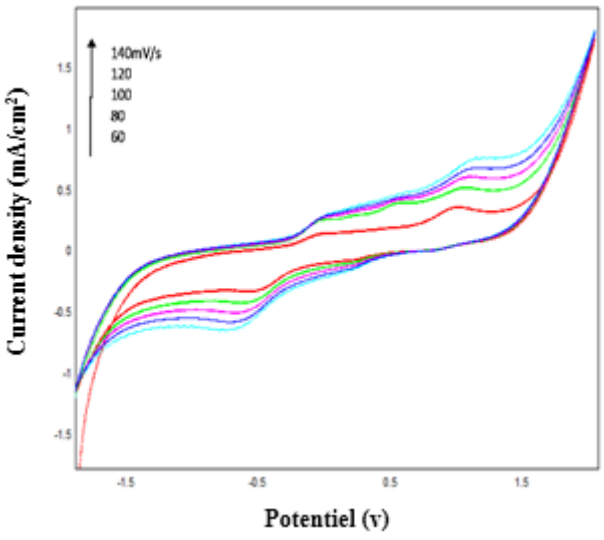


Fig. 8. CV's recorded at Clay-bacteria-CPE, in electrolytic medium containing phenol, at various scan rates

Fig. 9 shows the cyclic voltammograms, recorded in the presence of phenol in the electrochemical cell, at variable scan rates of 40 to 120 mV/s. We can see that the height of the peak relative to the oxidation of phenol increases with the scanning speed. Fig. 10 shows the linear relationship between the anode current densities and the scan rate.

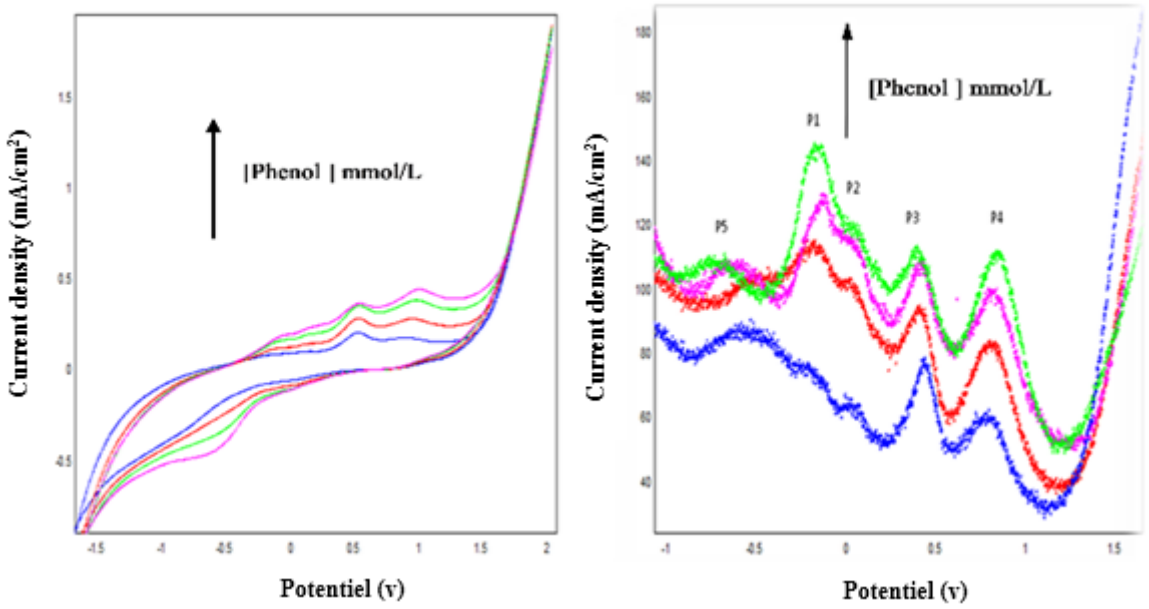


Fig. 9. CV's and SQW recorded at Clay-bacteria-CPE, in electrolytic medium containing various concentrations of phenol, at 100 mV/s

