

## Bioelectrochemical Systems for Clean Environment

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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. The results showed that the NP-bacteria-CPE exhibited excellent electro catalytic activity to phenol. The appearance of three peaks of oxidation shows that the degradation of the phenol was total.

**Keywords:** Modified electrodes; Cyclic voltammetry; Natural phosphate; Phenol

### Introduction

Phenol is considered as a toxic product, it is one of the first compounds inscribed into the List of Priority Pollutants by the US Environmental Protection Agency (US EPA). Phenol is really a refractory hazardous pollutant in wastewater. Phenolic compounds are present in effluents from coke production, food industries, and chemical industries, such as those associated to the production of resins and pesticides, and petroleum refineries [1]. Various technologies have been studied for the recovery or destruction of phenols [2,3]. These methods are mostly based on biological treatment [4], on the phenol polymerization on anode [5-7], or on electro-oxidation on a variety of electrodes. In this work, we couple biological and electrochemical treatment. The bioelectrochemical system developed is based on a carbon paste electrode modified by a natural phosphate matrix, in which we have introduced a well-defined quantity of bacteria.

### Experimental

#### Apparatus and software

All electrochemical measurements were invested by using a voltalab potentiostat (model PGSTAT 100, Eco Chemie BV., Utrecht, The Netherlands) driven by the general purpose electrochemical systems data processing software (Master 4 software) run under windows 2007. The three electrode system consisted of a modified carbon paste electrode as the working electrode a saturated calomel electrode (SCE) serving as reference electrode, and platinum as an auxiliary electrode.

#### Electrodes

Modified electrodes were prepared by mixing a carbon powder and the desired weight of natural phosphate doped with an amount of bacteria. The body of the working electrode for voltammetric experiments was a PTFE cylinder that was tightly packed with carbon paste. The geometric area of this electrode was 0.1256 cm<sup>2</sup>. Electrical contact was made at the back by means of a bare carbon.

#### Procedure

The prepared electrode is first characterized in electrolytic medium. In a second stage is tested for the electrooxidation 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 [7].

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

#### Natural phosphate characteristics

The morphological characterization of the natural phosphate (NP) used in this work, was invested by Scanning Electron Microscopy (MEB) (Figure 1). We find that the NP matrix is formed by compact particles fractions between 100 and 400 nm that is rich in phosphate and as can be seen that compact NP appearance was evident. The treated NP has following chemical composition:

CaO (54,12%), P<sub>2</sub>O<sub>5</sub> (34,24%), F<sup>-</sup> (3,37%), SiO<sub>2</sub> (2,42%), SO<sub>3</sub> (2,21%), CO<sub>2</sub> (1,13%), Na<sub>2</sub>O (0,92%), MgO (0,68%), Fe<sub>2</sub>O<sub>3</sub> (0,36%), K<sub>2</sub>O (0,04%) and several metals in the range of ppm.

We can notice that the surface of the NP presents an important porosity and a considerable roughness. The crystal structure of NP matrix is similar to that of fluoroapatite (Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>F<sub>2</sub>), as shown by X-ray diffraction (Figure 2) and infrared emission spectroscopy (Figure 3). The network of fluoroapatite is very tolerant of substitution in vacant sites, such as Ca can be replaced by Sr, Sb, Co and Na, PO<sub>4</sub> by AsO<sub>4</sub>, VO<sub>4</sub> and SO<sub>4</sub> and F<sup>-</sup> can be replaced by OH<sup>-</sup> and Cl. The NP has the characteristics of a good catalyst; in spite of its specific surface is relatively low 1 m<sup>2</sup>.g<sup>-1</sup> (Figures 1-3).

