New Electrode Based on Polymer Bacteria Modified Aluminum for Degradation of Phenol

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Abstract

The aims of this work were to examine the new electrode, based on polymer bacteria modified aluminum electrode for simultaneous production of electricity and degradation of phenol. This electrode is based aluminum modified by bacteria inserted in the polymer matrix, developed in situ on the surface. This electrode, designated subsequently by bacteria-polymer-aluminum, Showed stable response and was characterized with voltametric methods, as cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The experimental results revealed that the prepared electrode could be a feasible for degradation of hazardous phenol pollutants**.** The sensor was successfully applied to the determination of phenol in a real sample with satisfactory results.

Keywords: *Bacteria; Modified electrode; VC; EIS; Electrochemical polarization curves, polymer, phenol.*

Introduction

Removal of phenolic hydrocarbons from wastewater prior to their discharge is a prerequisite in many chemicalmanufacturing industries since they can be fatal to the environment or human health even at ppb levels [1]. A number of studies have been carried out to decompose phenolic pollutants dissolved in wastewater during the last few decades. [2].Ultrasonic irradiation [3] in conjunction with other methods such as addition of TiO2, [4]. photochemistry, [5] and ozonation [6] was utilized for the decomposition of phenolic compounds, in which the cavitation process generates reactive free radicals responsible for chemical oxidation of organic pollutants. Biological treatments of wastewater such as microbial [7] and enzymatic [8] oxidations are probably the most environmentally compatible method, but it often requires pretreatment for high concentrations of organic pollutants and may result in the generation of hazardous byproducts. Direct or indirect electro-oxidation of organic compounds was also studied. While the electron transfer takes place between electrodes and decomposable species in direct electrochemical oxidation, indirect oxidation mainly uses electrochemically oxidized species as mediators for the destruction of organic compounds. For indirect electrooxidation, destruction of organic compounds by anodically generated chlorine and hypochlorite is well known. [9] Reactive and high-valent metal ions which are electrochemically generated from stable and low valent state were also utilized to degrade organic pollutants.

The aim of this work was to combine two methods of destruction of a toxic, aromatic, non-biodegradable product such as phenol. The electrochemical method has been used as a pre-reprocessing, which transforms organic products "non-biodegradable" to "biodegradable" products, which will be treated biologically thereafter. The bacterium used in this work has proved highly effective as a catalyst for the electrochemical degradation of phenol.

Experimental

Reagents and apparatus

All chemicals were analytical grade and used without further purification. All solutions were prepared with distilled water. Voltammetric experiments were performed using a voltalab potentiostat (modelPGSTAT 100, Eco Chemie B.V., Utrecht, The Netherlands) driven by the general purpose electrochemical systems data processing software (voltalab master 4 software). The three electrode system consisted of a bacteria-polymer modified aluminum electrode as the working electrode a saturated calomel electrode (SCE) serving as reference electrode, and platinum as an auxiliary electrode. Prior to its modification the aluminum plate was polished with 0.05 µm alumina slurry for 2 min, rinsed with doubly-distilled water and sonicated in a water bath for 5 min.

Bacterial cultivation

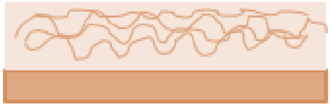
The bacterial strain used in this study was Staphylococcus aureus ATCC 25923. The strain was cultured in Luria Burtani broth at 37°C for 24 h after culture; the cells were harvested by centrifugation for 15 min at 8400 xg and were washed twice with and resuspended in KNO_3 solution with ionic strength 0.1 M. The physicochemical properties of this strain were measured by contact angle measurements.

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. The resuspended bacteria suspension was diluted with water to obtain needed suspension of different concentration before use.

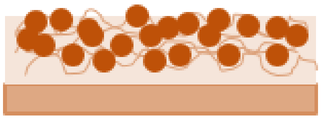
Electrode preparation

The polymerized aluminum electrode (1 cm × 1 cm × 1 mm) has been immersed in a suspension containing the suspensions of the bacteria, after immobilization of the bacteria the polymer-aluminum matrix, we launch a scanning cyclic voltammetry, 10 cycles, in the potential range between -1.5 V and 1.5 V at 50 mV / s in a 1 M solution NaCl.

Nu Electrode



Polymer- Electrode



polymer- bacteria -Electrode

Results and Discussion

Electrodeposition of polymer

Characterization by cyclic voltammetry

The polymerization of ε-caprolactone was carried out electrochemically, in a neutral electrolytic medium (0.1 M NaCl), the technique of successive scanning polymerization makes it possible to obtain stable films, the deposit can be controlled by following the decrease in intensity of current density.

Figure 1represents a series of voltammograms obtained during the electropolymerization of ε-caprolactone on an aluminum plate electrode, recorded with a scanning speed equal to 80 mV / S, in the NaCl solution (0.1 mol / l) containing 2 ml -caprolactam, in a range of potential between -2 V and 2 V.

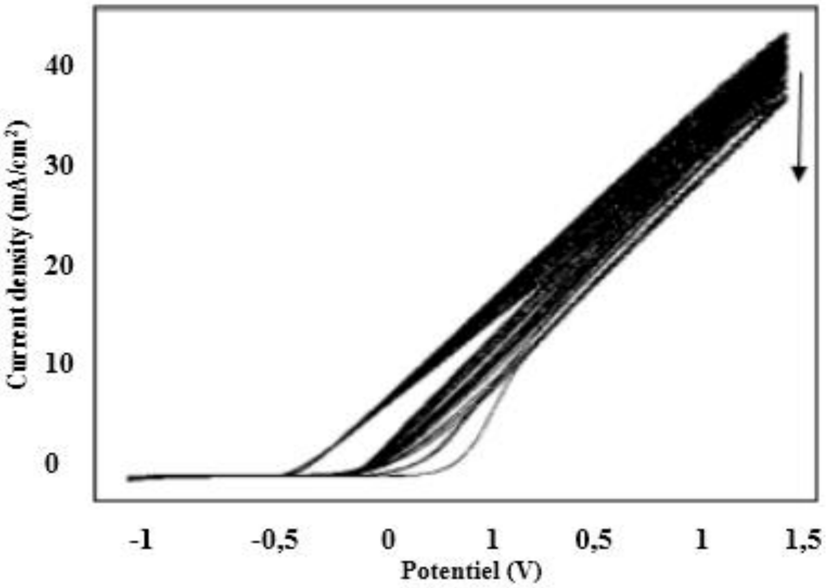


Figure 1: Voltammogram of electropolymerization of β-carprolactone in an electrolyte of 0.1 mol of NaCl at pH = 7, on the Al electrode with a scanning speed of 80 mV / s.

