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Phenol Removal from Wastewaters by Electrochemical Biosensor

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Abstract
The aim of this work is to introduce bacteria into the matrix of natural phosphate to catalyze the phenol oxidation in the wastewater.This electrode, designated subsequently by bacteria-NP-CPE, Showed stable response and was characterized with voltammeter methods, as cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and DRX. The experimental results revealed that the prepared electrode could be a feasible for degradation of hazardous phenol pollutants in the wastewater.

Keywords: Modified electrodes; Biosensor, Cyclic voltammetry; impedance spectroscopy; Bacteria; Phenol, wasterwater.

1. Introduction

The increase in the waste produced through industrial and domestic activities makes the investigation of alternative routes for the degradation and treatment of hazardous materials imperative [1]. Biological treatment of polluted water is the most economical process and it is used for the elimination of biodegradable organic pollutants present in wastewater; however, when the wastewater contains toxic and refractory organic pollutants, other processes must be employed [2]. One interesting possibility is to couple partial oxidation and biological treatment in order to decrease the toxicity and to increase the biodegradability of the wastewater before biological treatment [3].

The combination of electrochemical and biological method can bring benefit to the degradation of toxic materials such as phenol. The function of microbial bioelectrochemical systems is based on operating the microorganisms to catalyze an electrochemical reaction. The system allows for different tasks, such as, biodegradation, and electrochemical processes [4]. The aims of this work were to examine the new electrode , based on bacteria modified naturel phosphate electrode for simultaneous production of electricity and degradation of phenol in wastewater**.**

2. Experimental

2.1 Reagents and apparatus

Electrochemical measurements were performed using a Volta lab potentiostat (model PGSTAT 100, Eco Chemie B.V., Utrecht, The Netherlands) driven by the general purpose electrochemical systems data processing software (Volta lab master 4 software) run under windows 2007. The three electrode system consisted of a chemically modified carbon paste electrode as the working electrode a saturated calomel electrode (SCE) serving as reference electrode, and platinum as an auxiliary electrode. Phenol solution: was purchased from Merck.Potassium Chloride (KCl), Hydrochloric acid and sodium hydroxide were purchased from Aldrich (Milwaukee, USA) The natural phosphate samples were obtained from CERPHOS, Morocco.

2.2 Electrodes preparation

The working carbon paste electrode was prepared by mixing appropriate weight of natural phosphate (NP) with a graphite powder (CP) to give an appropriate ratio NP-CP. The whole cell modified carbon paste was subsequently packed firmly into the PTFE cylindrical
tube electrode cavity (0.1256 cm2) and polished to a smooth shiny finish by gently rubbing over an ordinary weighing paper. Electrical contact was established with a bar of carbon. The modified electrodes were immersed in a cell containing 2 ml of caprolactone monomer and
a quantity of the bacterium for 15 minutes. The resulting electrode is hereby denoted as bacteria-NP-CPE.

2.3 Procedure

The prepared electrode is first characterized in electrolytic medium. In a second stage is tested for the electro oxidation of phenol, added in the measurement cell. The mixture solution was kept for 20 s at open circuit and deoxygenated by bubbling pure nitrogen gas prior to each
electrochemical measurement. The cyclic voltammetry was recorded in the range from -1.5 V to 1,5V. Optimum conditions were established by measuring the peak currents in dependence on all parameters. All experiments were carried out under ambient temperature [5].

The bacteria used in this study are *Staphylococcus aureus*. The bacteria were cultivated in medium LB (Luria Burtani) solid. After sterilization in the autoclave of the culture medium, the bacteria were sown there and then incubation was done with 37°C during 24 h [6].
Provisions were taken for deoxygenation by splashing the solution.
with nitrogen gas during approximately 5 min. In order to obtain reliable and reproducible results, a new electrolyte was prepared for each handling.

3. Results and Discussion

3.1 Electrochemical characterization

3.1.1 Characterization by cyclic voltammetry

Figure 1 shows the recorded voltammograms (CV), respectively for the CPE-NP and CPE-NP-bacteria electrodes, after 15 min contact of the electrode with the bacterial suspension, at the same 100 mV / potential sweep rate. S, in electrolytic medium NaCl (0.1M), we can notice that the presence of bacteria on the surface of the electrode causes a slight increase in the electrical current densities [7]. The cyclic voltammogram has kept the same pace, which shows that the presence of bacteria on the surface does not modify the electrochemical characteristics of the electrode, but increases its activity.

