

Electro-Oxidation and Detection of Phenol on Metals Modified Carbon Paste Electrodes

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Abstract

A variety of electrodes based on the modification of the carbon paste electrode by various metals such as, Ti, Natural phosphate (NP), kaolin, were prepared. Cyclic voltammetry and square wave voltammetry tests were performed to evaluate the electrochemical performance. The results confirmed that the modification of carbon paste electrode by metals was successful. The presence of metal in the electrode matrix enhanced the electrode stability and increases its performance for the phenol oxidation. The electrochemical study of the complex mediated graphite electrode revealed its fast electron transfer property.

Keywords: Cyclic voltammetry; Square wave voltammetry; Modified electrode; Phenol

Introduction

Phenol is considered as one of the most serious environmental contaminants 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]. Various methods for the treatment of phenolic wastewater have been used, such as wet air oxidation [3], adsorption [4], chemical oxidation [5], photocatalyst [6], biological treatment [7], and ozone oxidation [8]. But there are few sufficiently efficient processes for the removal of phenol.

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 (.OH), 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 [10,11]. Recently, electrochemically activated carbon electrodes such as glassy carbon and screen printed carbon electrode (SPCE) have been broadly used for the detection of various analytes [12-15]. The activated carbon electrodes have showed more surface area and high electrochemical conductivity than that of bare electrodes due to the presence of more surfaces detects on the electrode surface. However, the electrochemically activated screen printed carbon electrode (EASPCE) has never been used for the detection of phenol in the industrial pollutants.

The goal of this work was to examine possible beneficial effect of metals modified carbon paste electrode in the electro oxidation of phenol.

Experimental

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) 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.

Reagents and chemicals

All chemicals were of the highest quality. Graphite powder (spectroscopic grade RWB, Ringsdorff-Werke GmbH, Bonn-Bad Godesberg, Germany) was obtained from Aldrich and was used without further purification, Titanium powder was obtained from Merck chemicals. Deionised water was used to prepare all solution.

Electrode preparation

Modified electrodes were prepared by mixing a carbon powder and the desired weight of Natural Phosphate (NP), titanium and/or clay. A 4% of modifiers was used through this work.

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 cm². Electrical contact was made at the back by means of a bare carbon. A Natural Phosphate (NP) used in this work was obtained in the Khouribga region (Morocco). Prior to use, this material was treated by techniques involving attrition, sifting, calcinations (900°C), washing, and recalcination. Kaolin was obtained in the north of Cameroun region.

Procedure

The initial working procedure consisted of measuring the electrochemical response at Metal-CPE at a fixed concentration of phenol. Standard solution of phenol was added into the electrochemical cell containing 100 mL of supporting electrolyte. 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 -1.8V to 1.8V. Optimum conditions were established by measuring the peak currents in dependence on all parameters. The square wave voltammetry was recorded in the range from -1.8V to 1.8V, for which the scan rate is 1 mV.s⁻¹, step potential 50 mV, amplitude 2 mV and duration 0.1 s. All experiments were carried out under ambient temperature. Supporting electrolytes have been known to enhance the reaction response of modified electrodes towards the electro oxidation of phenol by increasing either the current response and/or lowering the reaction potential. We studied the electrochemical response characteristics of the prepared electrodes in 0.1 mol L⁻¹ Na₂HPO₄, 0.1 mol L⁻¹ Na₂SO₄, and the best results were obtained with Na₂SO₄.

Results and Discussion

Electrode Ti-CPE

As shown in Figure 1 on the Titanium modified carbon paste electrode (Ti-CPE), the cyclic voltammograms (CV's) recorded respectively carbon paste electrode (CPE) and Ti-CPE in 0.1 M Na₂SO₄ solution, demonstrated two different behaviours. In the absence of Titanium, the work electrode shows no peaks (curve b). In the presence of Titanium, the CV shows an anodic peak, at about -0.3V, which probably corresponds to the surface oxidation.

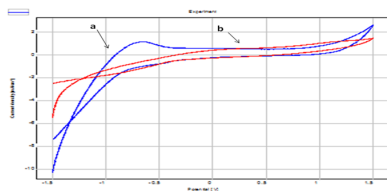
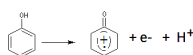


Figure 1: Cyclic voltammograms of a- Ti-CPE, b- CPE recorded successively, in 0.1 M Na₂SO₄ solution.