It can be seen that the decrease in the intensity of the currents during the sweeps accounts for the growth of the film deposited on the electrode surface with the number of cycles, the current densities of the voltammograms tend towards 0 indicating that the polymer developed has an insulating character [10].

Polymer modified aluminum electrode

Figure 2 represents the recorded voltammograms (CV) in an electrolytic medium (NaCl, 0.1 M) in the range of potential between -2 V and 2 V, respectively, by the electrode Al before (a) and after the polymerization (b) of the caprolactone monomer e at 100 mV.S -1. The voltammograms recorded for the two electrodes, in electrolytic medium, have different gaits, which suggests that the aluminum electrode is well modified by the polycaprolactone film.

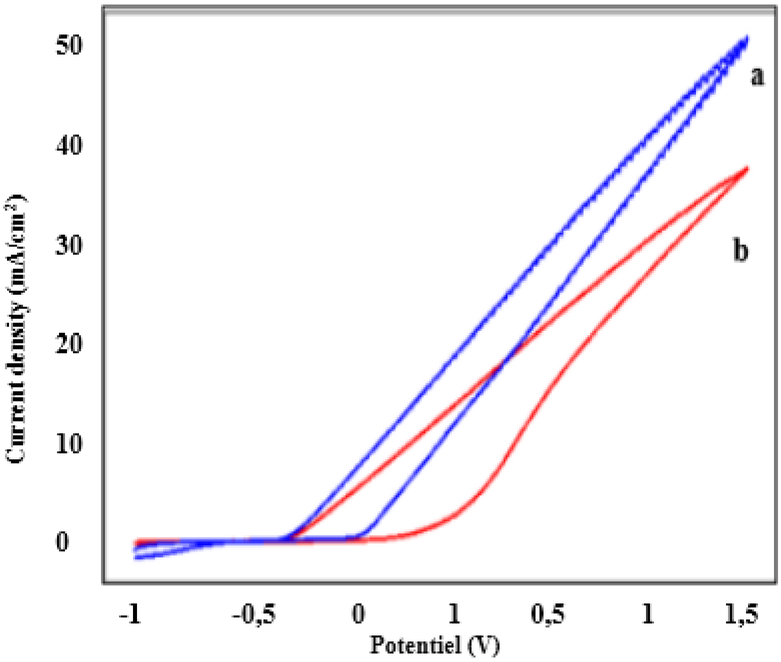


Figure 2: cyclic voltammograms obtained by the electrode Al before (a) and after the polymerization (b) of the caprolactone monomer in 0.9 M NaCl (pH = 7).

Electrochemical Impedance Spectroscopy (EIS)

Figure 3 shows the impedance diagrams (EIS) recorded, respectively for aluminum and aluminum electrodes modified by the polymer developed in situ on the surface of the aluminum electrode. The EIS recorded for the bare aluminum electrode has two time constants, the first at high frequency and corresponds to the transfer to the electron transfer at the metal / solution interface, the second at low frequency is a Warburg line who completes the diagram. The presence of a film on the surface of the electrode is illustrated by the appearance of two half loops entangled. The formation of the film on the surface of the electrode causes the reduction of the capacity of the double layer (Table 1) [11].

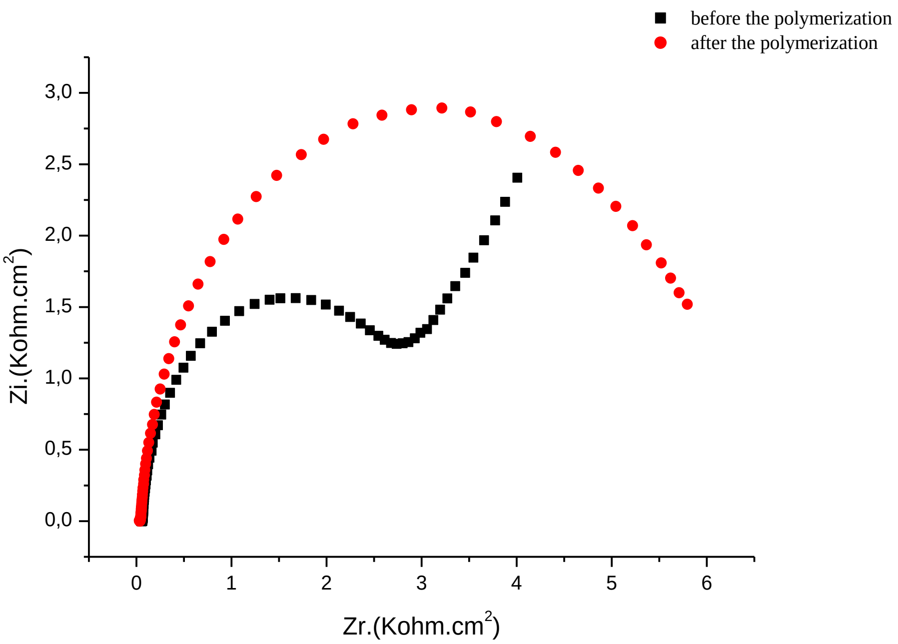


Figure 3: Impedance diagram obtained by the Al electrode before (a) and after the polymerization (b) of the caprolactone monomer in 0.1 M NaCl (pH = 7).

Table 1: Electrochemical impedance parameters (where R1 is 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)**
AL	63.83	31,182	28,15
AL -polymer	74,77	85,84	10,45

Electro oxidation of phenol on the surface of the Al / Polymer electrode

Figure 4 shows that the impedance diagrams recorded at the surface of the Al / polymer electrode in the absence and in the presence of phenol. In the cases the impedance diagrams are in the form of half-loops, the diameter of which corresponds to the electron transfer resistance, this resistance increases in the presence of the phenol, which suggests that the oxidation of the phenol is blocked by the formation of a polymer on the surface of the electrode.