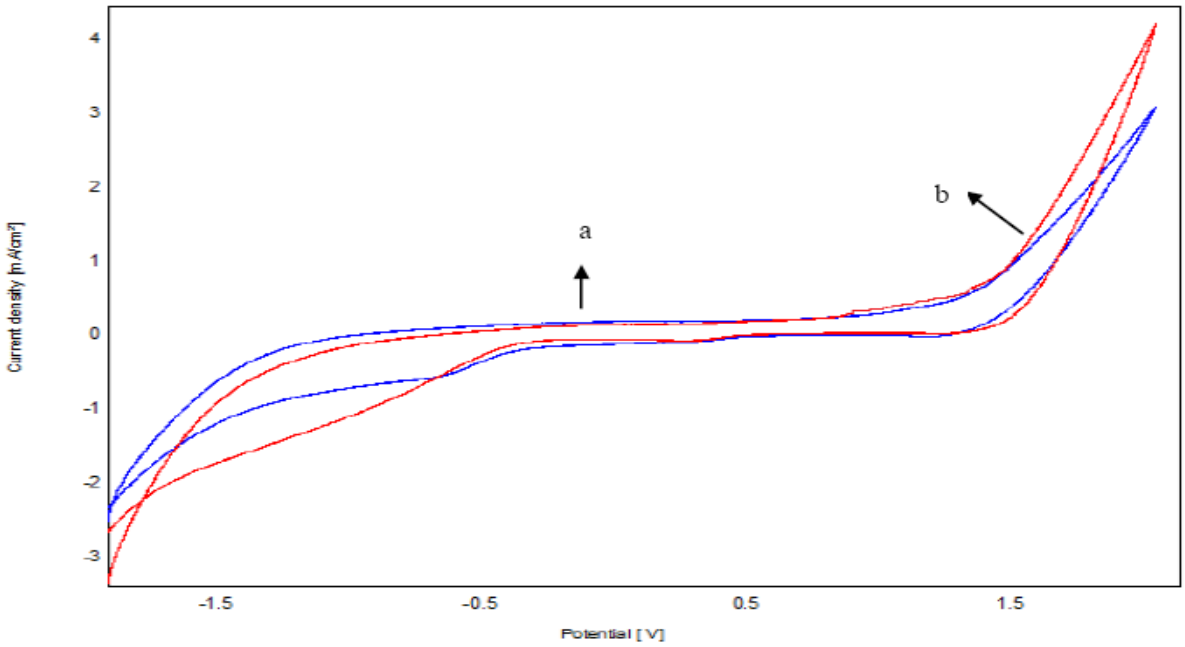

Figure 1: Cyclic voltammograms obtained by CPE-NP (a) and CPE-NP-bacteria (b) in 0.1M NaCl with a scanning rate of 100 mV / S.

3.1.2 Characterization by impedance spectroscopy

Both electrodes have led to EIS diagrams, which have the form of a half-loop that appears at high frequencies, and can be attributed to the process of electron transfer. The diameter of the half-loop corresponds to the transfer resistance of the electrons, the value of this resistance drops in the case of the electrode CPE-NP-bacteria, which confirms the immobilization of the bacteria on the surface of the electrode CPE-NP.

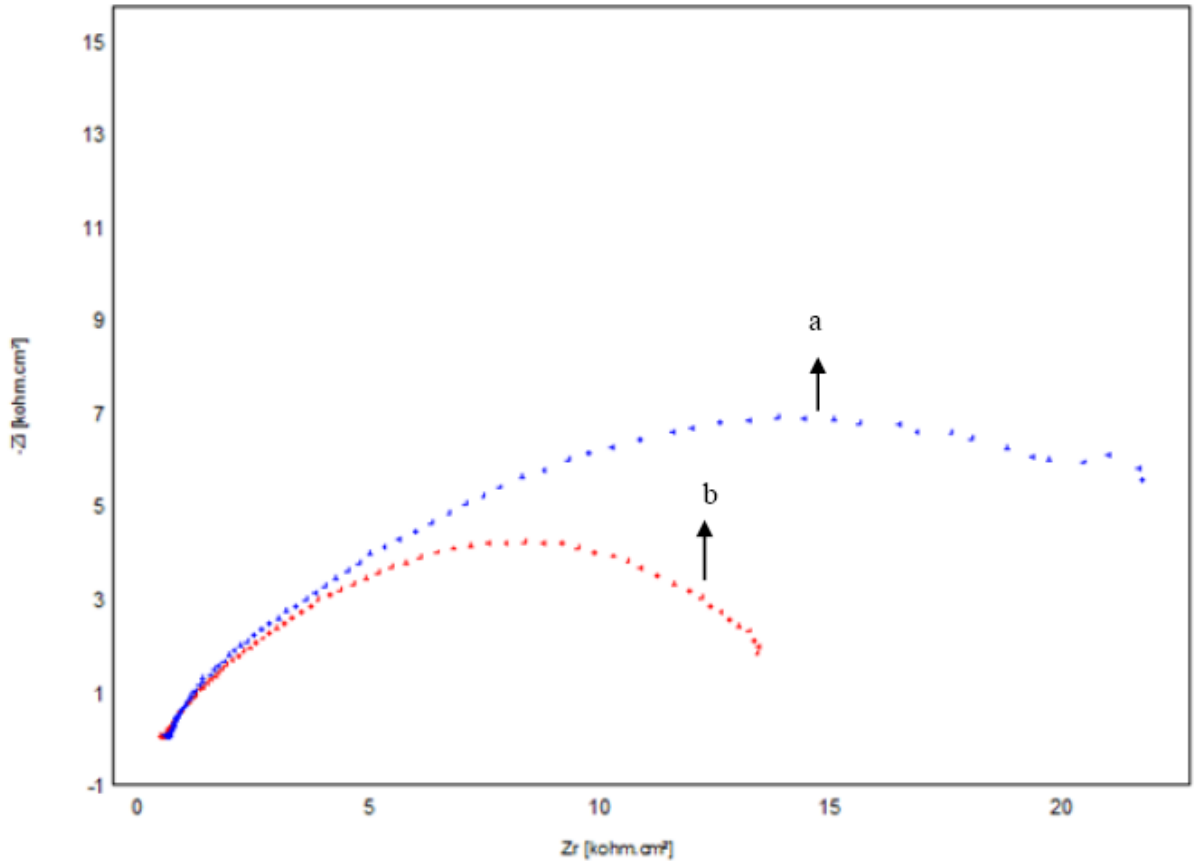

Figure 2: Impedance diagram obtained by CPE-NP (a) and CPE-NP-bacteria (b) in 0.1M NaCl.

