



Polymer Electrode Material for Microbial Bioelectrochemical Systems

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Abstract

Bioelectrochemical systems based on polymer-bacteria thin film modified electrode were explored. The prepared polymer-bacteria modified copper electrode was characterized with voltametric methods, as cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The proposed electrode indicated a definite redox response, high conductivity and electrochemical stability. The experimental results revealed that the prepared electrode could be a feasible for degradation of hazardous phenol pollutants.

Keywords: *Staphylococcus aureus*; Cyclic voltammetry; EIS; Phenol; Oxidation

Introduction

The chemical contamination of the environment is a serious problem across the world. Phenol is considered as one of the most products rejected by industrial plants such as pharmaceuticals, formaldehyde resins, pesticides, textiles, petroleum refineries, chemical industry and agricultural activities. Phenol is one of 129 chemical compounds considered important pollutants listed by the Agency for Environmental Protection (EPA) [1,2]. Due to severe legislative laws, prohibiting the discharge of toxic products into the environment, various methods for phenol treatment have been studied, such as wet air oxidation [3], adsorption [4], chemical oxidation [5], photo catalyst [6], biological treatment [7], and ozone oxidation [8]. But there are few sufficiently efficient processes for the removal of phenol. Microbial bioelectrochemical systems have evolved as a potential alternative technology for phenol treatment. The electrochemical oxidation methods has become a promising method for the toxic, bio refractory and highly concentrated organic wastewater treatment because of its simplicity, easy control, strong oxidation performance and environmental compatibility [9]. For anodic oxidation reactions, that the organic matter electro oxidation process, hydroxyl radicals ($\text{OH}\cdot$), produced by water discharge through the retardation of oxygen at high electrode over potential on metal/particle electrode surface, are required for organic matter elimination [10]. The combination of electrochemical and biological method can bring added value 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 [11]. The aims of this work were to examine the new electrode, based on polymer-bacteria modified copper electrode for simultaneous production of electricity and degradation of phenol.

Experimental

Reagents and apparatus

All chemicals were analytical grade and used without further purification. The monomer ϵ -caprolactone was purchased from Sigma-Aldrich. 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 polymer-bacteria modified copper 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 copper 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 8400xg 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 re-suspended bacteria suspension was diluted with water to obtain needed suspension of different concentration before use.

Electrode preparation

The bacteria suspension was versed onto the copper electrode plate (1 cm \times 1 cm \times 1 mm), after immobilizing the bacteria on the surface of copper plate, we launch a scan cyclic voltammetry, 10 cycles, in the potential range between -3 V and 2 V at 50 mV/s in a solution of 1 M NaCl.

Results and Discussion

Electrodeposition of polymer and bacteria

Electrochemical polymerization of the polymers can be carried out by either potential step or potential sweep methods, using a typical coating solution 0.1 M monomers in 1M NaCl solution (pH 5). In the

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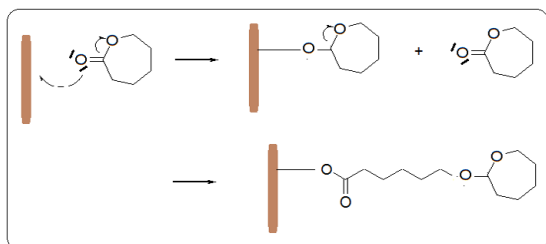
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cyclic voltammetric (CV) curves for the polymerization, the anodic current is even bigger during the early reverse scan than during the forward scan, leading to a cross-over. These features indicate [12,13] that deposition of the polymer proceeds through a nucleation and growth mechanism as reported for other conducting polymers.

The CV (Figure 1) exhibits three peaks, the first one (Ia), in the anodic scan, at about 0 V attributed to monomers oxidation, the second one at 0.5 V, corresponds to the evolution of the polymer, the third peak appears in the direction of cathodic scan may correspond to the polymer reduction.