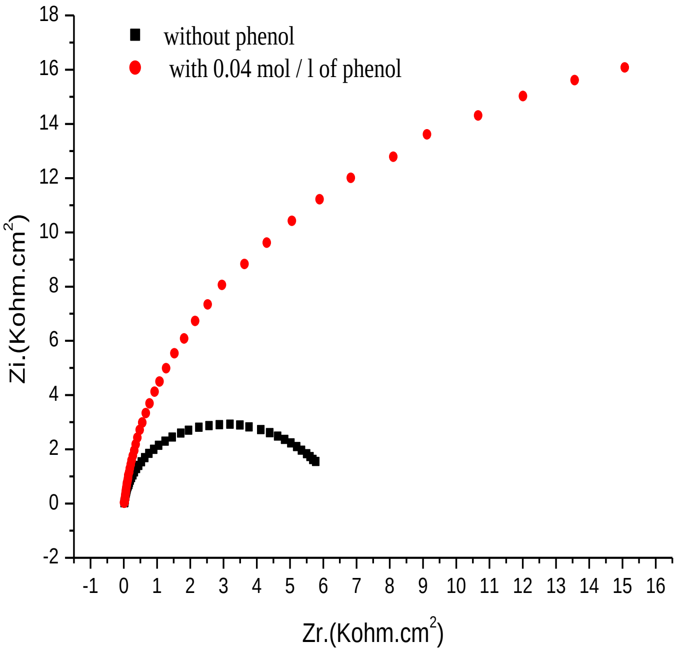


Figure 4: Impedance diagram obtained by the aluminum electrode-polymer in the presence (b) and absence (a) of 0.04M phenol in 0.1M NaCl (pH ~ 7).

Electrochemical study of the effect of phenol concentration

The concentration effect of phenol on the activity of the Al-polymer electrode towards the oxidation of phenol was studied by impedance spectroscopy. Figure 5 shows that the impedance spectroscopy curves have the shape of a semicircle for all concentrations of phenol in the high frequency region, which could be attributed to the electron transfer process. Increasing the concentration of phenol results in an increase in electron transfer resistance (Fig. 6).

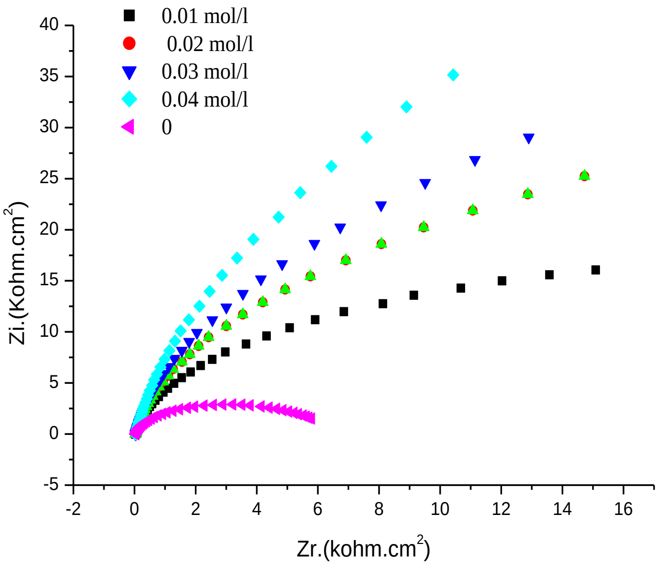


Figure 5: Impedance diagram at different concentrations of phenol (from 2 mM to 12 mM) in 0.1 M NaCl (pH = 7).

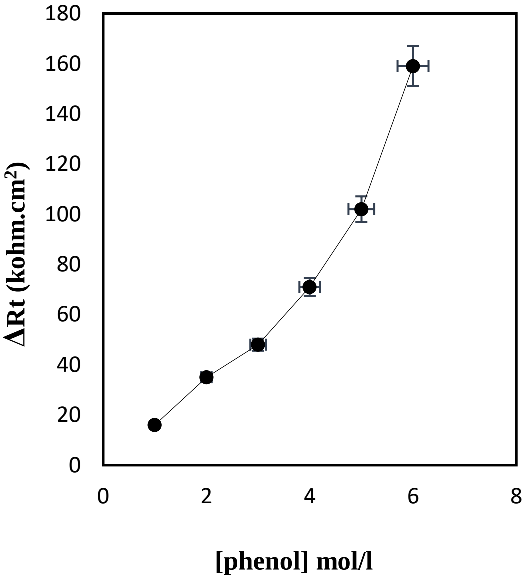


Figure 6: Influence of Phenol Concentration on Charge Transfer Resistance Obtained by Impedance Diagrams.

Electrodeposition of polymer and bacteria

Figure 7 shows the recorded impedance diagrams, respectively for the Al / polymer and Al / Polymer / Bacteria electrodes, in aqueous NaCl (0.1 M) solution. In both cases, the diagrams have the form of a half-loop that appears at high frequency, 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 decreases in the case of presence of the bacteria at the electrode surface. This confirms the adhesion of microorganisms to the surface of the electrode that create a significant charge at the metal / solution interface (Table 2).

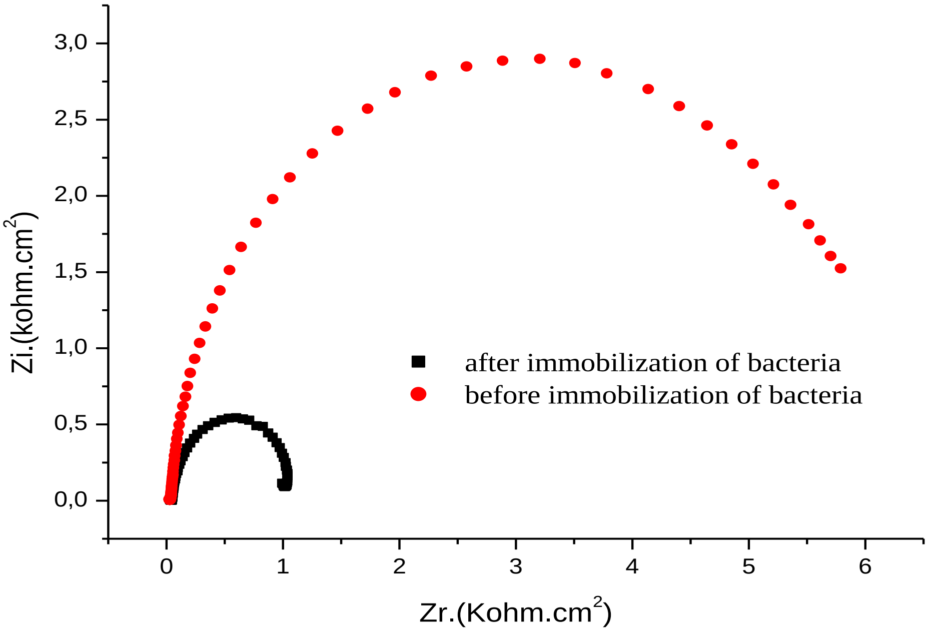


Figure 7: Impedance diagram obtained by the aluminum-polymer electrode (a) and Apolymer-bacteria (b) electrode in 0.1 M NaCl (pH ~ 7).