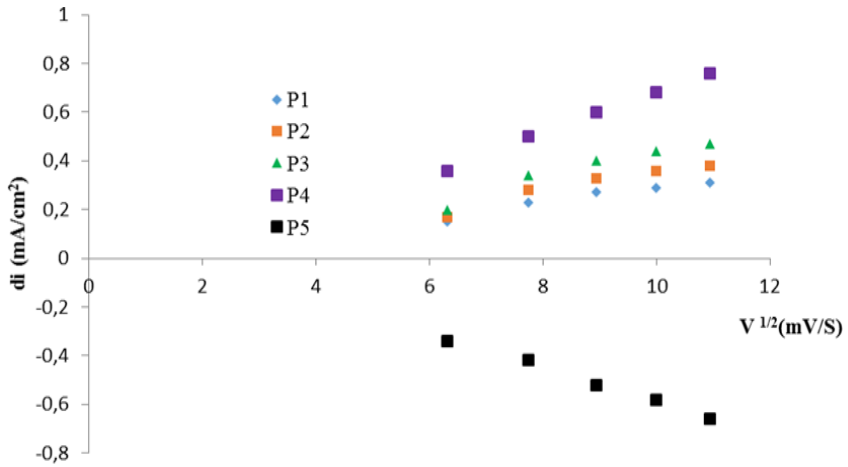


Fig. 10. Plot of peaks area versus scan rate

Figure 11 shows the cyclic voltammograms recorded on the surface of the CPE-clay-bacteria electrode, in a 0.05 mol/L solution of Na_2SO_4 (pH=5), containing different concentrations of phenol, at 100 mV/s. The current densities of the anodic peak increase linearly with the phenol concentration (Fig. 12).

The Table 1 shows that the limits of detections (D.L) and quantifications (Q.L) calculated for the bacteria-clay-CPE can reach, respectively $6.252.10^{-9}$ mol/L and $2.084.10^{-8}$ mol/L .

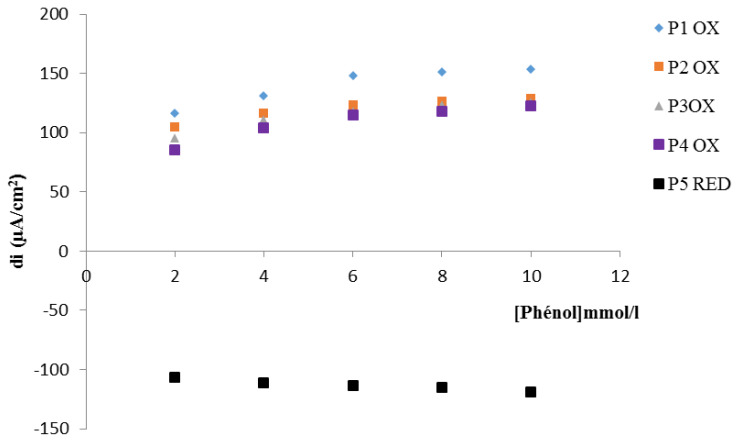


Fig. 12. Plot of peaks area versus concentration

Table 1. The correlation equations and the limits of detections and quantifications calculated for the clay–bacteria-CPE in the presence of phenol.

Peaks	P1 (OX)	P2 (OX)	P3 (OX)	P4 (OX)	P5 (RED)
Equation	di=3.574x+ 93.38	di=4.49x+82.09	di=4.74x+111.7	di=2.87x+102.8	di = -1.41x- 104.6
R^2	R^2 = 0.987	R^2 = 0.988	R^2 = 0.979	R^2 = 0.986	R^2 = 0.991
D.L (mol/L)	$1.11.10^{-8}$	$1.0652.10^{-8}$	$2.094.10^{-8}$	$6.252.10^{-9}$	$2.874.10^{-9}$
Q.L (mol/L)	3.728^{-8}	$3.550.10^{-8}$	$6.968.10^{-7}$	$2.084.10^{-8}$	$9.582.10^{-9}$

3.3. The activity of the immobilized bacterium

To evaluate the activity of the elaborate electrode, we propose the following equation:

$$\alpha = (1 - \frac{Ibact}{I}) \text{ x } 100$$

The activity of the bacterium adhered to the Clay-CPE electrode surface in the presence of 4 mmol/L of the phenol is in the order of: 54, 63%.

3.4. Global mechanism of degradation of phenol by bacteria-clay- CPE

Fig. 13 shows the evolution of the intensity of phenol oxidation peaks with the number of cycles recorded, for the bacteria-clay-CPE, pre-concentrated under optimal conditions in a

phenol solution, with a 100 mV/s sweep, in the electrolytic solution of NaCl (0.1 mol/L), in a potential range between -2 V and 2 V.