#### Electrochemical characterization of prepared electrode

The cyclic voltammograms (CV's) recorded, respectively, at NP modified carbon paste electrode (NP-CPE) (curve 1) and at NP doped with bacteria modified paste electrode (NP-bacteria-CPE) (curve 2), in

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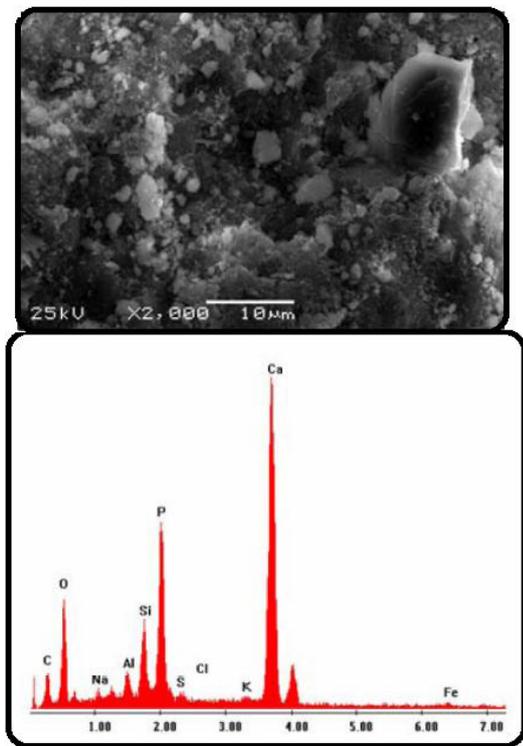


Figure 1: Scanning Electron Micrograph of Natural Phosphate.

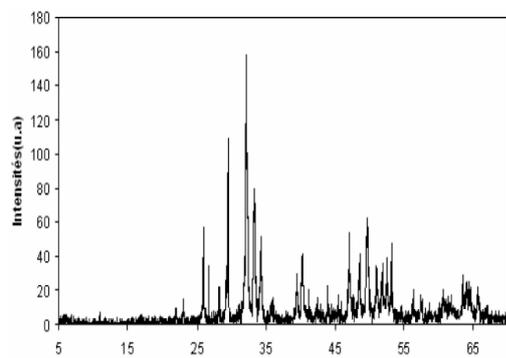


Figure 2: XRD pattern of the natural phosphate.

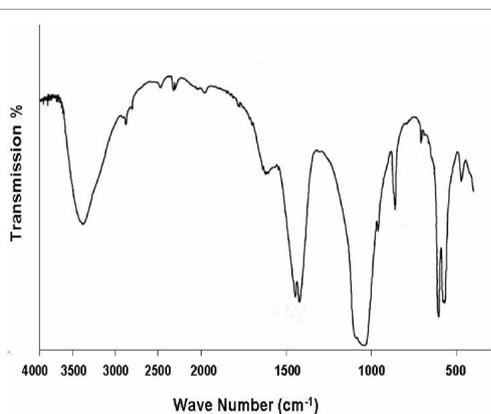


Figure 3: IR spectra of natural phosphate.

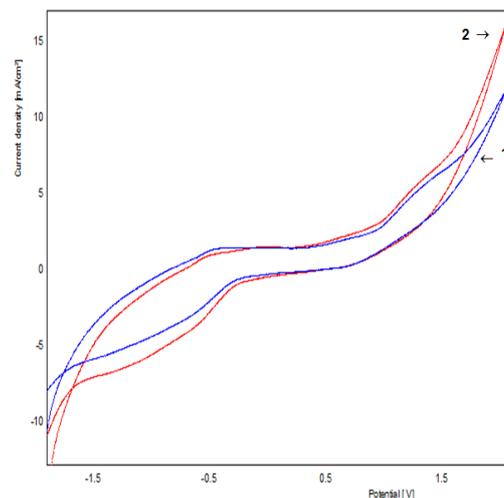


Figure 4: CV's recorded at, 1- NP-CPE and 2- NP-bacteria-CPE, in 0.1M Na<sub>2</sub>SO<sub>4</sub> solution.