Table 2: Electrochemical impedance parameters (where R1 is the resistance of the electrolyte, the transfer resistance, and C the capacity of the double layer

Electrode	**R_1 (ohm, cm^2)**	**R_2 (ohm, cm^2)**	**C (µF/cm^2)**
AL- polymer	73,38	85,84	10,38
AL-polymer - bacteria	44.04	84,411 om	94.97

Electro oxidation of phenol on Al electrode / Polymer / Bacteria

In Figure 8, we illustrate the impedance diagrams recorded respectively at the surface of the Al / Polymer and Al / Polymer / Bacteria electrodes in the presence of phenol. We clearly see that the presence of a biofilm on the surface of the electrode causes a remarkable decrease in the electron transfer resistance deduced from the diameter of the half-loop appears at high frequency. This shows that the presence of bacteria significantly activates the oxidation of phenol. The electrochemical parameters deduced from the impedance diagrams are summarized in Table 3.

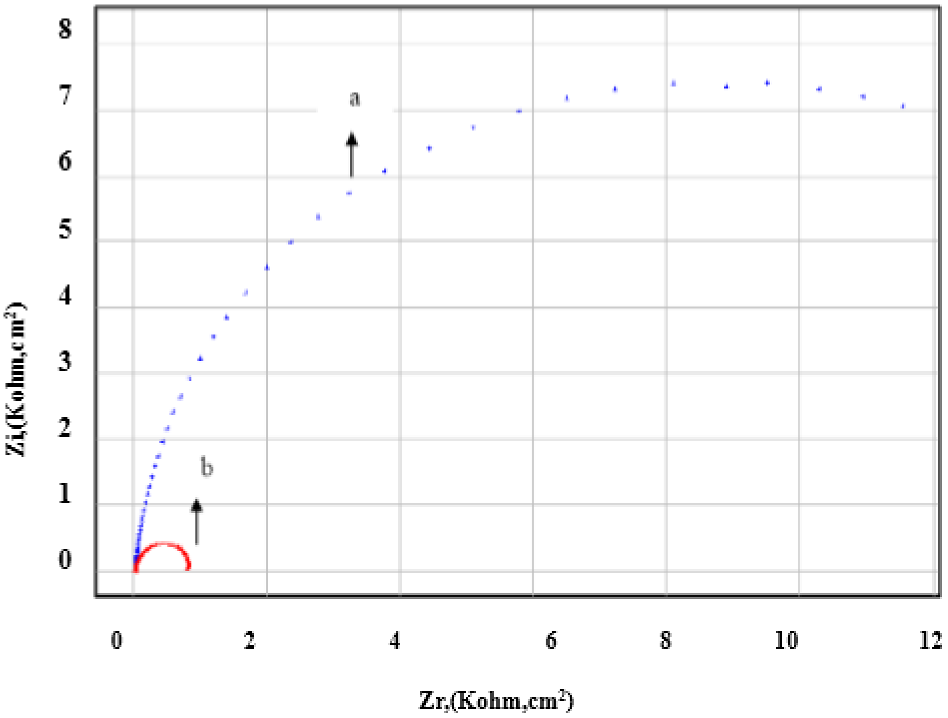


Figure 8: Impedance diagram obtained by the aluminum-polymer electrode (a) and Al-polymer -bacteria electrode (b) in the presence of phenol, in 0.1 M NaCl.

Table 3: Electrochemical parameters of impedance (R1 being the resistance of the electrolyte, the resistance of transfer, and C the capacity of the double layer).

Electrode	**R_1 (ohm, cm^2)**	**R_2 (Kohm, cm^2)**	**C (µF/cm^2)**
AL-polymer+ phenol	32,66	166,30	53,58
AL-polymer-bacteria +phenol	43,86	85,1	91.97

Influence of phenol concentration

The concentration effect of phenol on the Al-polymer-bacteria electrode was also studied by impedance spectroscopy. Figure 9 shows that the impedance spectroscopy curves are in the form of a semicircle for all concentrations of phenol in the high frequency region, which could be attributed to the electron transfer process. The increase in the concentration of phenol has a negative effect on the oxidation reaction, due to the formation of a polymer on the surface of the electrode Al / polymer / Bacteria, confirmed by the decrease in the capacity of the double layer (Figure 10), which hinders the biodegradation of phenol. The increase in electron transfer resistance is linear (Figure 11).

