Abstract

The voltammeter degradation of the phenol was carried out at a microbial electrode. This electrode is based on carbon graphite and clay and modified by bacteria. This electrode, later designated by bacteria-clay-CPE, showed stable response and was characterized by voltammetry methods, such as cyclic voltammetry (CV) and electrochemical Impedance spectroscopy (EIS). This electrode is tested to treat phenol-containing wastewater. Experimental results revealed that the prepared electrode could be a feasible solution. For the degradation of dangerous phenol pollutants.

Keywords: Cyclic voltammograms; EIS Electrochemical; oxidation Phenol; Biological sensor; removal of phenol.

Introduction

The electrochemical oxidation of hazardous organic species is a promising method for wastewater remediation. Phenols are a large group of pollutants in industrial effluents and, due to their low degradability by conventional effluent treatment, even at low concentrations they present toxicity and bioaccumulation problems [1]. Phenolic compounds are present in effluents from coke production, food industries, chemical industries, such as those associated to the production of resins and pesticides, and petroleum refineries [2]. Many different technologies are in use or have been proposed for the recovery or destruction of phenols [3], [4]. Among these technologies, there are processes dealing with collapse of micro bubbles [5], anodic polymerization [6], [7], [8], oxidation by photo-catalysis or by hydrogen peroxide [9], [10], [11], [12], as well as electro-oxidation with various electrode materials [13], [14], [15], [16].

The combination of electrochemical and biological method can bring benefit to the degradation of toxic materials such as phenol. The function of microbial bio-electrochemical systems is based on operating the microorganisms to catalyze an electrochemical reaction. The system allows for different tasks, such as, biodegradation, and electrochemical processes [17]. 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.

The purpose of this work is to study the applicability of cyclic, square wave voltammetry and electrochemical impedance spectroscopy (EIS) together with carbon paste electrode (CPE) modified with clay bacteria in the electro oxidation of phenol in wastewater solution.

Experimental

Reagents and apparatus

Electrochemical measurements were performed on a voltalab potentiostat (model PGSTAT 100, Eco Chemie B.V., Utrecht, The Netherlands) directed by software (voltalab master 4 software) run under windows 2007. The three electrode system consisted of a chemically modified carbon paste electrode as the working electrode platinum counter and SCE reference electrodes was used.

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.

Electrodes preparation

The clay modified carbon paste electrode (clay -CPE) was prepared by mixing a graphite carbon powder and the desired clay weight. The modified electrodes were immered in a cell containing bacteria for 15 minutes, thus the bacterial electrode is ready for use. The geometric surface of this electrode was 0.1256 cm2. The electrical contact was made at the back by means of a bare carbon.

Procedure

The prepared electrode is characterized in electrolytic medium. In a second stage is tested for the electro oxidation of phenol, added in the measurement cell. The cyclic voltammetry was recorded in the range from -2 V to 2 V. Optimum conditions were established by measuring the peak currents in dependence on all parameters. All experiments were carried out under ambient temperature [18]. 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.

**Results and Discussion**

**Clay characteristics**

The morphology of the electrode surface of Clay was observed by scanning electron microscopy (Figure 1).

![Figure 1: Electron Micrograph of CPE Modified by Clay](image)

We find that the matrix is formed by compact particles fractions between 1 and 15 μm. Clay treaty has the following chemical composition given by transmission electron 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 more metals order ppm (Figure 2). An examination of clay modified carbon paste electrode indicates some kind of agglomeration.

**Characterization by cyclic voltammetry**

The carbon paste electrode modified with clay and bacteria (CPE-Clay-Bacteria) was designed according to the procedure previously mentioned. Electrochemical characterization was studied by cyclic voltammetry (CV) (Figure 3) and polarization curves (Figure 4). The bacterial film is developed on the surface of the electrode by immersion of CPE-Clay in a solution containing the suspensions of bacteria. The presence of microorganisms on the surface of the electrode is manifested by a slight increase in current densities.
Figure 3: Cyclic voltammograms obtained by CPE-Clay (blue) and CPE-Clay-bacteria (red) in 0.1M NaCl with a scanning speed of 100 mV / S.

**Characterization by polarization curve**

The development of microbial film on the surface of the electrode resulted in a slight decrease in polarization resistance, due to the high susceptibility of clay to bacteria [1]. The bacterial-clay bond is so strong that it weakens the clay-carbon bond, which causes the detachment of the bacterial clay complex (Figure 4 and Table 1).