The proposed mechanism of polymerization is as follows:



The EIS experiments were carried out in 1.0 mol L⁻¹ NaCl in order to evaluate the effectiveness of the polymer modified copper electrode to oxidize the phenol. Figure 2 shows the Nyquist plot for phenol-free polymer-modified electrode and polymer-Cu/phenol system at different concentrations of phenol. In all cases (presence or absence

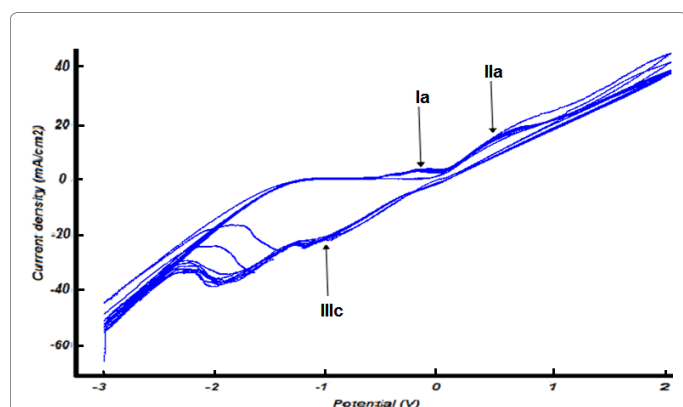


Figure 1: Cyclic voltammogram for electrochemical polymerization of 0.1 M monomer in 0.1 M NaCl, at copper electrode, at 50 mv/s, 10 cycles.

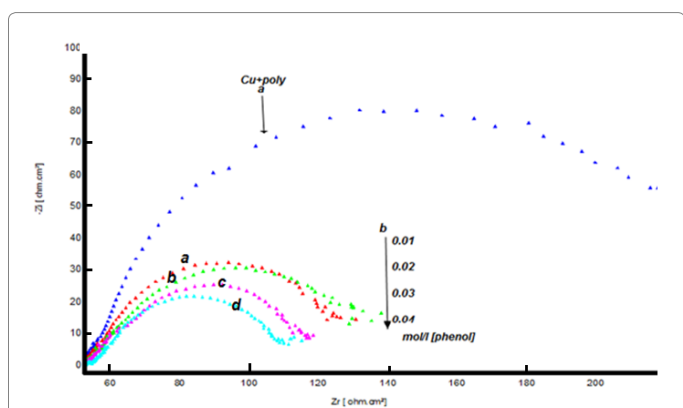


Figure 2: Impedance spectra in 1.0 mol L⁻¹ NaCl, at polymer modified copper electrode in 1 M NaCl solution containing different concentrations of phenol.

of phenol in the electrolytic solution) curves included a semicircle at higher frequencies corresponding to the electron transfer limited process and the linear part at lower frequencies corresponding to the diffusion process. It appears clearly from these data that the resistance became smaller in presence of phenol in electrolytical solution. This means that the modified electrode becomes more conductive, which can be explained by the presence of phenol on the electrode surface.

In the presence of bacteria in the polymer matrix, oxidation of phenol has been investigated by impedance spectroscopy (EIS). The same behavior in the absence of bacteria, the impedance diagrams have the shape of a semi circle, indicating that the mechanism of the phenol oxidation is not affected by bacteria (Figure 3).

In Figure 4, we illustrate the impedance diagrams recorded in the presence of phenol in the electrolytic medium, respectively for the electrodes, polymer modified copper electrode (curve a) and polymer-bacteria modified electrode (curve b), in the both cases EIS curves have the same shape, the mechanism of phenol oxidation has not changed. However, the electrochemical parameters deduced from these diagrams (Table 1) reveal that, in presence of phenol in electrolytical solution, the electron transfer resistance, Rt, recorded for polymer modified electrode, at the metal/solution interface is about 71.69 ohm.cm², while in the case of the polymer-bacteria electrode, Rt is of the

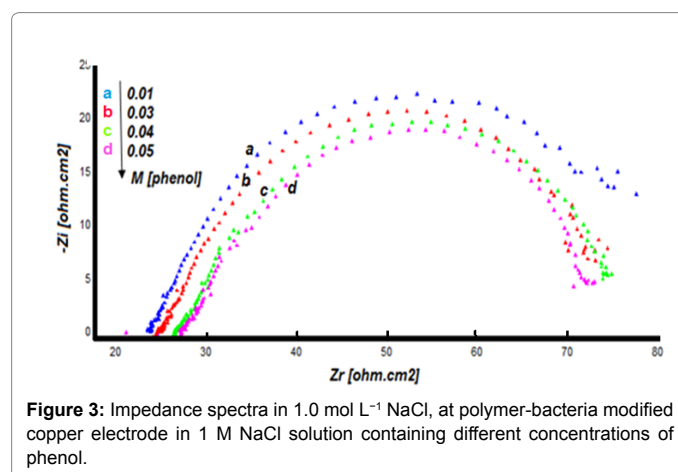


Figure 3: Impedance spectra in 1.0 mol L⁻¹ NaCl, at polymer-bacteria modified copper electrode in 1 M NaCl solution containing different concentrations of phenol.