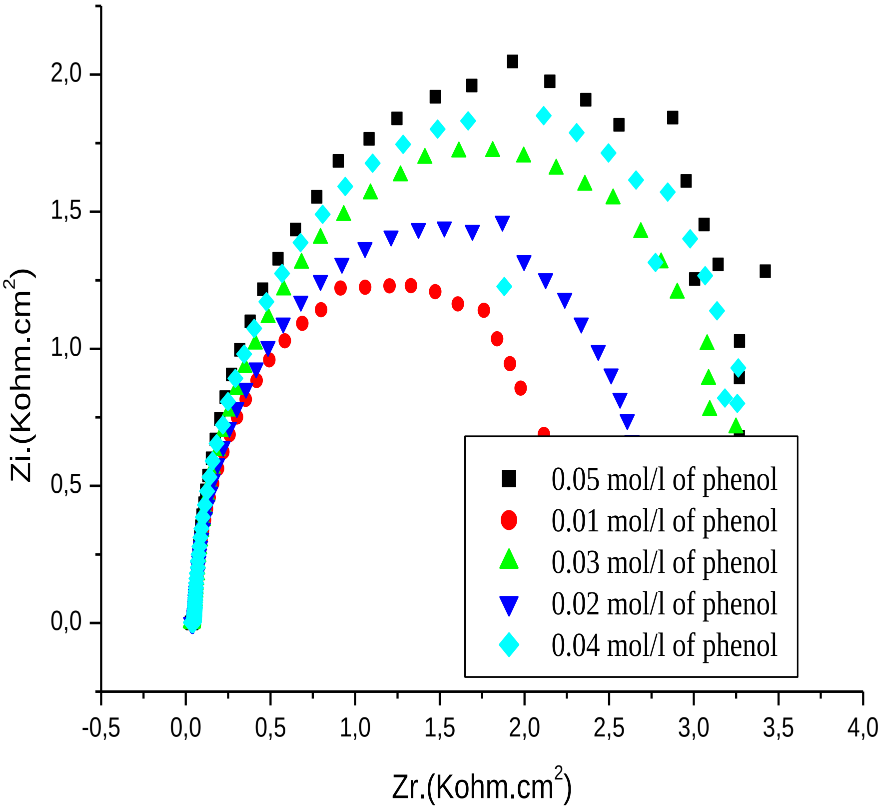


Figure 9: Impedance diagram at different concentrations of phenol (from 2 mM to 12 mM) in 0.1 M NaCl (pH = 7) on the Al-polymer-bacteria plate electrode.

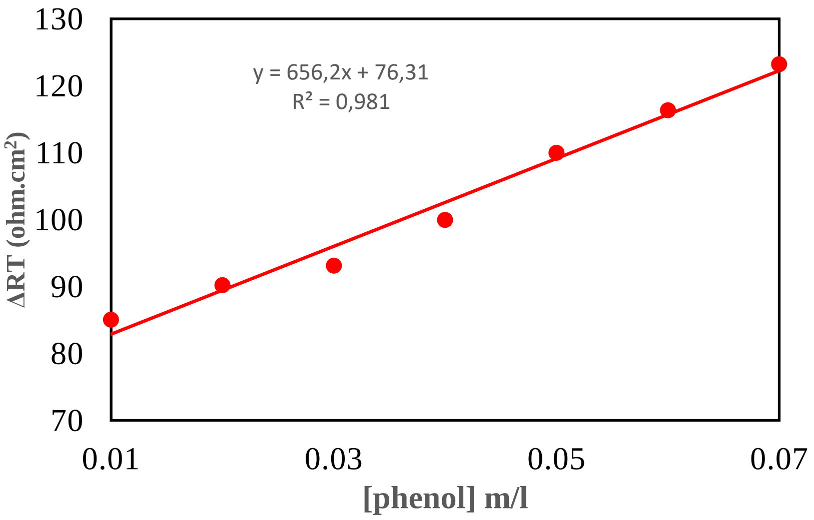


Figure 10: Influence of the concentration of phenol on the charge transfer resistance obtained by the impedance diagrams recorded by Al-polymer-bacteria electrode.

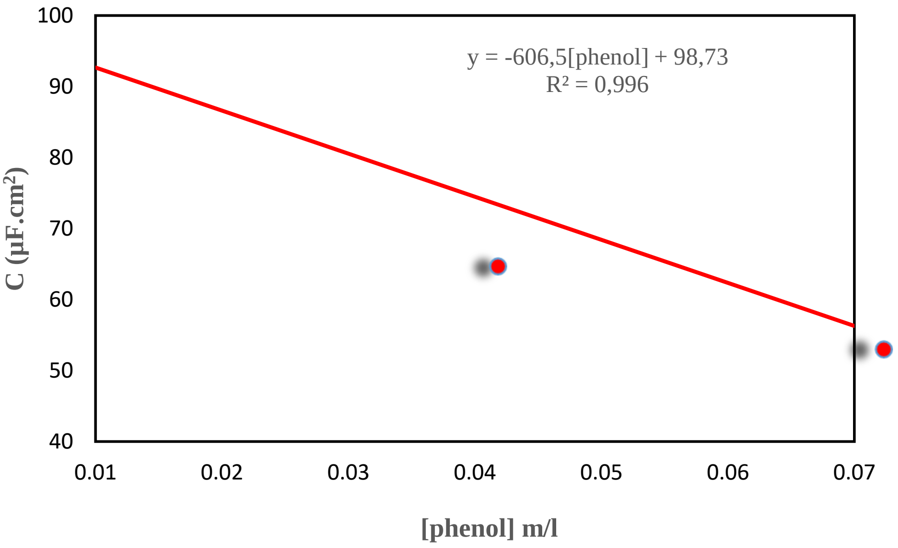


Figure 11: Influence of the concentration of phenol on the double layer capacity obtained by the impedance diagrams.

Morphological study of Al, Al / Polymer and Al / Polymer / Bacteria electrodes

This figure presents the morphological study results of the surface performed by Atomic Force Microscopy (AFM).

The AFM imaging taken respectively for the Al and Al / Polymer electrodes is given in Figure 12. The aluminum surface is relatively smooth; it has some defects, such as scratches that could be due to previous interventions. The surface of the Al / Polymer electrode has a different look, we see the disappearance of defects, the surface is homogeneous, and the organic film adheres to the entire surface of the electrode.