The parameters corresponding to these measurements are summarized in Table 1. The diameter of the capacitive loop decreases in the presence of bacteria at the electrode surface, which is explained by the decrease of the charge transfer resistance. The presence of bacteria on the surface increases the conductivity of the metal / solution interface. The capacity of the double layer, which models the effect of the potential drop near the electrode, increases in the presence of bacteria due to the attachment of bacteria to the surface of the CPE-NP electrode.

Table 1: Electrochemical impedance parameters (R1 being the resistance of the electrolyte, the transfer resistance, and C the capacity of the double layer).

Electrode	R_1(ohm,cm^2)	R_2(Kohm,cm^2)	C(µF/cm^2)
CPE-NP	487,1	27,9	12,77
CPE-NP-bactérie	461,1	15,35	18,6

3.2 Electrochemical analysis of phenol in tap water medium

3.2.1 Voltammetric study

Catalysis of the oxidation of phenol by the elaborated bioelectrode, CPE-NP-bacteria, was invoked by cyclic voltammetry (VC) at 100 mV / s in 0.1M NaCl electrolyte solution (FIG. absence of phenol (4 mmol / L), in a

potential range between -2 V and 2 V. There are two anodic peaks, respectively at 0.59 V and at 1.04 V, attributed to the oxidation of phenol and its derivatives.

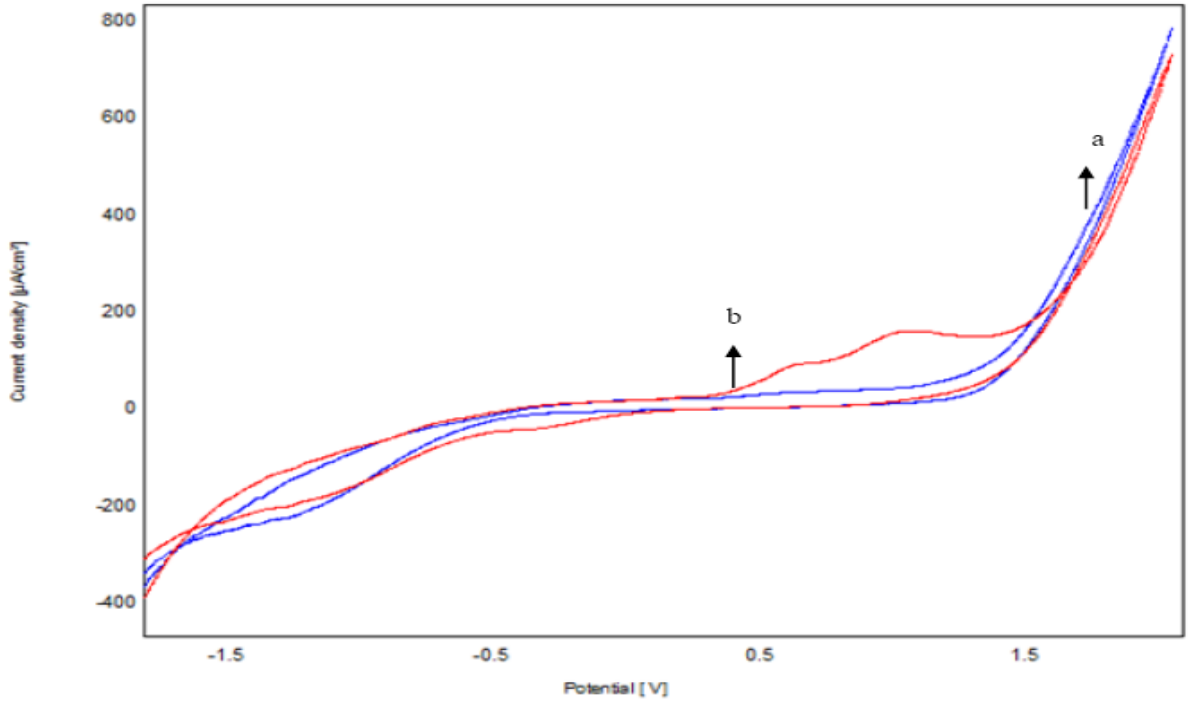

Figure 3: Cyclic voltammograms obtained by CPE-NP-bacterium in the absence (a) and in the presence (b) of 4 mM phenol in 0.1 M NaCl with a scanning speed of 100 mV / S.

3.2.2 Characterization by impedance spectroscopy

Figure 4 illustrates the impedance diagrams recorded by a CPE-NP-bacterium electrode, in the presence and absence of a 4mM concentration of phenol in tap water. The charge transfer resistance decreases remarkably in the presence of phenol (Table 2), which shows that the bacteria favor the oxidation of phenol.