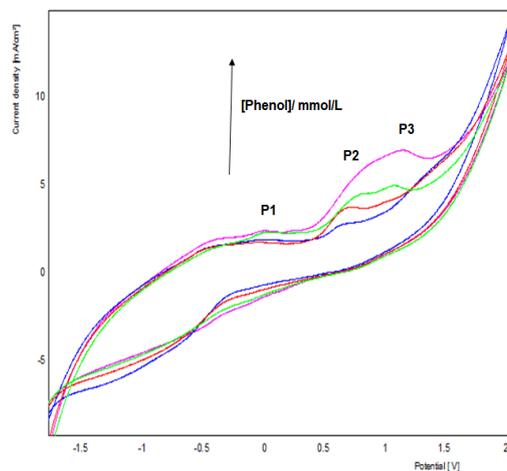
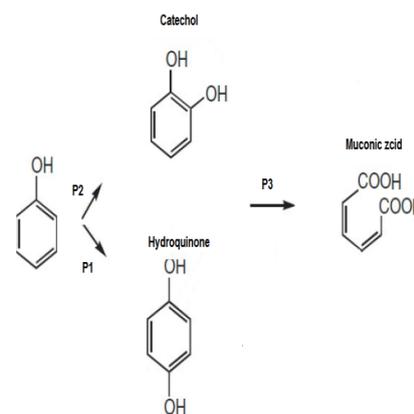


Figure 5: CV's recorded at NP-bacteria-CPE, in electrolytic medium containing various concentrations of phenol, at 100 mV.s<sup>-1</sup>.



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

supporting electrolyte (0.1M Na<sub>2</sub>SO<sub>4</sub>), are shown in Figure 4. We can notice that in both cases CV's keep the same speed, with a light increase of electric currents densities for the NP-bacteria-CP electrode [3].

Electrooxidation of phenol was studied at NP-bacteria-CPE, by cyclic voltammetry (CV) and by square wave voltammetry (SWV). Figure 5 shows the CV's unregistered when phenol was added to electrolytic medium. The CV's exhibited three defined anodic peaks P1, P2 and P3, respectively at 0, 1 and 1.4 V. The presence of only anodic peaks, suggests that the electrochemical oxidation of phenol is totally irreversible, and we propose the following scheme, in agreement with the previous works (Figures 4 and 5 and Scheme 1).

The influence of scan rate on the oxidation peak potentials (E<sub>p</sub>) and peak current (I<sub>p</sub>) of phenol, were studied by CV (Figure 6). The current density, of phenol oxidation peak, increase considerably with concentration. The Figure 7 shows the linear relationship between the scan rates and the current density of anodic peak (P2), suggesting that the electron transfers of phenol at NP-bacteria-CPE is adsorption controlled reaction (Figures 6 and 7) [6].

The evolution of the peak of the phenol oxidation (P2) with according the concentration was also followed by SWV. The current

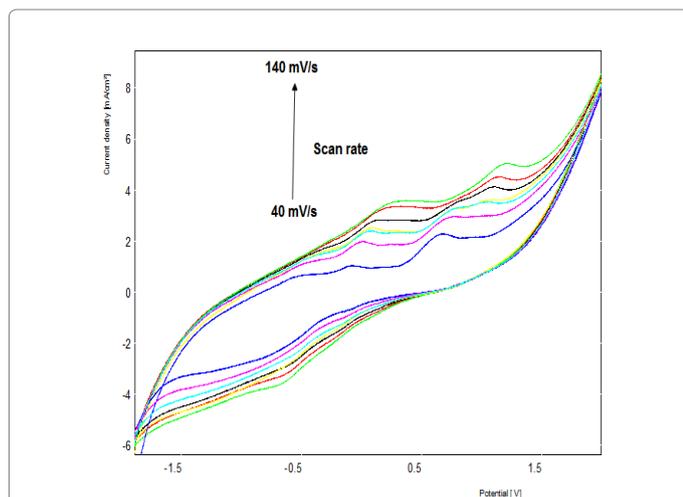


Figure 6: CV's recorded at NP-bacteria-CPE, in electrolytic medium containing phenol, at various scan rates.

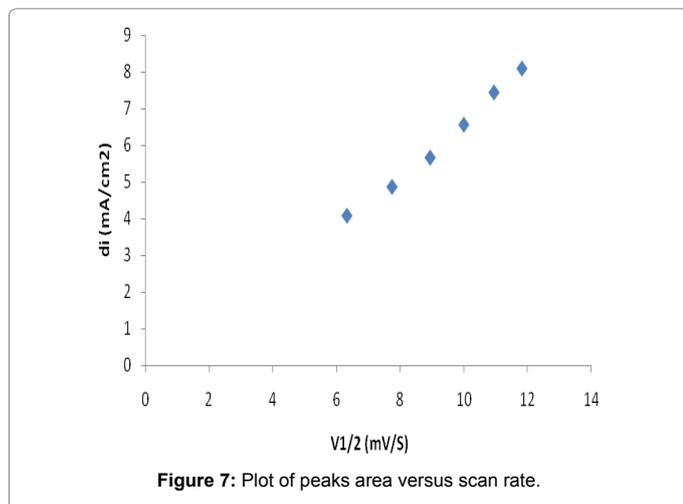


Figure 7: Plot of peaks area versus scan rate.