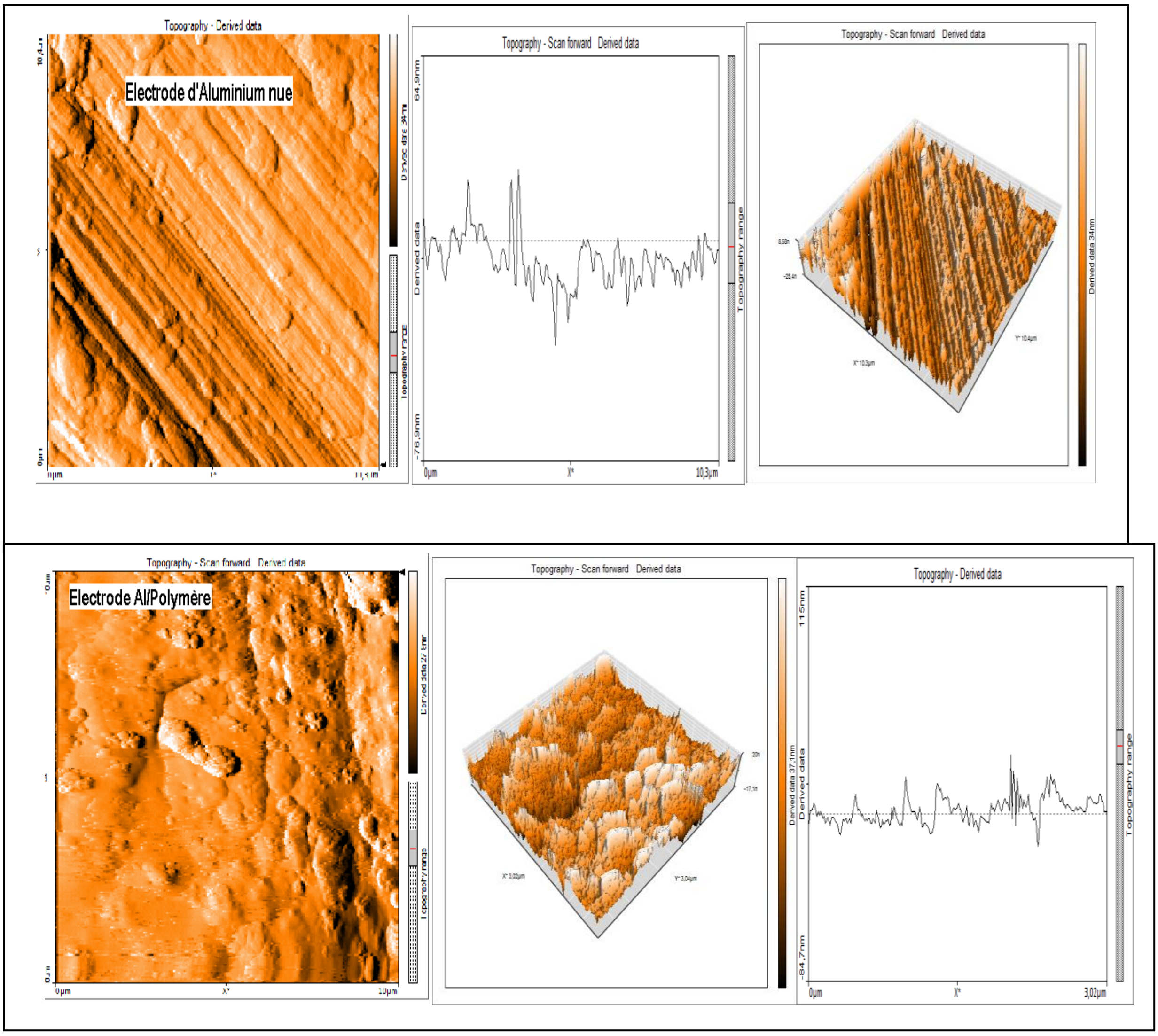


Figure 12: AFM imaging taken for Al and Al / Polymer electrodes.

The appearance of a very dense bacterial population in the case of an optimized surface, with a predominantly oval shape of particle size with a very important coverage rate of the surface occupied by the bacteria (fig13) [12].

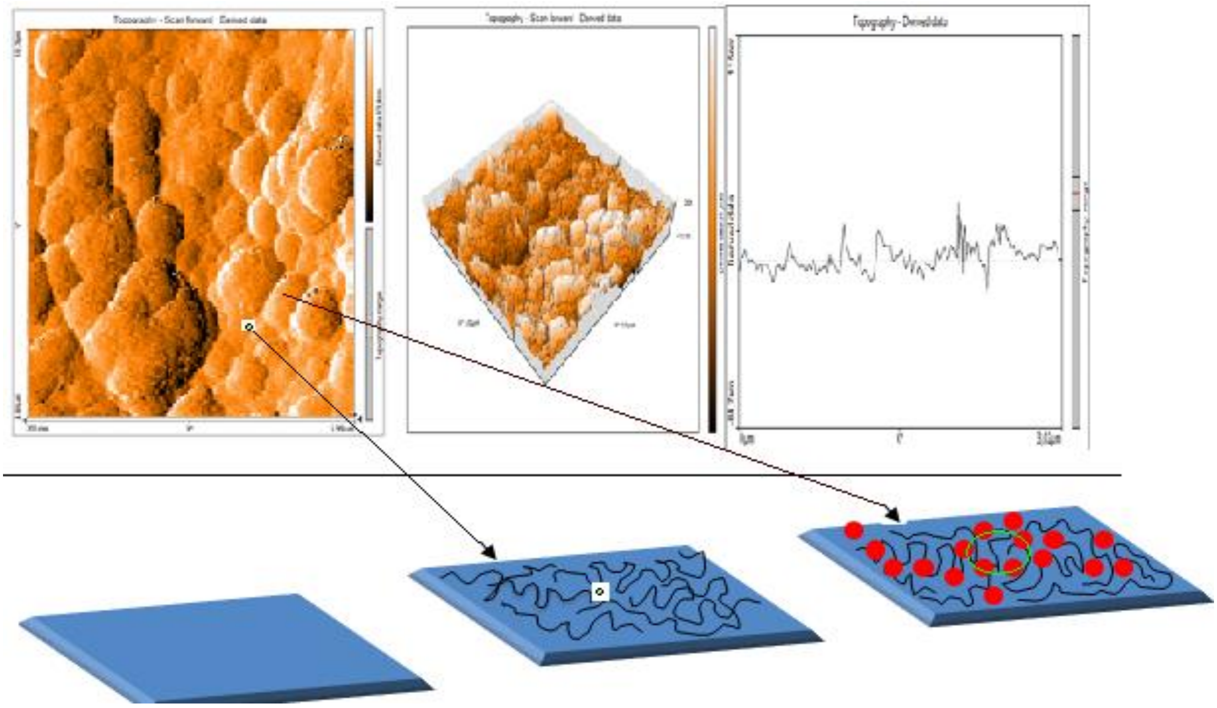


Figure 13: AFM results for an Al-polymer-bacterium electrode surface; 3D topographic images.

These results show the studied electrodes Al, Al / Polymer and Al / Polymer / Bacteria, have very different surfaces, whose average roughness, shown in Table 5, and measured at places in the sample where the film was homogeneous without aggregates too large, varies significantly [9] (Table 4).

Table 4: Evolution of the roughness of modified surfaces.

Area	**Al -sensor**	**Al-polymer sensor**	**Al-polymer-bacteria sensor**
Roughness Ra (nm)	4.63	5.23	7.32

Practical application: in tap water

In order to evaluate the performance of bacteria-Polymer modified aluminum electrode by practical analytical applications, the determination of phenol was carried out in tap water without any pre-treatment.