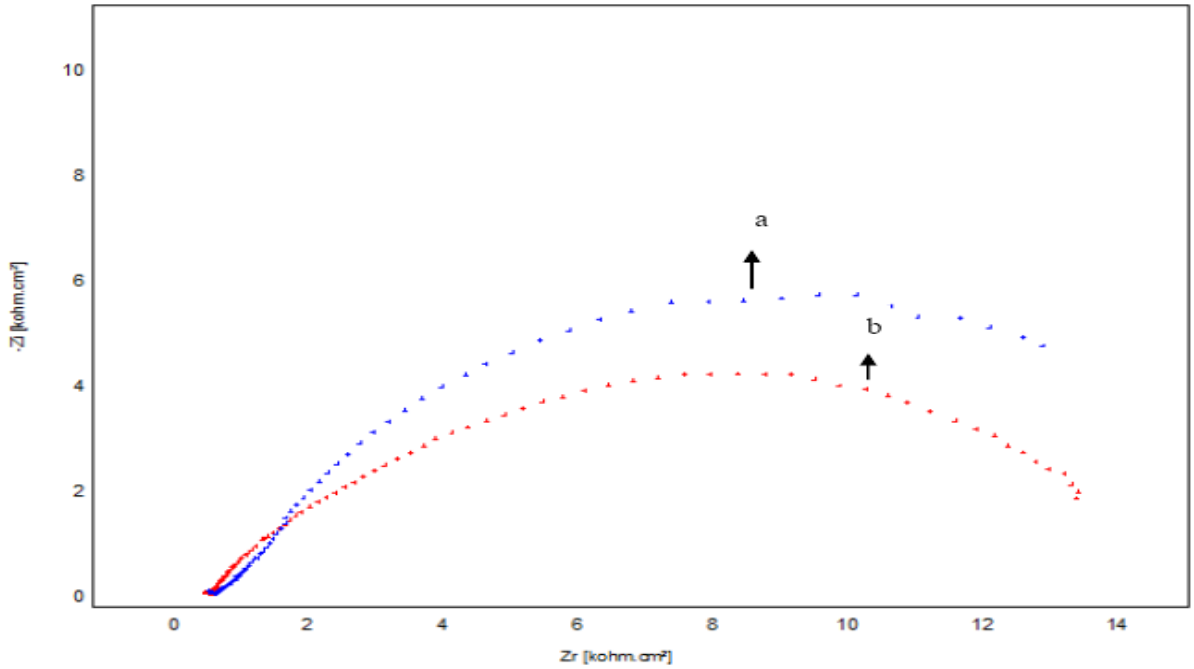

Figure 4: Impedance diagram obtained by CPE-NP-bacteria in absence (a) and in the presence (b) of 4 mM phenol in 0.1 M NaCl with a scanning speed of 100 mV / S.

Table 2: Electrochemical impedance parameters (R1 being the resistance of the electrolyte, the transfer resistance, and C the capacity of the double layer).

Electrode	R_1 (ohm,cm^2)	R_2 (Kohm,cm^2)	C(µF/cm^2)
CPE-NP-bactérie	461,1	15,35	18,6
CPE-NP-bactérie+phénol	492,9	13,38	51,88

3.2.3 Effect of scanning speed

Figure 5 shows the cyclic voltammograms recorded by the CPE-NP-bacterium electrode, at different scan rates, in tap water containing phenol.

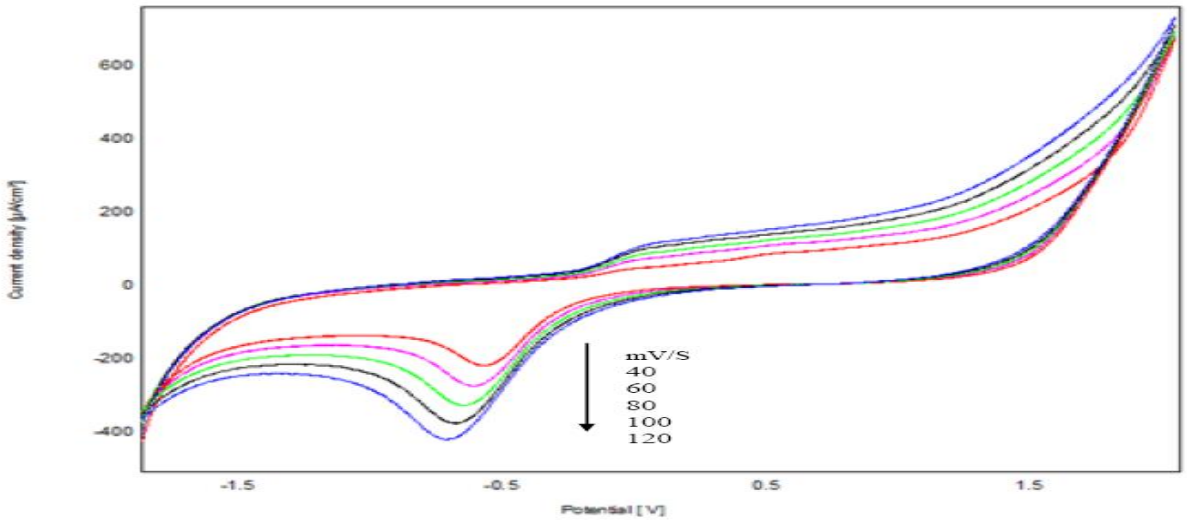

Figure 5: Voltamograms recorded by CPE-NP-bacterium with 8 mM phenol in 0.1 M NaCl at different scan rates from 40 to 140 mV / S.