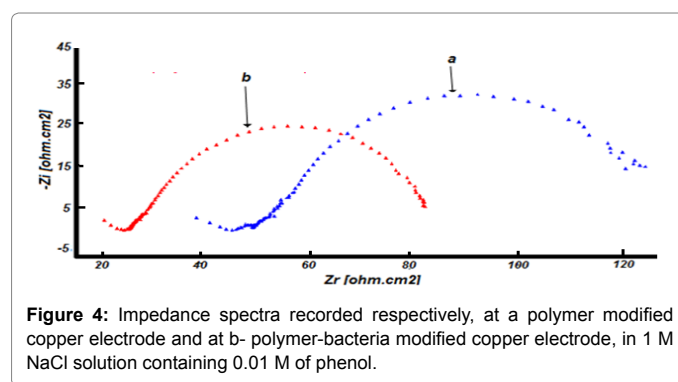
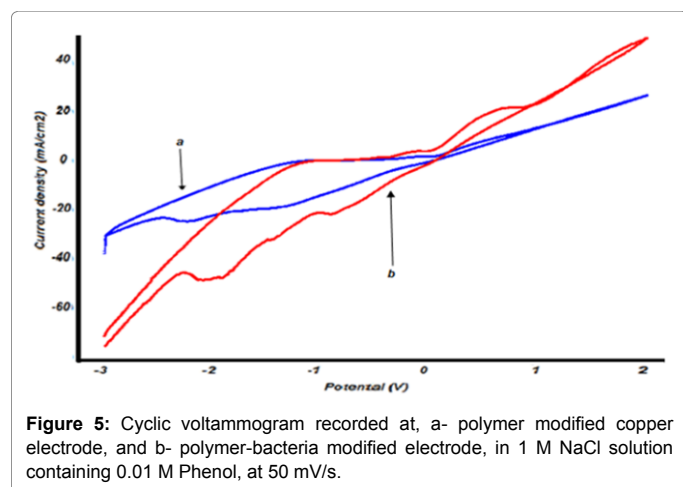


Figure 4: Impedance spectra recorded respectively, at a polymer modified copper electrode and at b- polymer-bacteria modified copper electrode, in 1 M NaCl solution containing 0.01 M of phenol.

| Electrode | R ₁ (ohm.cm ²) | R ₂ (ohm.cm ²) | Diameter (ohm.cm ²) |
|-------------------------|---------------------------------------|---------------------------------------|---------------------------------|
| Polymer-Copper | 55.86 | 70.24 | 71.69 |
| Polymer-bacteria-Copper | 30 | 53.25 | 53.48 |

Table 1: Parameters of the electrochemical spectra of impedance.



order of 53.48 ohm.cm². Which shows that the electrode polymer-bacteria modified copper electrode is more active for the oxidation of phenol than polymer modified copper.

Figure 5 illustrates the CV's registered respectively at (curve a) and polymer-bacteria modified copper electrode, in electrolyte medium containing 0.01 M phenol. We note that, the oxidation current densities are very important in the case of the electrode modified by bacteria, confirming the previous results; bacteria catalyze the oxidation of phenol connection which facilitates the adsorption of the molecule of phenol.

Conclusion

In this study, we experimentally prepared two electrodes, polymer modified copper electrode and polymer-bacteria modified copper electrode. The presence of bacteria onto polymer matrix improves sensitivity towards phenol and provides a rapid response.

Oxidation of phenol was investigated by cyclic voltammetry and EIS. EIS diagrams resulted in separate time constants; the oxidation of phenol is mostly represented by half a circle, whose diameter corresponds to the electron transfer resistance. Electron transfer resistance produced by polymer-bacteria modified copper electrode is less than that obtained

by polymer modified copper electrode. The presence of bacteria in the polymer matrix increases the activity of the electrode and catalyzes the oxidation of phenol.

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