Phenol oxidation

Cyclic voltammetry (CV) at a scan rate of 100 mV/s was the electrochemical technique applied to study the oxidation behaviour of phenol (Figure 2). We can see that in the presence of phenol, the current densities are remarkably very important. The CV shows the appearance of three peaks, two in the anodic scan, at about 0.6 V and 1.7 V and a reduction peak at -0.1 V. Taking into account the positions of the anodic peaks and the cathodic peak, we can conclude that it is not the same redox system. The oxidation of phenol is thus irreversible. The proposed mechanism is the following:



The ability of the Ti-CPE to oxidizing phenol was also studied by square wave voltammetry (SWV). Figure 3 shows the SWV obtained in 0.1 mol L⁻¹ Na₂SO₄ in presence and absence of phenol. When the electrolytic solution was enriched by phenol, square wave voltammetry shows two well defined peaks. These peaks were due to the oxidation of phenol.

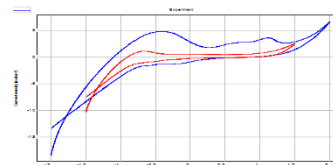


Figure 2: CVs recorded for 0.11 M phenol at pH=5 at Ti-CPE, scan rate 100 mV/s.



Figure 3: Square wave voltammograms recorded at Ti-CPE electrode, in 0.1M Na₂SO₄ containing 0.11M phenol (pH ~ 5).

The increase in the concentration of phenol decreased the current density of the anodic peaks, which can be explained by the saturation of the electrode surface (Figure 4). The Figure 5 shows the linear relationship between the scan rate anodic peak currents of phenol at Ti-CPE, deducted from SWV's.

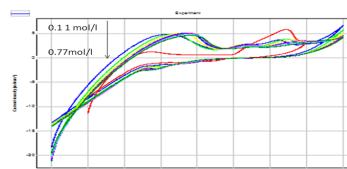


Figure 4: Cyclic Voltammograms of different concentration of phenol 0.11 M to 0.77 M) at Ti-CPE in 0.1 M Na₂SO₄ pH=5, Scan rate 100 mV/s.

Electrode kaolin-CPE

Typical metal matrix modified carbon paste electrode have been shown to be able to participate in the electro oxidation of phenolic solution, such as, NP and kaolin. Figure 6 shows the CV's recorded respectively at NP-CPE electrode, in electrolytic solution containing phenol (curve b) and in without phenol (curve a). A strong peak can be observed at a potential range from around 0.5 to 1.5 V, as it can be seen the double oxidation of phenol is characterized by two well defined peaks. Current densities are 10 times higher than the one observed on Ti-CPE electrode. The same behavior was observed when the concentration of phenol increase, the oxidation current densities decrease, which confirms the saturation of the electrode surface.

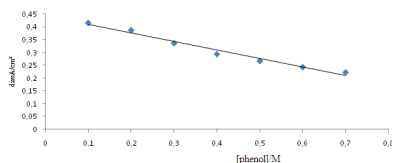


Figure 5: Effects of phenol concentration on peak currents.

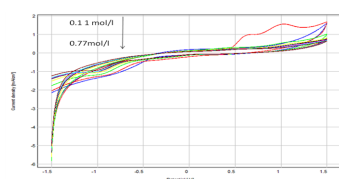


Figure 6: Cyclic Voltammograms of different concentration of phenol 0.11 M to 0.77 M at kaolin-CPE in 0.1 M Na₂SO₄ pH=5, Scan rate 100 mV/s.

Electrode NP-CPE

When the clay is replaced by the NP, the oxidation current densities are slightly improved. The structure is characterized by the presence of connection which facilitate the adsorption of the molecule of phenol, but at high concentrations of the phenol, we find a power drop due to the passivation of the electrode surface (Figure 7).

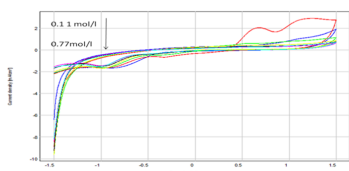


Figure 7: Cyclic Voltammograms of different concentration of phenol 0.11M to 0.77M) at NP-CPE in 0.1 M Na₂SO₄ pH=5, Scan rate 100 mV/s.

Conclusion

This work the electro oxidation of phenol on various prepared electrodes was carried out. On all studied electrodes, the oxidation of phenol is characterized by the appearance of two well defined anodic peaks. With clay and NP, as modifiers, oxidation current densities of the phenol are 10 times greater than in the case of Ti-CPE electrode. The porous nature of metallic matrix, NP and kaolin, facilitate the

adsorption of phenol at electrode surface and catalyzes the oxidation. We noted that the current density of the anodic peaks falls remarkably when the concentration of phenol becomes significant, probably due to saturation of the electrode surface, which confirms that the adsorption of phenol constitutes the decisive step of the reaction of oxidation. Nevertheless there is a strong relationship between the peak current density and phenol concentration.

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