The intensities of the anodic and cathodic peaks vary linearly with the scanning rate, in the range of 40 to 140 mV / S, indicating that the kinetics of the reaction are limited by diffusion.

The linear regression equations are as follows:

Ipa = 14,28x - 36,60 R=0.997

Ipc = -44,35x + 52,42 R=0.999

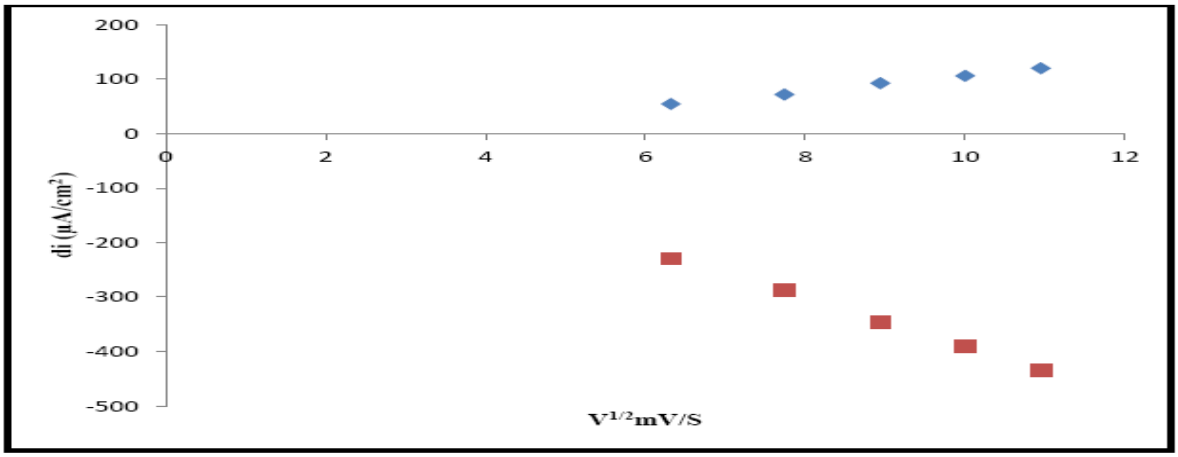

Figure 6: Influence of the root of the sweep rate on the intensity of the phenol redox peaks obtained by VC on the surface of CPE-NP-bacteria.

3.3 Effect of phenol concentration

3.3.1 Characterization by cyclic voltammetry

Figures 7 and 8 show the effect of the change in the amount of phenol on the cyclic voltammograms recorded for the phosphate-modified carbon electrode and the bacteria (CPE-NP-bacteria), the scanning rate is set to 100 mV / s. We note that the increase in the concentration of phenol leads to the increase of the current densities of the anodic and cathodic peaks, no poisoning was observed. The CPE-NP-bacteria electrode does not promote the formation of poison derivatives on its surface. The linear regression equations corresponding to the peak of oxidation and reduction respectively are as follows:

Ipa = 2,464 [phénol] + 76,47 R2 = 0,993

Ipc = -17,50 [phénol] - 0,558 R2 = 0,989

The detection limit is 8.24 × 10-8 mol l-1 and 8.11 × 10-9 mol l-1 for the oxidation peak and the reduction peak respectively. The limiting quantification is 2.74 × 10-7 mol l-1 and 2.70 × 10-8 mol l-1 respectively for the oxidation peak and the reduction peak.

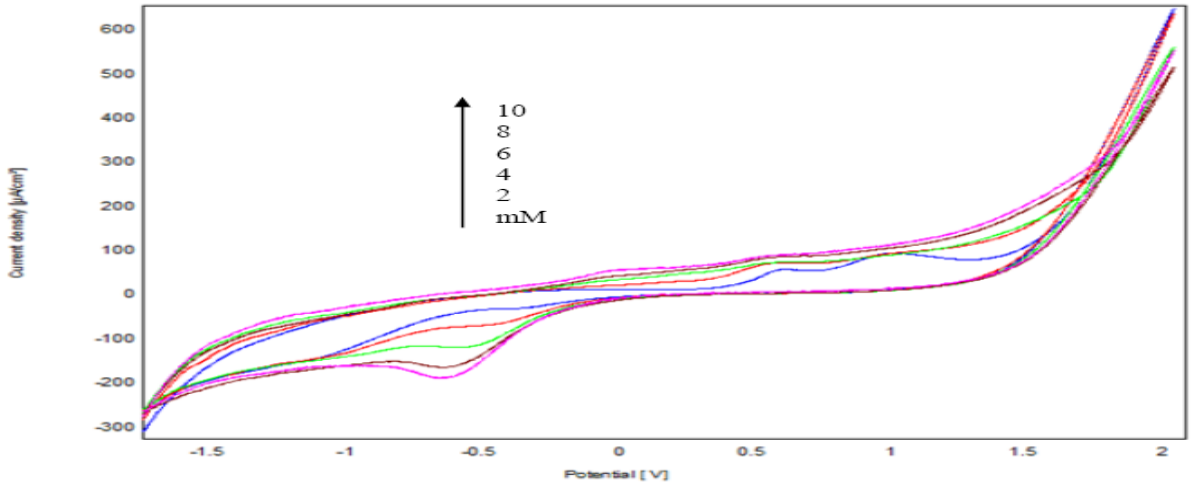

Figure 9: Cyclic voltammograms at different concentrations of phenol (from 2 mM to 12 mM) in 0.1 M NaCl on CPE-NP-bacterium, V = 100 mV.S-1.