We observe the presence of 4 anodic peaks corresponding to the oxidation of phenol, P1, P2, P3 and P4 respectively, at -0,2 V, 0.05 V, 0,3 V and 0.8 V.

These peaks disappear gradually with the number of cycles, and give rise to four peaks which are subsequently disappeared in turn, and two one peaks remains after 110 cycles because the paste of the electrode is detached. This can be explained by the electrochemical reactions following:

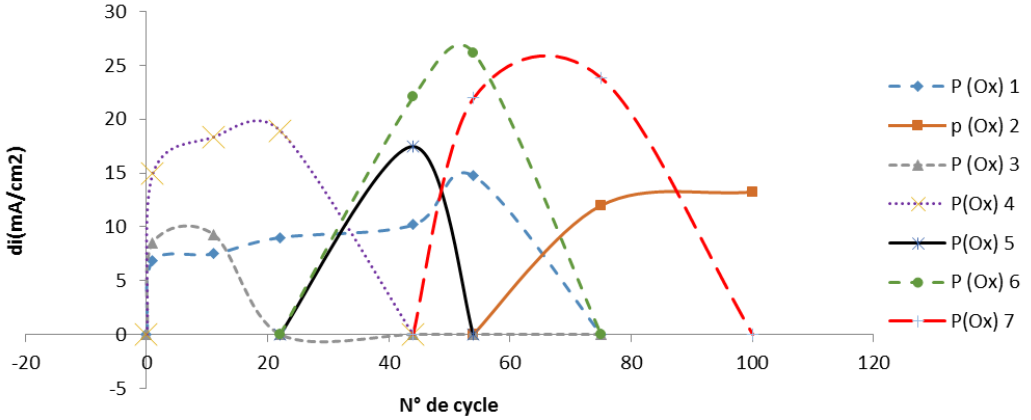
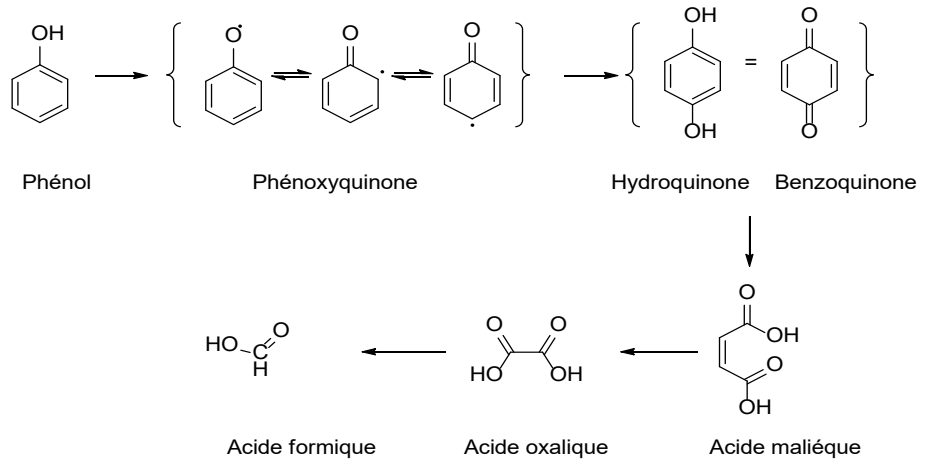


Fig. 13. Influence of the current density of the oxidation peaks as a function of the number of cycles recorded by the bacteria-clay-CPE



Scheme 2. Global mechanism proposed for the electrochemical oxidation of phenol, at bacteria-clay-CPE

The oxidation of phenol on the bacteria-clay-CPE electrode led to the intermediates: Hydroquinone, Benzoquinone, Maleic acid, Oxalic acid, and Formic acid.

4. CONCLUSION

From the results obtained, it can be seen that bacteria-clay-CPE can be successfully investigated in the electro-oxidation of phenol. Bacteria-clay-CPE was prepared with a simple method. The oxidation of phenol on the bacteria-clay-CPE electrode led to the intermediates: Hydroquinone, Benzoquinone, Maleic acid, Oxalic acid, and Formic acid. The activity of the bacterium adhered to the Clay-CPE electrode surface in the presence of 4 mmol/L of the phenol is in the order of: 54, 63%.

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