Figure 4: Polarization curves recorded for the two CPE-Clay (a) and CPE-bacterium (b) electrodes.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>E (i = 0) (mV)</th>
<th>Rp (Kohm.cm²)</th>
<th>icorr (mA/cm²)</th>
<th>Ba (mV)</th>
<th>Bc (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPE-Clay</td>
<td>623.3</td>
<td>41.67</td>
<td>0.8686</td>
<td>217.1</td>
<td>-203.7</td>
</tr>
<tr>
<td>CPE-Clay bacteria</td>
<td>449.11</td>
<td>38.87</td>
<td>0.9387</td>
<td>273.7</td>
<td>-167.9</td>
</tr>
</tbody>
</table>

Table 1: Electrochemical parameters and polarization curves recorded for the two CPE-Clay and CPE-bacteria electrodes.
Degradation of phenol

The electrochemical degradation of phenol on the surface of the CPE-Clay-bacteria electrode was studied respectively by cyclic and square-wave voltammetry. The VC recorded in the presence of phenol (0.45 mmol / L) in tap water, has 2 peaks in the anodic sweep direction (Figure 5), respectively at 0.6 V, and 1.2 V and a cathode peak near 0. The anodic peaks correspond to the oxidation of phenol to intermediate products. Square wave voltammograms show the 3 peaks observed in the CV.

Figure 5: Cyclic voltammograms obtained by CPE-Clay-bacteria 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.

Characterization by impedance spectroscopy

The impedance diagrams recorded for the CPE-Clay-bacteria electrode are given in Figure 6. The part of the high-frequency curve is eclipsed by the scattering phenomenon. Clay because of its porous structure favors the diffusion phenomenon. The electrochemical parameters deduced from the impedance diagrams are summarized in Table 2. The high value of the capacity of the double layer recorded in the presence of phenol is probably due to the biodegradation of phenol and its derivatives [18].

Figure 6: Impedance diagram obtained by CPE-Clay-bacteria in the absence (a) and in the presence (b) of 4 mM phenol in 0.1 M NaCl.
Table 2: Electrochemical impedance parameters (R1 being the resistance of the electrolyte, the transfer resistance, and C the capacity of the double layer).

<table>
<thead>
<tr>
<th>Electrode</th>
<th>$R_1$(ohm,cm$^2$)</th>
<th>$R_2$(Kohm,cm$^2$)</th>
<th>C($\mu$F/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPE-NP-bactérie</td>
<td>175,7</td>
<td>23,7</td>
<td>67,12</td>
</tr>
<tr>
<td>CPE-NP-bactérie+phénol</td>
<td>225,7</td>
<td>31,39</td>
<td>50,68</td>
</tr>
</tbody>
</table>

Effect of scanning speed

In Figure 7, we present the cyclic voltammograms, recorded for the graphite carbon electrode modified by clay and bacteria, at different scanning speeds, in tap water containing phenol. The current densities of the different peaks increase linearly with the scanning speed (Fig. 8). The anodic peaks move towards the positive potentials, as the scanning speed increases, while the cathodic peaks move towards the negative potentials at high scanning speeds [19].

Figure 7: Voltammograms recorded by ECP-Clay-bacteria with 8 mM phenol in 0.1 M NaCl at different scan rates of 40 to 140 mV.s$^{-1}$. 
Figure 8: Influence of the root of the sweep rate on the intensity of the phenol redox peaks obtained by (CV) on the surface of CPE-Clay-bacteria.

**Effect of phenol concentration**

The change in anodic peak intensity as a function of phenol concentration was followed by cyclic voltammetry (Figure 9), and impedance spectroscopy (Figure 10). We have established the calibration curve by progressive addition of phenol in the electrolytic solution. This curve is shown in Figure 11. The linear regression equation corresponding to the reduction is expressed as follows:

\[
I_{pc} = -0.032 \text{[phenol]} - 0.056 R^2 = 0.955
\]

The detection limit is \(6.23 \times 10^{-9}\) mol l\(^{-1}\) and the limit quantification is \(2.37 \times 10^{-8}\) mol l\(^{-1}\) for the reduction peak.

Figure 9: Cyclic voltammograms at different concentrations of phenol (from 4 mM to 10 mM) in 0.1 M NaCl on CPE-Clay-bacteria, \(V = 100 \text{ mV / S}\).
Figure 11: Influence of phenol concentration on peak reduction intensity obtained by (CV) on the surface of CPE-Clay-bacteria.

Figure 12: Impedance diagram at different concentrations of phenol (from 2 mM to 12 mM) in 0.1 M NaCl on CPE-Clay-bacteria.
Evaluation of the activity of the modified bacteria-Clay-CPE electrode for the oxidation of phenol.

Voltage study

Figures 160 and 161 show that the oxidation peaks corresponding to the oxidation of phenol are more intense in the presence of bacteria. Bacteria catalyze the oxidation of phenol.

The activity of the bacterium adhered to the Clay-CPE electrode surface calculated for the oxidation of phenol in a solution of tap water is: \( \alpha = (1 - (0.23 / 0.135)) \times 100 = 70.37\% \)

Conclusion

The electrode developed, CPE-Clay, modified by bacteria (Staphylococcus aureus) showed a high sensitivity to the detection of phenol in tap water.

The CPE-Clay biosensor showed the best efficiency for the detection of phenol in tap water, of the order of 70.37%. Optimization of the experimental conditions yielded the following values of the following detection limits (DL) and quantification limits (LQ):

- LD = 6.23.10^-9 mol l^-1, and LQ = and 2.37.10^-8 mol l^-1.

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.

References