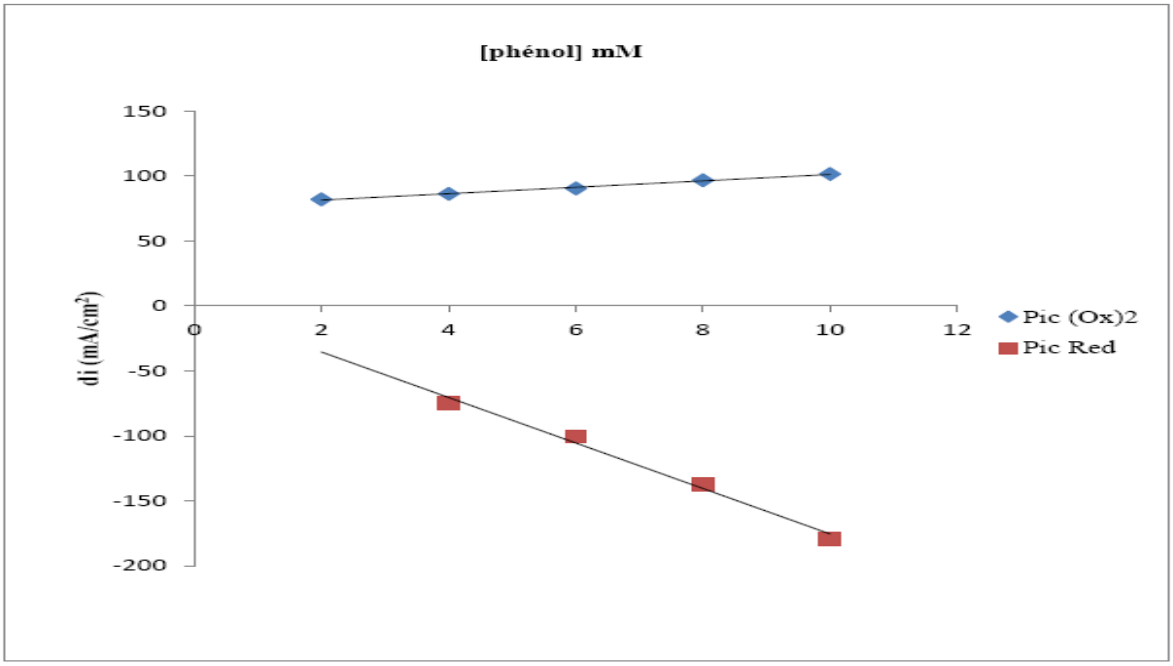

Figure 10: Influence of the phenol concentration on the intensity of the oxidation-reduction peaks obtained by VC on the surface of CPE-NP-bacterium.

3.3.2 Characterization by impedance spectroscopy

The effect of phenol concentration was also studied by impedance spectroscopy. Figure 11 shows that the impedance spectroscopy curves have the form of half-circles for all concentrations of phenol in the high-frequency region, which could be attributed to the electron transfer process. The electron transfer resistance decreases with the concentration of phenol, which shows that the electrode surface has a large number of active sites.