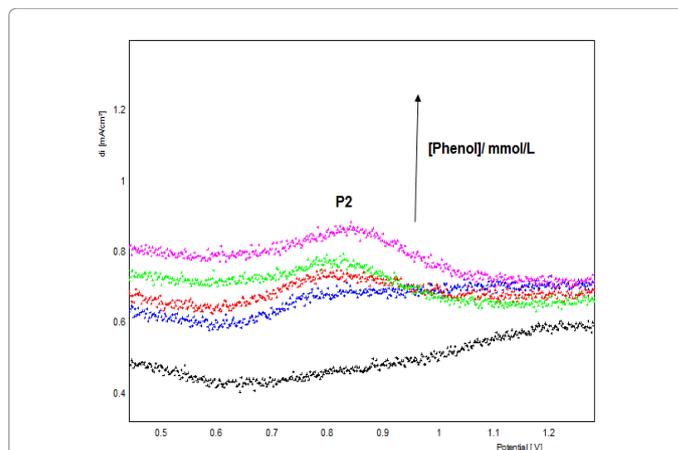


Figure 8: SWV recorded at NP-bacteria-CPE, in electrolytic medium containing phenol.

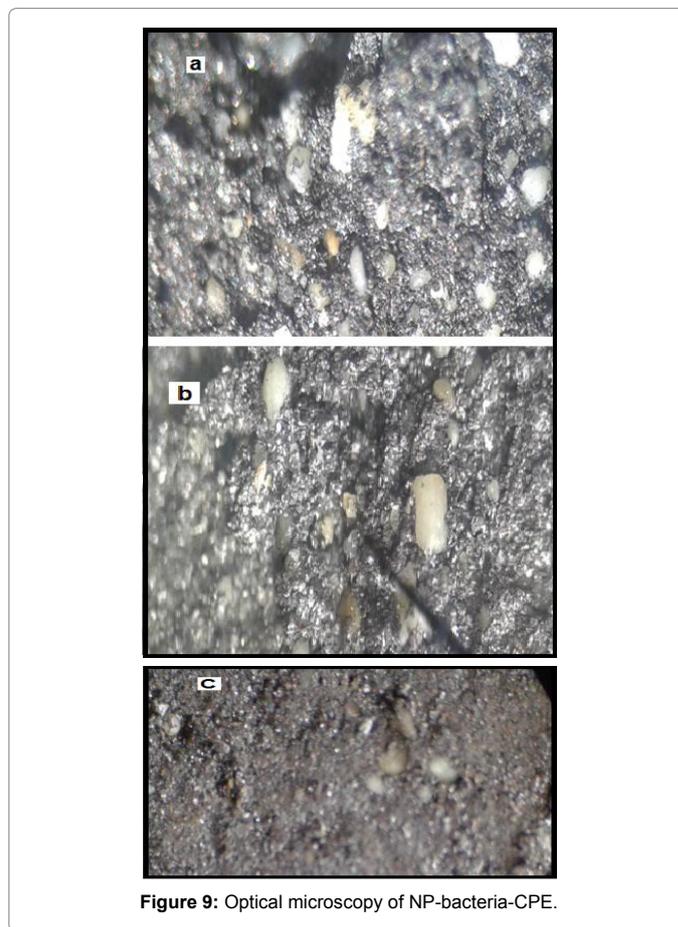


Figure 9: Optical microscopy of NP-bacteria-CPE.

density increases with the concentration of the phenol, what means that the prepared electrode possesses a significant number of active site (Figure 8).

The morphological study of the surface of the prepared electrode was investigated by metallographic microscopy (Figure 9). The prepared electrodes were imaged by optical microscopy. After phenol oxidation, the morphology of the prepared electrode surface changes aspect, it shows agglomerates scattered on the entire surface.

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