Electrochemical Impedance Spectroscopy (EIS)

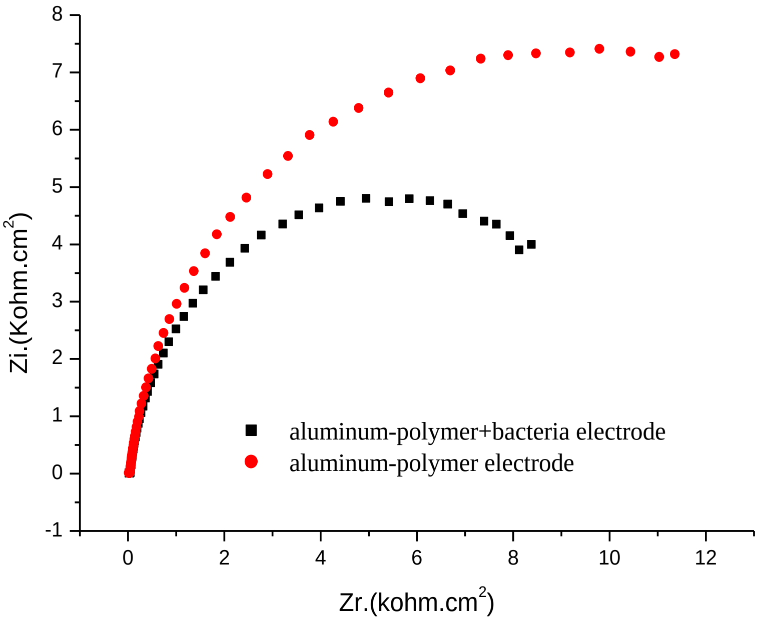


Figure 14: Impedance diagram obtained by the aluminum-polymer electrode (a) and Al polymer -bacteria electrode (b) in 100 ml tap water.

Table 5: Electrochemical parameters of impedance (R1 being the resistance of the electrolyte, the resistance of transfer, and C the capacity of the double layer).

Electrode	**R_1 (ohm.cm^2)**	**R_2 (ohm. cm^2)**	**C (µ. cm^2)**
Al +polymer	60.38	98,50	21.56
Al–polymer-bacteria	40.58	72,54	27.84

Electrochemical analysis of phenol

Electrochemical Impedance Spectroscopy (EIS)

Figure 15 shows the recorded impedance diagrams, respectively for Al-polymer and bacteria-polymer-Al electrodes, in 100 ml medium of tap water contains 4 M of phenol, we can notice that the presence of bacteria to the surface of the electrode causes a decrease in the diameter of the semicircle, which corresponds to the decrease of the load transfer resistance. The accumulation of bacteria at the bacteria-polymer-Al electrode surface promotes the oxidation of phenol in a real sample.

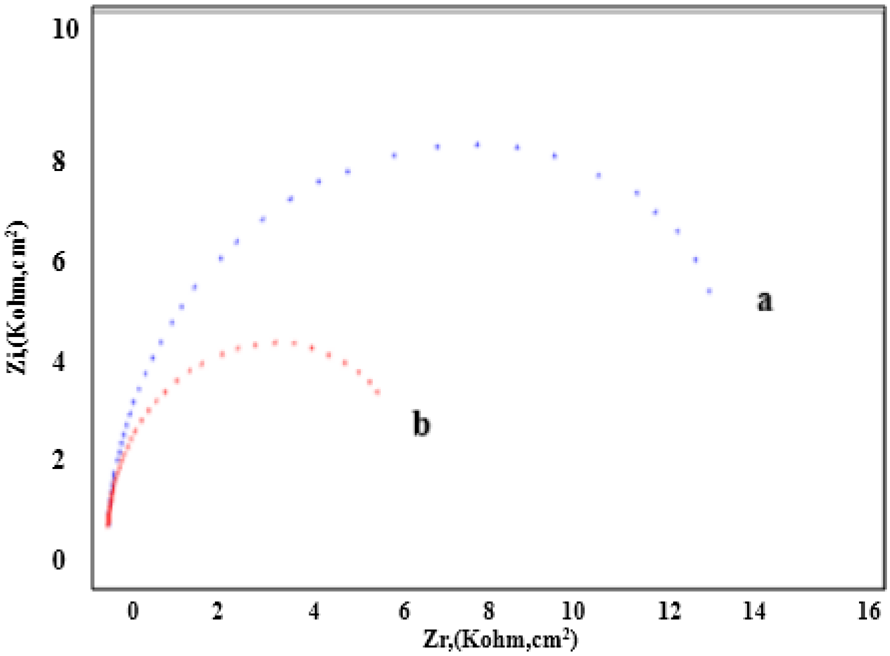


Figure15: Impedance diagram obtained by the aluminum-polymer electrode (a) and bacteria-polymer -Al electrode (b) in the presence of 4 mM of phenol in 100 ml tap water.

Table 6: Electrochemical parameters of impedance (R1 being the resistance of the electrolyte, the resistance of transfer, and C the capacity of the double layer).

Electrode	**R_1 (ohm.cm^2)**	**R_2 (ohm.cm^2)**	**C (µF.cm^2)**
Al+ polymer + phenol	40.58	100,54	17.64
Al+ Polymer+ bacteria +phenol	46,2	34 ,80	20,97

Electrochemical polarization curves

The polarization curves are in the form of Tafel right, the presence of bacteria on the surface of the electrode leads to an increase in the densities of anodic and cathodic currents. Corrosion potential moves to negative values with the presence of the bacteria. These results confirm those found by impedance spectroscopy. The detection of phenol has an influence on the charge density in the vicinity of the electrode. This results in increasing the double layer capacity.