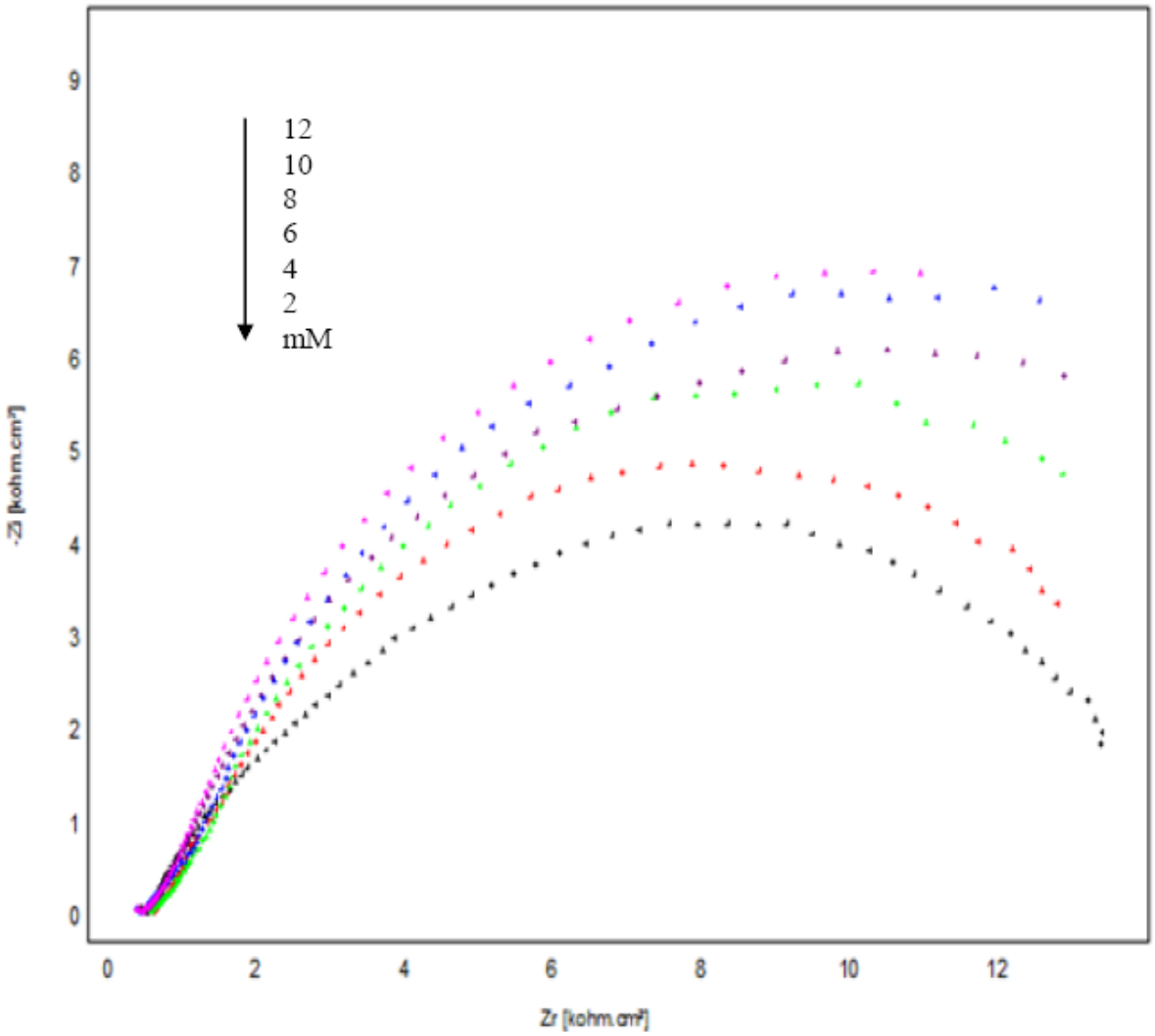

Figure 11: Impedance diagram at different concentrations of phenol (from 2 mM to 12 mM) in 0.1 M NaCl on CPE-NP-bacteria.

3.4 Evaluation of the activity of the bacteria-NP-CPE modified electrode for the detection of phenol in tap water medium.

3.4.1 Voltage study

In this part we compare the behavior of the CPE-NP and CPE-NP-bacterium electrodes for the oxidation of phenol in tap water to examine bacterial activity.

Figures 12 show that the current densities of the oxidation peaks are more intense in the presence of bacteria on the surface of the CPE-NP-bacteria electrode. This shows that the presence of bacteria on the surface improves the catalytic activity of the oxidation of phenol.

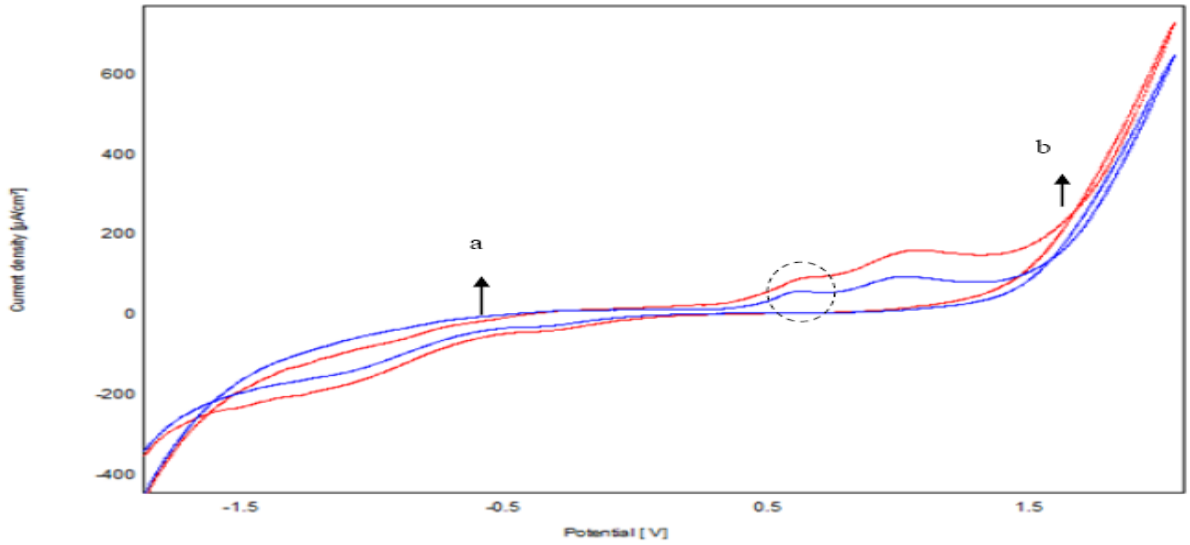

Figure 12: Cyclic voltammograms obtained by CPE-NP (a) and CPE-NP-bacterium (b) in the presence of 4 mM phenol in 0.9 M NaCl with a scanning speed of 100 mV / S.