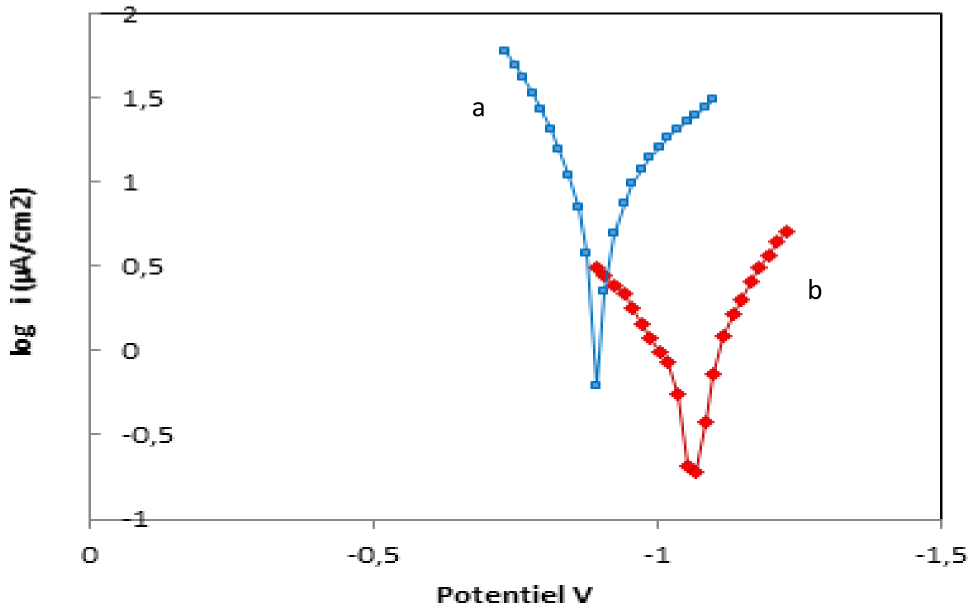


Figure 16: Polarization curves obtained by (a) the aluminum-polymer electrode and (b)Al-polymer -bacteria electrode in 100 ml tap water.

Table 7: The electrochemical polarization curve parameters recorded for the two 'Al-polymer electrodes and Al-polymer-bacteria electrode.

Electrodes	E (i = 0) (mV)	Rp (Kohm.cm²)	icorr (mA/cm²)	βa (mV)	βc (mV)
Al- polymer+ phenol	-902,7	5,46	8,5211	194,2	-354,7
Al-polymer-bacteria+ phenol	-1057,7	48,92	0,9614	292,5	-237,6

Electrochemical study of the effect of phenol concentration

Figure 17 illustrates the impedance diagrams recorded by the bacteria-polymer- aluminum electrode at different concentrations of the phenol. The increase in concentration leads to a linear increase in the electron transfer resistance, justified by the formation of an organic film on the surface.

The capacity of the double layer decreases with phenol concentration, probably due to the formation of an organic film on the surface of the electrode (Figure 18).

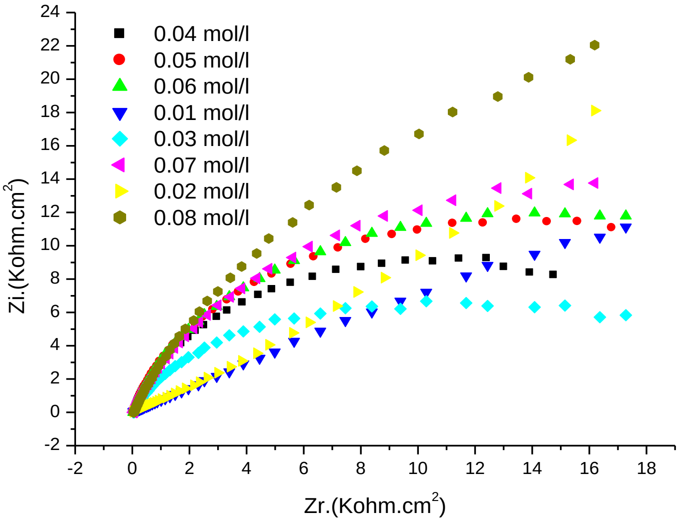


Figure 17: Impedance diagram at different concentrations of phenol (from 2 mM to 12 mM) in tap water 100 ml on the Al-polymer-bacteria electrode.

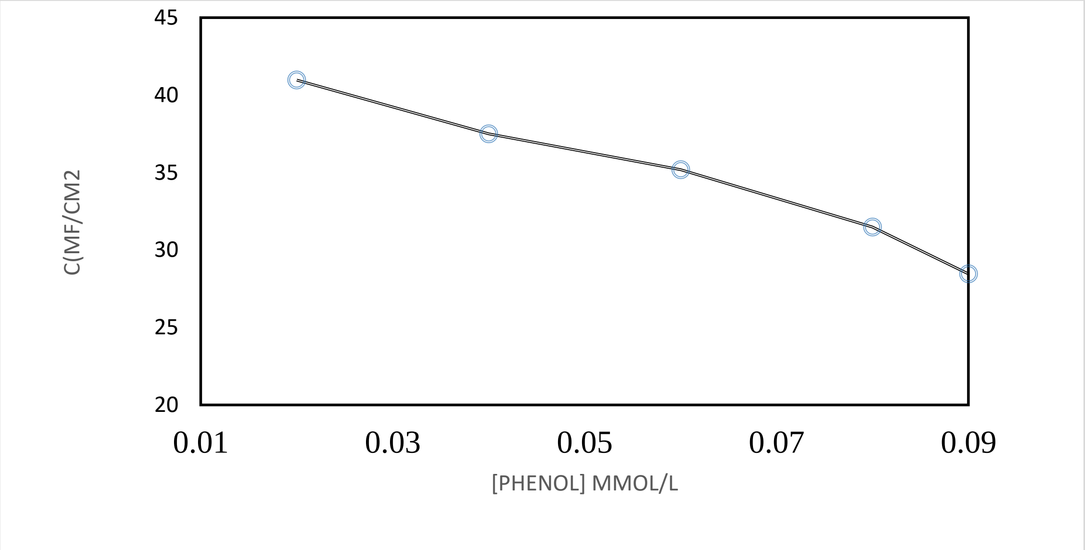


Figure 18: evolution of the double layer capacity according to different phenol concentration.

Conclusion

The aim of this work was to group two methods of destruction of toxic organic products, of which phenol is the simplest molecule, the electrochemical method which is often blocked by the poisoning of the surface of the electrode by the formation of intermediates of the reaction and the biological method based on the biodegradation of phenol by bacteria. This biodegradation is limited by the nature of the toxic products that could expand the microorganisms hence the need to present a process of preliminary destruction of non-biodegradable toxic products. The Al / Polymer / Bacteria electrode has proved a great activity with respect to the oxidation of phenol. Electropolymerization took place in situ on the surface of the aluminum electrode by subjecting the Al electrode to a series of cyclic voltammograms. Deposition of the bacteria took place by contact of the Al / Polymer electrode with a solution containing the bacteria. AFM imaging has shown that the polymer adheres perfectly to the entire aluminum surface and the biofilm is composed of populations of bacteria dispersed over the entire surface.

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