As a result, the activity of the bacterium immobilized on the NP-CPE electrode surface, for the oxidation of phenol in a solution of tap water contaminated with phenol is:

α = (1-(89.29/55.4)) x 100
=61,11%

3.4.2 Characterization by DRX

The compositional analysis of the elaborated electrode surface was performed by DRX, The results obtained, respectively, for the natural phosphate modified carbon paste electrode (NP-CPE), show that the surface composition is mainly composed of the composition of the surfaces consists mainly of graphite carbon analysis, fluoroapatite in addition of the phenol in case of phenol-NP-CPE.

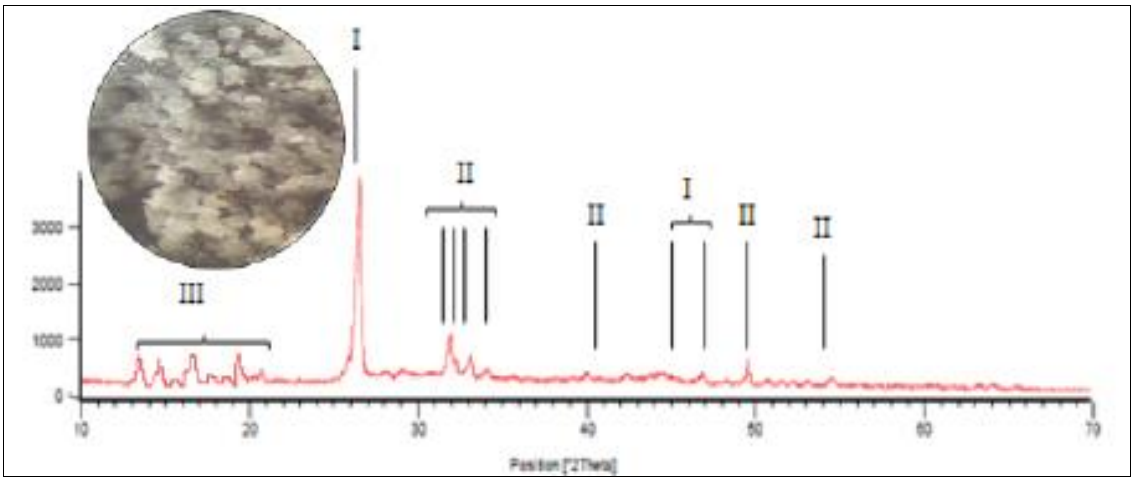

Figure 13: The XRD spectra recorded by the surface of the CPE-NP-phenol

Peaks I: correspond the graphite carbon
Peak II: correspond to the structure of fluoroapatite of natural phosphate
Peak III: correspond the overlap of phenol

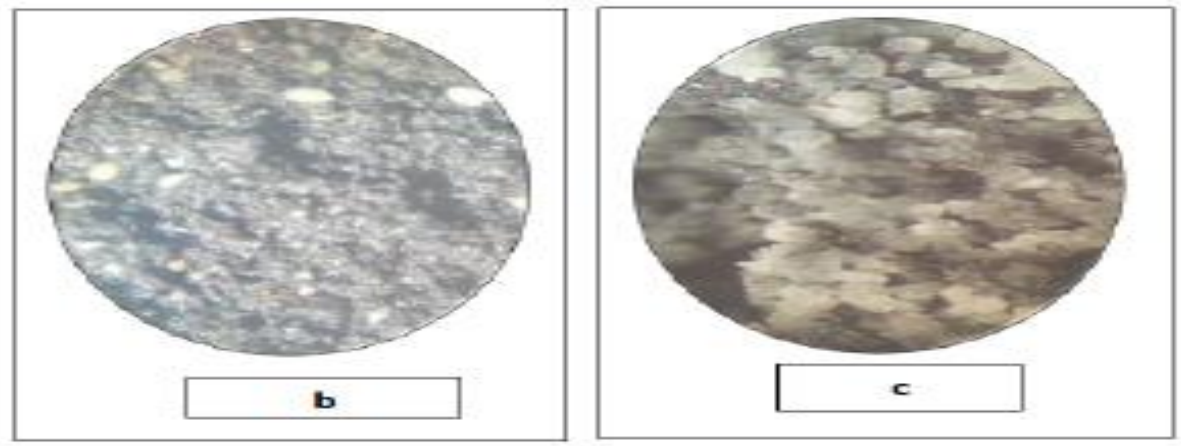

Figure 14: Natural phosphate- carbon paste electrode before detectiono phenol (b) and after detection of phenol (c).

The figure shows the observation of the electrode surface by optical microscopy:
(b) The surface of the carbon paste electrode modified by the natural phosphate before the detection of phenol and (c) After the detection of the phenol.

4. Conclusion

The elaborate electrodes, CPE-NP, modified by bacteria (Staphylococcus aureus) showed high sensitivity to the detection of phenol in tap water contaminated with phenol.
The CPE-NP biosensor showed the best efficiency for the detection of phenol in tap water, of the order of 61.11%. Optimization of the experimental conditions yielded the following values of the following detection limits (LD) and quantification (QL):
- DL = 8.11.10-9 mol / L for CPE-NP / bacteria.
- QL = 2.7.10-8mol / L for CPE-NP / bacteria.

We have noted that the presence of other species in the solution to be analyzed is a factor that can influence the analytical results. This method is very simple and easy to implement. It is inexpensive compared to other methods and applicable in the field.

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